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Reactions of Group 6 Fischer Carbene Complexes with Alkynes: Effect of the Metal on the Product Distribution and the Isolation of a Nontautomerized Cyclohexadienone Complex

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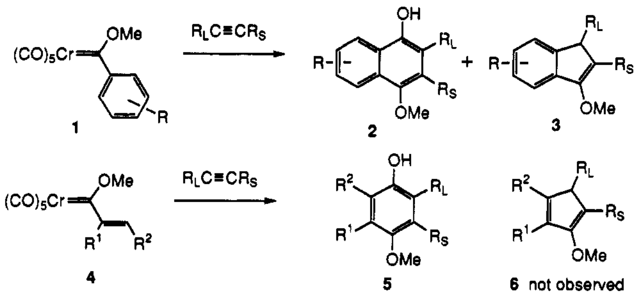
The first comparative study on the effect of the nature of the metal on the reactions of unsaturated group 6 Fischer carbene complexes with alkynes is reported. The scope of the study includes both aryl- and alkenylcarbene complexes of chromium, molybdenum, and tungsten for both internal and terminal alkynes. Twenty-one different organic structural types have been isolated and characterized from these reactions, but in most instances phenols and indene (cyclopentadiene) products are the two most frequently observed. The general observation made is that phenol formation is favored over indene (cyclopentadiene) formation in the order chromium > tungsten > molybdenum. The effect of the concentration of the alkyne on the distribution between phenol and indene (cyclopentadiene) was also examined and was found to be most prevalent in the order molybdenum > chromium > tungsten. The bis(alkyne)(η^4-cyclohexadienone)molybdenum complex **107** has been isolated in which the final tautomerization to the phenol product has not occurred. This complex has been characterized by X-ray diffraction and provides support for the previous interpretations of the concentration effects for the reactions of chromium complexes. This complex is the first example of the long-proposed ultimate intermediate in these reactions. Crystal data for **107**: space group $P2_1/c$, $Z = 4$, $a = 19.088(4)$ Å, $b = 10.101(1)$ Å, $c = 14.578(3)$ Å, $\alpha = 90.0°$, $\beta = 109.917(13)°$, $\gamma = 90.0°$, $R = 0.0598$, and $R_w = 0.0788$ for the 2405 reflections observed.

Introduction

Fischer carbene complexes of the group 6 metals are valuable reagents in organic synthesis, and a dramatic increase in the interest in these reagents by synthetic organic chemists in recent years can be noted.[1] The reaction of these complexes that has been most utilized in natural product synthesis to date is the benzannulation reaction of unsaturated complexes with alkynes. This reaction was first reported[2] for an aryl complex of the type **1** and depending on conditions can produce a number of different types of organic products, the most predominant of which is the 4-methoxy-1-naphthol species **2**, which is accompanied in many cases by the indene **3** as a side product.[2,3] The 4-methoxy-1-naphthol products **2** have attracted the most attention to date in natural product synthesis,[4] since they can be oxidatively converted to naphthoquinones, which are abundant molecular subunits on the bioscape. The annulations of alkenyl complexes of type **4** are more chemoselective, giving high selectivities for the 4-methoxyphenol products, which have also been employed as key steps in natural product synthesis.[5] Unlike the indene products **3**, which are often undesired side products accompanying the formation of the naphthols **2**, the products corresponding to the indene **3** (cyclopentadienes **6**) have never been observed from the reaction of an alkenyl carbene complex and an alkyne[6b] except in one special case with a nitrogen-substituted alkenyl complex,[6a]

Scheme 1



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[*] Abstract published in *Advance ACS Abstracts,* December 1, 1993.

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

(3) For leading citations to the literature, see: Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293.

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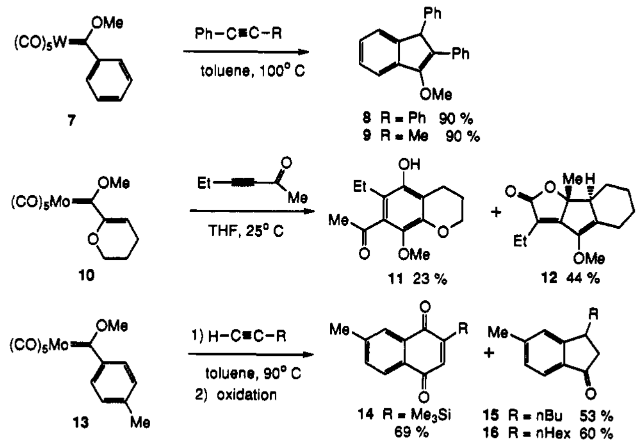
where five-membered-ring formation might have been expected.[7]

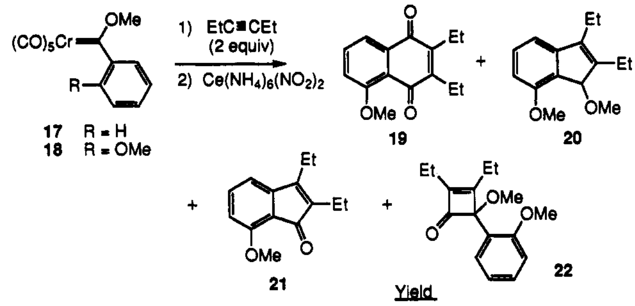
Background

The benzannulation reaction was discovered with a chromium carbene complex, and the reaction has been almost exclusively synthetically developed with chromium.[1] Surprisingly, given the importance of this reaction, the benzannulation reactions of molybdenum and tungsten carbene complexes have been largely ignored and are limited to just a few reports, all of which are summarized below. None of these reports have examined the reactivity of all three group 6 metals with the same alkynes and under the same conditions. The first annulation reaction with a tungsten complex was from the work of Geoffroy in 1983, when he reported that the phenyl complex **7** reacted with diphenylacetylene and phenylpropyne to give only indene products.[8] These were the only two thermal reactions described in this report, and it is difficult to compare these reactions to those of chromium, since these same reactions have never been performed in toluene with chromium and since it has been noted that the product distribution from these reactions is very sensitive to the nature of the solvent,[3,9] especially for the reactions with diphenylacetylene.[3,9] Indene products have also been observed for the reaction of a 4,4′-bis(tungsten carbene) complex with diphenylacetylene.[10] The first benzannulation of a molybdenum complex with 1 equiv of alkyne[11] was reported for the keto acetylenes, which give in addition to the 4-methoxyphenol **11** the novel tricyclic lactone **12**.[12] Both tungsten and chromium complexes give similar distributions of these products, but all three were not compared with the same alkyne. Recently, the molybdenum *p*-tolylcarbene complex **13** was reacted with three terminal alkynes to give either the six-membered- or five-membered-ring products as indicated in Scheme 2, but again the reactions of the corresponding chromium complex with the same alkynes in toluene have never been reported in the literature.[13]

Scheme 2



Scheme 3



solvent	[complex]	Yield 19	Yield 20 + 21	Yield 22
heptane	0.5 M	81	<6	
THF	0.5	61	23	
	0.005	5	75	
CH_3CN	0.5	6	11	78

The synthetic potential and utility of these reactions are matched by their mechanistic intrigue. A measure of the intrigue is reflected in the effect of the concentration of the alkyne and the effect of solvent on the product distribution from these reactions. This is illustrated in Scheme 3 for the reaction of the (*o*-methoxyphenyl)carbene complex **18** with 3-hexyne. With the indicated changes in the solvent and/or concentration the reaction can produce an 81% yield of the quinone **19**, a 75% yield of indenes, or a 78% yield of the cyclobutenone **22**.[3] While the effects of concentration and solvent have been ex-

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(6) (a) One example of a cyclopentadiene product is known for a nitrogen-substituted alkenyl complex where five-membered-ring formation is expected:[7] Duetsch, M.; Lackmann, R.; Stein, F.; de Meijere, A. *Synlett* **1991**, 324. (b) Professor Daniel Harvey has informed us that he has also observed cyclopentadienes from the reactions of molybdenum alkenylcarbene complexes with alkynes: Harvey, D. F.; Grenzer, E. M.; Gantzel, P. K. Unpublished results.

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(11) (a) The comparative study of chromium, molybdenum, and tungsten complexes in a two-alkyne annulation reaction has been reported: Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1060. (b) Reactions with propargylic ketones have been observed to give bicyclic lactones as the major product.[12]

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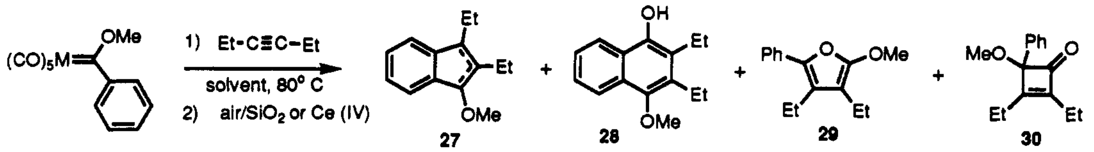
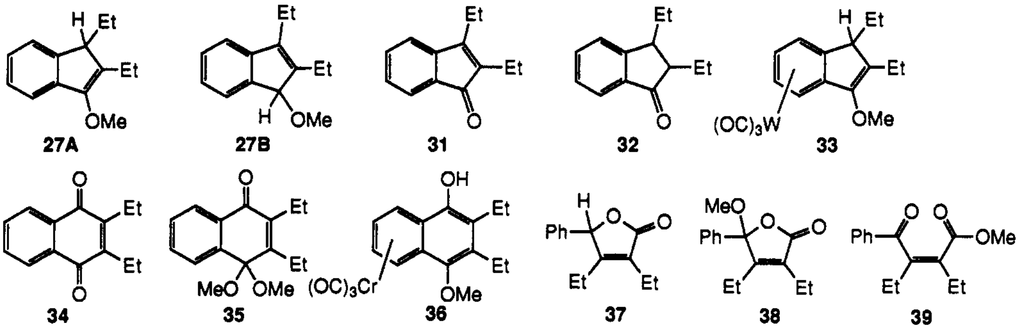
Table 1. Reactions of Aryl Complexes with 3-Hexyne[a]



entry no.	complex	solvent	[complex], M	time, h	oxidant	yield, %				mass balance	six/five (28/27)
						27 (A/B)[b]	**28**[b]	**29**[c]	**30**[c]		
1	**17**, M = Cr	THF	0.10	47	Ce(IV)	1.3[d]	97.4[e]	≤1[f]		98.7	74.9
2			0.005	34	Ce(IV)	1.7[g]	96.6[e]	1.3		99.6	56.8
3		benzene	0.10	46	Ce(IV)	≤0.7[h]	96.5[e,q]	≤1[f]		96.5	≥136.9
4			0.005	64	Ce(IV)	≤0.6[h]	95.7[e,r]	≤0.9[f]		95.7	≥159.9
5		CH_3CN	0.10	20	air/SiO_2	25 (13/12)	32	≤2	7	64	1.28
6			0.005	48	air/SiO_2	65 (38/27)	12	1	11	89	0.19
7			0.10[i]	17	Fe(III)	14 (9/5)	38[k]	≤1	23[k]	75	2.7
8			0.005[j]	30	Ce(IV)	29 (15/14)	24[k]	ND[t]	19[k]	72	0.83
9	**26**, M = Mo	THF	0.10	24	air/SiO_2	67 (66/1)	9	5		81	0.13
10			0.005	36	air/SiO_2	71 (71/0)	3	2		76	0.04
11		benzene	0.10	28	air/SiO_2	74 (74/0)	6	15		95	0.08
12			0.005	40	air/SiO_2	66 (66/0)	5	8		79[l]	0.08
13		CH_3CN	0.10	27	Ce(IV)	6 (>5/1)	39[e]	6	16	67	6.5
14			0.005	50	Ce(IV)	5 (>5/1)	67[e]	6	3	81	13.4
15	**7**, M = W	THF	0.10	42	air/SiO_2	53 (46/7)	6	33		92	0.11
16			0.005	75	air/SiO_2	57 (51/6)	8	26[m]		91	0.14
17		benzene	0.10	42	Ce(IV)	86[n,s]	3	6		95	0.04
18			0.005	73	Ce(IV)	67[o,s]	2	1		70	0.03
19		CH_3CN	0.005	62	air/SiO_2	7 (5/2)	4[k]	2	3	16[p]	0.65

[a] 1.9 equiv of alkyne in all cases. For the reactions of **7** an additional 1.9 equiv of alkyne was added at the halfway point. $(CH_3CN)M(CO)_5$ was observed in substantial amounts (30–75% by ^1H NMR) in all reactions in acetonitrile. [b] Isolated yields unless otherwise specified. Structures of isomers A and B are shown in Chart 1. Naphthol **28** isolated as quinone. [c] Yield by ^1H NMR analysis of crude reaction mixture prior to oxidation. [d] Yield by ^1H NMR; **27B** only, **27A** not observed. [e] Isolated yield of **34** and the side product **35**, which was present with **34** in 4–10 mol %. [f] Maximum possible yield of **37** + **39**. [g] **27B** only, **27A** not observed. [h] Maximum possible yield of **27A** + **27B**. [i] 45 °C.[9a] [j] 45 °C.[3] [k] Isolated yield. [l] $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ observed in 30% yield by ^1H NMR. [m] Obtained as a 9/17 ratio of **39**/**37**. [n] Obtained as a 44/42 mixture of **32**/**31**. [o] Obtained as a 36/31 mixture of **32**/**31**. [p] Also a 3% yield of methyl benzoate was observed and a 43% yield of $(CH_3CN)W(CO)_5$, which was the major product. [q] Obtained as a 6/1 ratio of **28**/**36** prior to oxidation. [r] Observed as a 1.5/1 ratio of **28**/**36** prior to oxidation. [s] Observed as a variable mixture of **27A**, **31**, **32**, and **33** prior to oxidation. [t] ND = not determined.

Chart 1



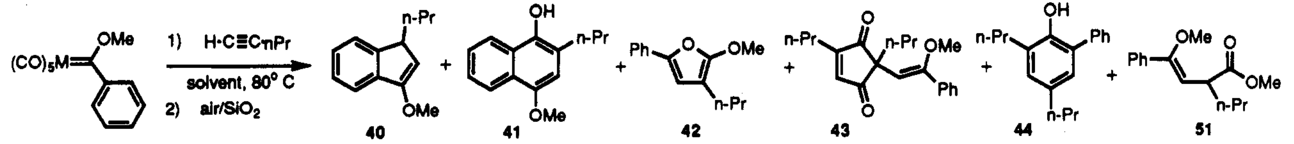
amined for a number of chromium complexes, these types of studies have never been reported for molybdenum or tungsten carbene complexes.

The purpose of the present work is to provide the first comparative study of the benzannulation reactions of all of the group 6 Fischer carbene complexes. The results described herein will detail the comparisons of the benzannulation of both aryl- and alkenylcarbene complexes of chromium, molybdenum, and tungsten with both terminal and internal alkynes, where it is found that the order of chemoselectivity for phenol over indene formation is chromium > tungsten > molybdenum. We also report the first observations of the formation of the five-membered-ring products from the benzannulation of simple alkenyl carbene complexes.[6] In addition, we report the first study of the effect of the metal on the process of substrate regulation of product distribution, where it is found that the reactions of molybdenum complexes display the greatest sensitivity of the product distribution to the concentration of the alkyne (allochemical effect).[3] Finally, we report the isolation and characterization of the first example of the ultimate intermediate in the benzannulation reaction, a nontautomerized chromacyclohexadienone intermediate of the type **87** in Scheme 4.

Benzannulation of Aryl Complexes of Chromium, Molybdenum, and Tungsten

The reactions of the parent phenyl complexes of all three of the group 6 carbene complexes with 3-hexyne were carried out, and the results are presented in Table 1. The chromium complexes give the highest selectivity for the phenol product, the optimal conditions being found with higher concentrations and with less polar and/or coordinating solvents. However, a clear distinction can be seen between chromium and the other two group 6 metals. The reaction of the chromium complex **17** with diethylacetylene gives the phenol **28** as the major product in all solvents

Table 2. Reactions of Aryl Complexes with 1-Pentyne[a]



40 41 42 43 44 51

entry no.	complex	solvent	[complex], M	time, h	yield, % 40^{b,c}	41^{b}	42^{b}	43^{b}	44^{b}	51^{d}	52^{d}	mass balance	six/five (41/40)
1	**17**, M = Cr	THF	0.10	24	2 (2)	84^{e} (66)	10 (6)		0.5 (<0.5)			98.5^{l}	42.0
2			0.005	50	12	61.6	7		0.5			81.1	5.13
3		benzene	0.10	36	1	64^{e} (60)	4	10 (8)	1			80	64
4			0.005	70	1	59	8	5 (6)	3			76	59
5		CH_3CN	0.10	38	9	60^{f}	19^{f}		2		0.5	90.5	6.7
6			0.005	50	3	76^{e}	1		5		3	88	25.3
7	**26**, M = Mo	THF	0.10	27	21	5^{d}	25 (22)		20 (15)	20		91	0.24
8			0.005	60	27	12^{d}	27		6	11		83	0.44
9		benzene	0.10	36	62 (53)	4^{d}	2 (3)	1.3 (1.8)	21 (29)	2.5		92.8	0.16
10			0.005	65	80	3^{d}	3	3	6	1		96	0.04
11		CH_3CN	0.10	26	10	17.5^{g}	15.5^{g}		4	30	3	80^{h}	1.7
12			0.005	60	3	9^{e}	2		2	1	2	46^{i}	3.0
13		MeOH	0.10	27	19	2	0.2		25	41		87.2	0.11
15	**7**, M = W	THF	0.10	8^{m}	6	6 (6)	37 (31)		10	18		77	1.0
16			0.005	48	9	10	38		7	20	4	88	1.1
17		benzene	0.10	10^{m}	57 (50)	7	12 (13)	1.2	19 (15)	2		98.2^{j}	0.12
18			0.005	70	60	6	5	6	14	1		92	0.10
19		CH_3CN	0.005	30	9	10^{e}	5 (5)		1	5	2	35^{k}	1.1

[a] 1.9 equiv of alkyne in all cases. For the reactions of **7** in THF (0.005 M), benzene (0.005 M), and CH_3CN (0.005 M) an additional 1.9 equiv of alkyne was added at the halfway point. For the reactions of **7** in THF (0.1 M) and benzene (0.1 M) 1.9 equiv of alkyne was added every 12 h until the reaction was complete. $(CH_3CN)M(CO)_5$ was observed in substantial amounts (30–95% by ^{1}H NMR) in all reactions in acetonitrile. [b] GC yields measured with response factors determined relative to triphenylmethane. Yields in parentheses are isolated yields. [c] No significant amounts of the isomeric indene **45** could be detected in any of the reactions by ^{1}H NMR ($\leq$0.2%). [d] Yield by ^{1}H NMR. [e] $\leq$1.5% **48** by ^{1}H NMR. [f] Includes 12% from **48**. [g] Includes 12.5% from **48**. [h] $\leq$0.5% **53** by ^{1}H NMR. [i] Includes a 27% yield of **53** (1.3/1 mixture of isomers. [j] 20–30 equiv of alkyne used. Poly-1-pentyne was isolated in 53–76% yield. [k] Includes a 3% yield of **53** (1.4/1 mixture of isomers); $(CH_3CN)W(CO)_5$ was observed as the major product in 80% yield. [l] Upon isolation a compound was obtained which was identified as **55** in 3% yield. [m] In units of days.

and concentrations, except at the lowest concentration in acetonitrile. In contrast, the molybdenum complex **26** gives the indene product **27** as the major product in all solvents except acetonitrile. This behavior of molybdenum is quite unexpected, since it has long been known that for the benzannulation of chromium complexes polar coordinating solvents favor indene products, especially DMF.[14] The tungsten complex gives predominately indene products in THF and benzene; however, in acetonitrile the mass balance falls precipitously and no conclusions can be made.

In previous studies on the benzannulation of chromium arylcarbene complexes, it was observed that the partition between phenol and indene products was dependent upon the concentration.[3,9a] Although there are slight trends consistent with these previous observations on chromium, for the most part, the reactions of all three complexes are fairly selective for either the indene or phenol product and there are not sufficient changes in the phenol to indene partition with concentration to make any conclusions. The biggest change in this regard is in the reaction of the chromium complex in acetonitrile, in which the partition drops by a factor of 3–5 depending on the temperature when the concentration is lowered from 0.10 to 0.005 M.

In addition to the indene and phenol products, the other primary products observed in these reactions are the furan **29** and the cyclobutenone **30**, both of which are precedented in the benzannulation of chromium complexes.[15,16] The cyclobutenone is only seen in the reactions in acetonitrile and is more prevalent with chromium, although it is seen in small amounts in the reactions of both the molybdenum and tungsten complexes in acetonitrile. The furan **29**, on the other hand, can only be detected in trace amounts in the reactions of the chromium complex and is a much more common side product in the reactions of both molybdenum and tungsten complexes, and significant amounts of the furan product were observed in the reactions of the tungsten complex in THF. The furan product is sensitive to air oxidation, particularly in the presence of silica gel, and thus the yields of the furan were generally determined by ^{1}H NMR integration on the crude reaction mixture prior to workup. Isolation of the furan leads to significant and/or complete conversion to a mixture of the oxidation product **39** or the hydrolysis product **37**.

The reactions of the chromium, molybdenum, and tungsten phenylcarbene complexes **17**, **26**, and **7** with 1-pentyne are summarized in Table 2. The chromium complexes predominately give the phenol product **41**, but the molybdenum and tungsten complexes give predominately indene product **40**. For chromium the partition between phenol and indene is in favor of phenol in all solvents and at all concentrations, while indene formation is least favored in benzene, where only trace amounts were detected. In contrast, for both the molybdenum and tungsten complexes indene formation is strongly enhanced in benzene relative to THF and acetonitrile. As was the case for the same reactions with diethylacetylene, there is only a small or negligible effect of the concentration on

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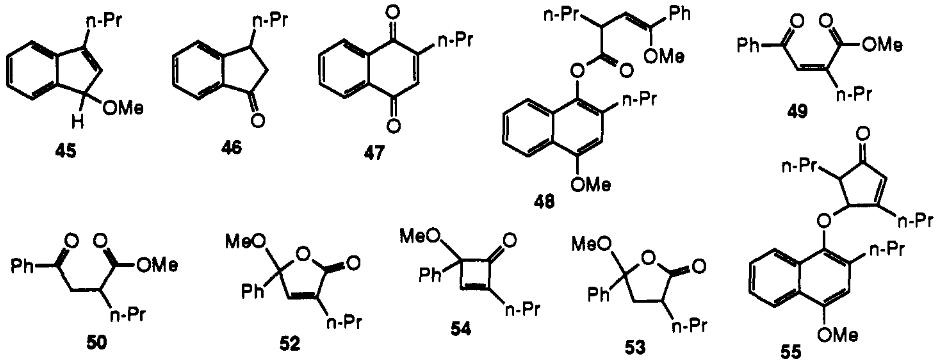
(14) (a) Wulff, W. D.; Tang, P.-C.; Chan, K.-S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (b) Yamashita, A. *Tetrahedron Lett.* **1986**, *27*, 5915. (c) Chan, K.-S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9.

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

(16) Cyclobutenones: see refs 9a and 15a.

Chart 2



the partition between phenol and indene formation for each of the three metals. Most interestingly, the strong preference for phenol formation that is observed for the molybdenum complex in acetonitrile in its reaction with 3-hexyne (67%, entry 14, Table 1) is not found for the same reaction with 1-pentyne, where instead a low mass balance is observed and where the predominate product is the lactone **53**.

A number of other products are observed in these reactions with 1-pentyne in addition to the phenol and indene products, but the cyclobutenone **54** was not found in any of these reactions, even in acetonitrile, where this was a significant product in the reaction with 3-hexyne. Unlike the reactions with 3-hexyne, the furan product is now a significant side product in the reactions of the chromium complex with 1-pentyne, but like the reactions with 3-hexyne, the furan product is more pronounced for the reactions of the molybdenum and tungsten complexes in the reaction with 1-pentyne than it is for chromium. In fact, the furan **42** is the predominate product of the reaction of the tungsten complex in THF. The cyclopentenedione **43** is observed as a minor product for all of the complexes, but only in benzene solvent.[17] The ketene trapping product **51** is observed as a substantial side product in the reactions of the molybdenum and tungsten complexes, and although its origins were not investigated, it suggests that free methanol is formed in these reactions. The stereochemistry of **51** was determined to be only *Z* in all cases and suggests that it results from the trapping of the (*Z*)-vinylketene intermediate which cannot cyclize to the naphthol product (Scheme 4) as has been previously observed.[15b] Although the ketene trapping product **51** was not observed in the reactions of the chromium complexes shown here, it has been reported for other chromium complexes, where it was also not determined if free methanol was involved.[18] The ketene trapping product **48** was observed in a small amount from a reaction of the chromium complex **17**, but only in acetonitrile as solvent, and related observations have been previously made.[19]

On the basis of prior observations made by Geoffroy and Katz, it was expected that a competing process in the reaction of tungsten complex **7** with alkynes would be alkyne polymerization.[20] This would be expected to be a more severe problem with terminal acetylenes than for internal alkynes. For example, both the thermal and photochemical reactions of the tungsten complex **7** with diphenylacetylene and phenylmethylacetylene gave good yields of indene products; however, the photochemical reaction of **7** with terminal acetylenes gave rise to no detectable cyclized products and only to polyacetylene products.[8] Related to this process is the formation of the phenol **44**, which results from the insertion of 2 equiv of the alkyne but then cyclizes, preventing multiple insertion of the alkyne.[21] Although the two-alkyne phenol is formed in significant amounts in the reactions of both the molybdenum and tungsten complexes, polymerization is apparently only a serious problem with the tungsten complex, and then only at high concentration. All of the reactions of the chromium and molybdenum complexes in Table 2 go to completion with 1.9 equiv of alkyne (it was not investigated whether this would be true with less equivalents of alkyne). The reactions of the tungsten complex **7** go to completion with 3.8 equiv (but not 1.9) for those reactions at 0.005 M, but for the reactions at 0.1 M large excesses (20–30 equiv) of 1-pentyne were required. Nonetheless, a very good mass balance was observed, indicating that the polymerization is the result of only a few percent of the carbene complex. As expected, polymerization was less of a problem with 3-hexyne compared to 1-pentyne; in all of the examples in Table 1 with the tungsten complex, the reactions went to completion with 3.8 equiv of 3-hexyne even at high concentration.

Benzannulation of Alkenyl Complexes of Chromium, Molybdenum, and Tungsten

In past studies on the benzannulation of chromium carbene complexes substantial differences were observed between the reactions of aryl complexes and alkenyl complexes. Specifically, it has been found that the benzannulations of alkenyl complexes result in more six-membered-rings (phenol) than five-membered rings (cyclopentadienes) and this selectivity is much greater than that for the corresponding reactions of aryl complexes.[9a] In fact, with only a single special exception, five-membered-ring annulation products (cyclopentadienes) have never been reported from the reaction of an chromium alkenylcarbene complex.[6] It has also been observed that solvent does not have much of an effect on the efficiency of phenol formation from the benzannulation of alkenyl complexes. In contrast, for the benzannulation of aryl

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[17] (a) 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. (b) Anderson, B. A.; Bao, J.; Brandvold, T. A.; Challener, C. A.; Wulff, W. D.; Xu, Y. C.; Rheingold, A. L. *J. Am. Chem. Soc.*, in press.

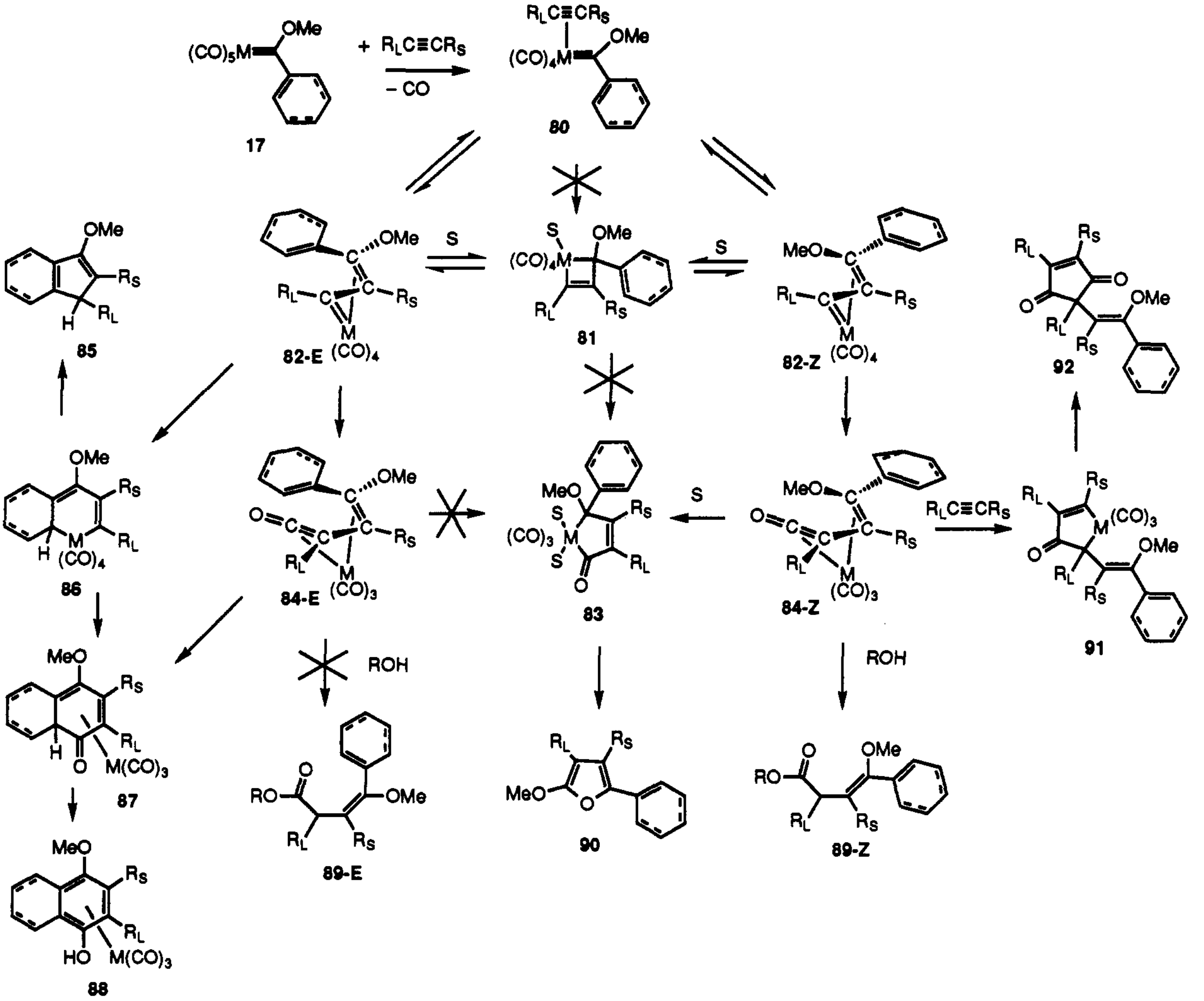
[18] Yamashita, A. *J. Am. Chem. Soc.* **1985**, *107*, 5823.

[19] See ref 9a and: Yamashita, A.; Timko, J. M.; Watt, W. *Tetrahedron Lett.* **1988**, *29*, 2513.

[20] Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

[21] (a) Bao, J.; Dragisich, V.; Wenglowsky, S.; Wulff, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 9873. (b) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1060.

Scheme 4

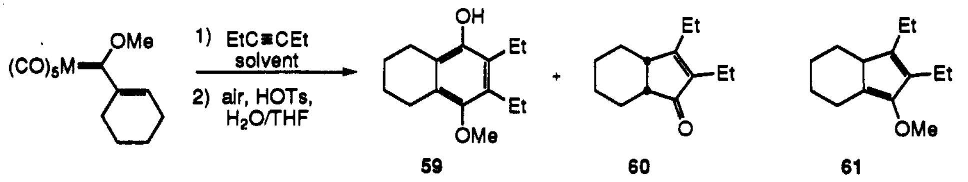


complexes phenol formation can be largely suppressed in many cases with the use of polar coordinating solvents.[3] While it has been noted for some time that the efficiency of phenol formation can be closely associated with the concentration in the reactions of chromium aryl complexes,[3] this has never been investigated in the reactions of chromium alkenyl complexes. Finally, there are no reports in the literature of a benzannulation of an alkenyl complex of either molybdenum or tungsten with simple alkynes (the only exception is with ketoalkynes, Scheme 2).[11b]

The study of the effect of the metal on the benzannulation of alkenyl complexes began with the reactions of the cyclohexenyl complexes with 3-hexyne (Table 3) and immediately uncovered some surprises. The reactions of the molybdenum cyclohexenyl complex **57** with 3-hexyne indicated in Table 3 are unprecedented in two aspects. First, it is the first example where five-membered rings are formed in the benzannulation of a simple alkenyl carbene complex.[6] The expected product from benzannulation without CO insertion is the cyclopentadiene **61**; however, since this compound can exist as five isomers due to 1,5-sigmatropic hydrogen shifts, the crude reaction mixture is hydrolyzed with tosic acid which, unless otherwise specified, selectively provides the product as the single regio- and stereoisomer **60**. Other than the phenol and cyclopentenone products, no other significant products were observed in any of the benzannulation reactions of alkenylcarbene complexes described in this work. In many cases analysis of the crude reaction mixture by ^{1}H NMR reveals the presence of several minor products that were present in such small amounts that they were not isolated or characterized.

The second surprise that is most prominently revealed in the reaction of the molybdenum carbene complex **57** with 3-hexyne is that these are the first examples of a benzannulation of an alkenyl complex where the partition between six- and five-membered-ring products is dependent on the concentration. In fact, for those reactions in THF, the major product of the reaction can be changed simply by changing the concentration. The product partition can be changed by a factor of 20 by changing the concentration by a factor of 100. At 0.1 M the phenol **59** is the major product by a factor of 2:1, but at 0.005 M the cyclopentenone **60** is the major product by a factor of 10:1. The magnitude and direction of the change in the partition between six- and five-membered-ring products in this reaction are the same as has been observed in the largest effect thus far seen for the reaction of a chromium carbene complex.[3] The product partition from the reaction of the molybdenum complex **57** is in favor of the cyclopentenone product in polar coordinating solvents such as acetonitrile and is selective for the phenol product in the nonpolar noncoordinating solvent heptane, and this is the same type of solvent dependence that has been observed in the benzannulation of chromium aryl complexes.[3] It can be seen from the data in Table 3 that molybdenum complexes are more sensitive to this allochemical effect.[3] The

Table 3. Benzannulation of Cyclohexenyl Complexes with 3-Hexyne



complex	solvent	[complex], M	[alkyne], M	temp, °C	time, h	yield, %		six/five	total yield, %
						59	**60**		
56, M = Cr	heptane	0.5	1.0	50	42	58	≤0.1	≥580	58
		0.005	0.010	50	42	73	≤0.1	≥730	73
	THF	0.5	1.0	50	19	67	≤3	≥22.3	67
		0.005	0.010	50	18	60	≤1	≥60	60
	CH_3CN	0.5	1.0	50	37	41	≤1	≥19	41
		0.005	0.010	50	37	23	22	1.05	45
57, M = Mo	heptane	0.5	1.0	50	18	33	7	4.7	40
		0.005	0.010	50	18	33	9	3.7	42
	THF	0.5	1.0	50	8	48	22	2.3	70
		0.005	0.010	50	8	6	64	0.09	70
	CH_3CN	0.1	0.2	25	19	5	27	0.19	32
58, M = W	heptane	0.1	0.2	90	19	51	23	2.2	74[a]
		0.005	0.010	90	18	50	38	1.3	88
	THF	0.1	0.2	90	20	45	7	6.4	52[a]
		0.005	0.010	90	32	56	8	7.0	64[a]
	CH_3CN	0.1	0.2	90	19	24	24	1.0	48
		0.005	0.010	90	18	8	47	0.17	55[a]

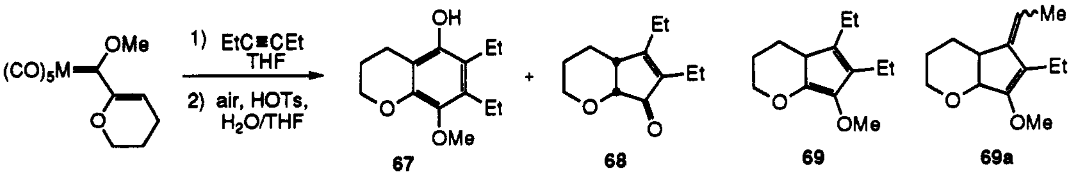
[a] Small amount of a minor product observed; see Experimental Section.

chromium complex only gives the phenol product in THF and heptane with no detectable amount of cyclopentenone products from reactions that differed in concentration by a factor of 100. In acetonitrile the chromium complex **56** shows a slight concentration effect, in contrast to the tungsten complex **58**, which gives both the phenol and cyclopentenone products, but over concentration changes of a factor of 100 the changes in the product partition are quite small except perhaps in acetonitrile as solvent. The effect of solvent on the product partition for the benzannulations of the tungsten complex **58** is out of line with the trend for the molybdenum complex, since the reaction is most selective for the phenol **59** in THF and not in heptane.

The dependence of the product distribution on the concentration that was observed for the molybdenum complex **57** was also observed for the reaction of the molybdenum dihydropyranylcarbene complex **65**. In the reaction of complex **65** with 3-hexyne, a change in the partition ratio of a factor of 29 favoring the phenol was observed for an increase in the concentration by a factor of 100. Unlike the reaction of tungsten complex **58** with 3-hexyne, the reaction of the tungsten complex **66** mirrors that of the chromium complex **64** in this case, in that it is completely selective for the phenol **67** and no detectable amount of the cyclopentenone **68** was observed from their reactions even at low concentrations. The origin of the concentration effect was examined in more detail for the reaction of the molybdenum complex **65** with 3-hexyne, and as the data in Table 4 reveal, the product partition is dependent on the concentration of the alkyne but not on the concentration of the carbene complex. This was also demonstrated to be the case in the reaction of the chromium *o*-methoxyphenyl complex **18** with 3-hexyne.[3] It should be noted that no concentration effects were noted for the reactions of the molybdenum complexes **57** and **65** with 3-hexyne in heptane solvent, and possible origins of these effects will be discussed later. Finally, if an acid workup is not employed for the reaction in entry 4 in Table 4, the cyclopentenone **68** (10%) and the enol ether **69a** (12%) are isolated.

The effect of solvent on the product partition in the reaction of the molybdenum cyclohexenyl complex **57** with 3-hexyne was very pronounced compared to the negligible effects seen for the chromium and tungsten complexes **56** and **58**. A similar effect of solvent was also observed and studied more intensively for the reaction of the molybdenum dihydropyranyl complex **65** with 3-hexyne. These data along with those from studies on the effects of temperature and various additives on the product partition from this reaction are presented in Table 5. Benzene, heptane, and methylene chloride are the only solvents that give exclusively the phenol product and share the common property of being noncoordinating. The cyclopentenone product **68** is only seen in a set of solvents that can be characterized as polar and/or coordinating. The trend seen in the data in Table 5 can best be interpreted as that expected where the product partition is dependent on the coordinating ability of the solvent. The only exception to this trend is from the reaction in 2,5-dimethyltetrahydrofuran (DMTHF) where, on the basis of previous observations for the reaction of the chromium complex **18** with 3-hexyne,[3] a significant change in partition between THF and DMTHF would have been expected. In addition, the decreasing mass balance for the reaction that is observed with increasing polarity and/or coordinating ability of the solvent also obscures the significance of this trend. In consonance with this trend is the small effect seen by the addition of 1 equiv of triphenylphosphine to the reaction mixture, where a small but real increase in the yield of the cyclopentenone is observed for a reaction where the mass balance actually increases (entries 11 and 13). This reaction was carried out at 60 °C, since the addition of triphenylphosphine slowed down the reaction slightly and the control experiment in entry 11 reveals that there is a slight effect of raising the temperature from 25 to 60 °C, although the yield of cyclopentenone is essentially constant. The effect of temperature on the

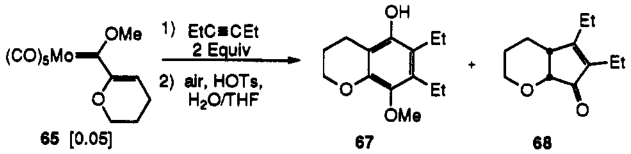
Table 4. Benzannulation of Dihydropyranyl Complexes with 3-Hexyne



complex	solvent	[complex], M	[alkyne], M	temp, °C	time, h	yield, %		six/five	total yield, %
						67	**68**		
64, M = Cr	THF	0.5	1.0	50	24	73	≤0.1		73
		0.005	0.010	50	96	75	<1.0		75
65, M = Mo	THF	0.5	1.0	25	18	49	12	4.1	61[a]
		0.05	0.10	25	12	31	33	0.91	64[a,b]
		0.005	0.010	25	21	8	59	0.14	67
		0.05	1.0	25	9	58	16	3.6	74[a]
		0.005	1.0	25	18	36	10	3.6	46
	heptane	0.5	1.0	25	17	69	<3		69
		0.05	0.10	25	19	68	<5		68
		0.005	0.010	25	17	69	<1		69
66, M = W	THF	0.5	1.0	90	24	58	<3		58[c]
		0.05	0.10	90	24	65	<3		65
		0.005	0.010	90	48	77	<2		77

[a] 3–5% of **107** observed along with two other minor organometallic compounds. [b] Without an acid workup a 10% yield of **68** and a 12% yield of **69a** are obtained. [c] 3% yield of **108** analogous to **107**.

Table 5. Effect of Solvent and Additives on the Product Distribution[a]



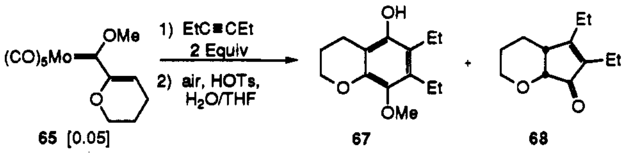
entry no.	solvent	additive (amt, equiv)	temp, °C	time, h	yield, %		six/five	mass balance
					67	**68**		
1	heptane	none	25	19	68	≤5	≥13.6	68
2	benzene		25	36	65		≥30.0	65
3	CH_2Cl_2		25	22	53		≥30.0	53
4	DME		25	18	57	14	4.1	71
5	TMF		25	24	31	33	0.94	64
6	DMTHF[b]		25	36	28	36	0.77	64
7	DMF		25	13	9	14	0.64	23
8	CH_3CN		25	54[c]	5	25	0.20	30
9	CH_3OH		25	15	11	40	0.27	51
10	CH_3NO_2		25	*d*	≤10	<10		
11	THF		60	13	16	36	0.44	52
12	THF		110	0.5	6	25	0.24	31
13	THF	PPh_3 (1)	60	48	14	47	0.30	61
14	THF	PBu_3 (1)	60	10	*e*			
15	THF	$P(OMe)_3$ (1)	60	24	*e*			
16	THF	CO (1 atm)	60	72	33	11	3.0	44

[a] All reactions run at 0.05 M in **39** with 2 equiv of alkyne. All yields are isolated. [b] 2,5-Dimethyltetrahydrofuran. [c] Additional 1 equiv of alkyne added after 48 h. [d] Analysis by GC: crude ^1H NMR was quite complicated, and the products were not isolated from this reaction. [e] Neither **35a** nor **36a** could be detected by GC or ^1H NMR analysis of the crude reaction mixture.

partition is not clarified by the experiment at 110 °C, since the mass balance drops significantly. The addition of more electron rich phosphines leads to the complete suppression of all annulation products. An atmosphere of carbon monoxide also slows down the reaction, which is not surprising and leads to a slight shift of the partition in favor of the CO-inserted product, but this effect has not been further investigated in other reactions.

From the point of view of synthesis of cyclopentenones, the two trends revealed by the solvent studies in Table 5 lead to a mixed prognosis. On one hand, the yield of cyclopentenone increases with increasing coordinating ability of the solvent, but on the other hand, the mass balance goes down. The set of experiments that are summarized in Table 6 were carried out to probe the ability of the $2e^-$ donor acetonitrile to affect the partition in favor of five-membered-ring formation and to identify the optimal conditions for the two opposing trends. As the data reveal, there is a correlation between the percentage of cyclopentenone and the number of equivalents of acetonitrile that are added to the reactions carried out in benzene, and the effect appears to maximize at about 40 equiv. A greater effect can be achieved with less acetonitrile in THF, since THF has a greater inherent propensity to give cyclopentenones than does benzene. In fact, the best yield of the cyclopentenone **68** and the highest mass balance for the reaction is achieved in THF with 10 equiv of acetonitrile. The 59% yield of **68** for this reaction is the same yield that is obtained in pure THF at 0.005 M. This is a synthetically useful result, since the reaction can

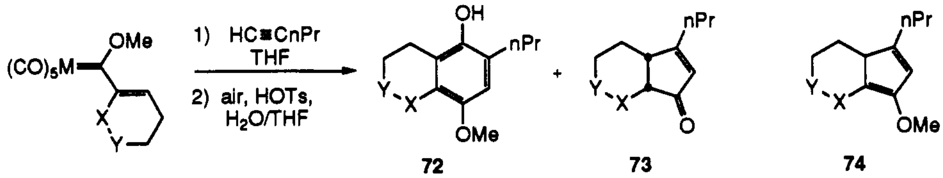
Table 6. Effect of Added Acetonitrile on the Product Distribution[a]



entry no.	solvent	amt of CH_3CN, equiv	time, days	GC yield,[b]		isolated yield, %		six/five	mass balance
				67	**68**	**67**	**68**		
1	benzene	0	1.5			65		≥30.0	65
2		2	1.7	54	6			9.0	60
3		4	2.7[c]	27	28	24	34	0.83	56
4		10	4.3[c]	16	33			0.48	49
5		38[d]	4.5[c]	7	46			0.15	53
6		114[e]	4.5[c]	7	43			0.16	50
7	THF	0	2.5			31	33	0.94	64
8		10	3.5[c]	11	57	10	59	0.17	68
9		100	0.8			tr	6		6
10		100	2.5			7	58[f]	0.12	65[g]
11	CH_3CN	380	2.3[c]			5	25	0.20	30

[a] All reactions run at 25 °C and 0.05 M in **39** with 2 equiv of alkyne. [b] Anthracene as internal standard. [c] Additional 1 equiv of alkyne added after 48 h. [d] 10% CH_3CN/90% benzene. [e] 30% CH_3CN/70% benzene. [f] Contains 14% of the nonconjugated cyclopentenone. [g] 0.005 M in **65**.

Table 7. Benzannulation of Alkenyl Complexes with 1-Pentyne



complex	[complex], M	[alkyne], M	temp, °C	time, h	yield, %		six/five	total yield, %
					72	**73**		
			X–Y = O–CH_2[j]					
64, M = Cr	0.3	0.45	50	24	67[a]			67
	0.005	0.010	50	21	57	≤0.2	>285	57
65, M = Mo	0.05	0.10	25	24	51	10	5.1	61
	0.005	0.010	25	28	35	14	2.5	49[b]
66, M = W	0.5	1.0	80	108	43	≤0.4	108	43[c]
	0.005	0.010	80	120	54			54[c]
			X–Y = CH_2–CH_2[k]					
56, M = Cr	0.5	1.0	50	19	69	≤2		69
	0.005	0.01	50	18	65	≤6		65
57, M = Mo	0.5	1.0	25	45	86	≤0.2		86
	0.005	0.010	25	18	77			77
	0.5	1.0	50	15	72	<0.8		72[d]
	0.005	0.01	50	15	80	<3		80[d]
58, M = W	0.1	0.2	90	38	88[e]			88
	0.005	0.010	80	64	96[f]			96
			X–Y = CH_2[l]					
77, M = Cr	0.3	0.45	45	24	54			54[g]
78, M = Mo	0.1	0.2	25	14	80			80[h]
79, M = W	0.005	0.01	80	61	87			87[i]

[a] Isolated as quinone.[5e] [b] No acid workup; yield of **73** refers to 8% **73** and 6% of isomeric enone with double bond at ring fusion. [c] 4–6 equiv of alkyne total. [d] Reaction in heptane. [e] Isolated as quinone: 2 equiv of alkyne added after 16 h. [f] Isolated as an 81/14 mixture of **72b** and complex **109** analogous to **107**: 2 equiv of alkyne added after 48 h. [g] In hexane this reaction produced a 51% yield of **72c** and a 9% yield of cyclopentenedione **110** analogous to **92** in Scheme 4.[17b] [h] Two unidentified minor products observed. [i] 8 equiv of alkyne added in four portions. [j] Yields given for **72a** and **73a**. [k] Yields given for **72b** and **73b**. [l] Yields given for **72c** and **73c**.

be carried out on a 10-fold greater concentration with 10 equiv of acetonitrile.

The reactions of the molybdenum and tungsten alkenyl complexes with 1-pentyne (Table 7) are in sharp contrast to the reactions of the molybdenum and tungsten aryl complexes with 1-pentyne (Table 2). The cyclohexenyl and cyclopentenyl complexes of all three metals are completely chemoselective, giving only the phenol products **72** at all concentrations. The only cyclopentenone observed was for the reaction of the molybdenum dihydropyranyl complex **65**, and even then it was a minor product even at low concentration. Another surprising feature is that both benzannulations of the molybdenum and tungsten cyclohexenyl complexes give higher yields of the phenol **72b** than does the chromium complex. The molybdenum cyclopentenyl complex **78** gives a significantly higher yield of phenol (80%) than does the chromium complex **77** (54%).[17b] The reaction of the tungsten cyclopentenyl complex **79** also gives an excellent yield of the phenol (87%) but suffers from competing polymerization of the alkyne (8 equiv of alkyne). The benzannulation of the tungsten cyclohexenyl complex **58** with 1-pentyne goes to completion at either 0.1 or 0.005 M with 4 equiv of alkyne, whih is in stark contrast to the 20–30 equiv required to drive the reaction of the tungsten phenyl complex 7 with 1-pentyne to completion (Table 2). From a synthetic point of view this is an attractive reaction, since the yield of **72b** is still 88% at 0.1 M; the same reaction of the chromium complex only goes to 69% yield. The results from the reactions in Table 7 were surprising, since it was anticipated on the basis of the reactions of molybdenum and tungsten aryl complexes that the advantages of these alkenyl complexes over chromium might be in their selectivity for five-membered-ring annulation products, but instead the advantages of these complexes, with terminal alkynes at least, appear to be that they generate phenol products in higher yields compared to those for the chromium alkenyl complexes.

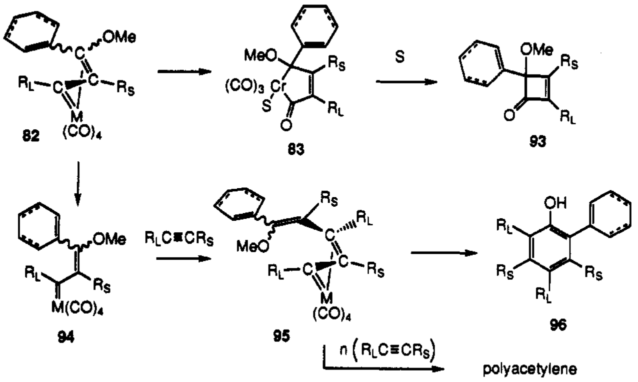
Mechanistic Discussion

Background. The mechanism of the reaction of Fischer carbene complexes with alkynes has traditionally not been considered from the point of view of the stereochemistry of the reactive intermediates involved, but it is becoming increasingly clear that this is necessary.[3,9a,15b,22b,23] To account for and discuss the formation of all of the products that we observed in this work, we will first consider those products in which the stereochemistry of the reaction intermediates is known to be important in their formation (Scheme 4), and then we will focus on the partition between the indene and phenol products (Scheme 6), since these are the two major products for nearly all of the reactions of the group 6 carbene complexes described in this work.

These reactions are thought to involve a rate-limiting loss[24] of a cis carbon monoxide ligand[25] followed by addition of an alkyne to generate the η^1:η^3-vinylcarbene-complexed intermediates 82 as a mixture of the diastereomers 82-*E* and 82-*Z*. The formation of 82 was originally postulated as occurring via a ring opening of 81,[28] but recent calculations show that the direct formation of 82 from 80 would be more energetically favorable.[22] For chromium the bulk of the reaction flux must pass through the *E* isomer of 82, since the reaction of chromium carbene complexes with alkynes is a generally useful method for phenol formation. The phenol products are thought to arise from CO insertion in 82,[26] giving the vinylketene complex 82-*E*,[27] which undergoes electrocyclic ring closure to give the cyclohexadienone complex 87 followed by tautomerization to 88. The indene product has been postulated to arise from a reductive elimination from the chromacyclohexadiene intermediate 86[28] and thus also must arise from the *E* isomer of 82.

The cyclopentenedione products 92 are always observed as a single diastereomer about the pendant double bond, and in all cases that have been described before, and in the present work as well, these products are always obtained exclusively as the *Z* isomers, suggesting that they are formed from the *Z* isomer of the vinylcarbene-complexed intermediate 82.[17] Furthermore, it was observed that cyclopentenedione products can be the major products of the reactions of carbene complexes with alkynes in situations where the formation of the *E* isomer of the vinyl carbene complex is geometrically impossible.[17] Finally, it has been established that, in intramolecular reactions, the cyclopentenedione products are formed via the intermediacy of the vinylketene complex 84-*Z* and not directly from the vinylcarbene-complexed intermediate 82-*Z*.[17]

Scheme 5



It has been established at least in one case for the reaction of a chromium carbene complex that the vinylketene complexes 84-*E* and 84-*Z* do not interconvert rapidly with respect to the formation of phenol and furan products.[15b] That work also demonstrated that furan formation occurs via the *Z* isomer of the vinylketene complex 84.[15b] While there are no such data in the literature concerning whether the vinylcarbene-complexed intermediates 82-*E* and 82-*Z* can equilibrate, recent theoretical considerations reveal that the barrier to such an isomerization may be small and that equilibration of the vinylcarbene-complexed intermediates 82-*Z* and 82-*E* may be rapid with respect to the subsequent CO-insertion step, giving rise to the vinylketene complexes.[22b]

At this time there is not enough information to identify the stereochemistry of the reaction intermediates which are responsible for the formation of the cyclobutenone and two-alkyne phenol products. It has been proposed that the cyclobutenone product is the result of a reductive elimination from the metallacyclopentenone complex 83.[9a] However, it has been proposed that the furan product also is formed from the complex 83 under conditions where 83 is formed from the *Z* isomer of 84 but not the *E* isomer.[15b] This does not mean that cyclobutenones are also formed only from the *Z* isomer of 84, since cyclobutenone formation is usually only seen in acetonitrile[9a] (Table 1), which may be a strong enough coordinating solvent to intercept both isomers of 84. Also as indicated in Scheme 5, the stereochemistry of the reactive intermediates is lost in the formation of the two-alkyne phenol 96 in the penultimate step involving the cyclization of the vinylketene complex derived from 95.[21b] Finally, is should also be pointed out that the only intermediate in the mechanism presented in Scheme 4 that has been isolated from the reaction of a group 6 pentacarbonyl carbene complex and an alkyne is an amino vinylketene complex analogous to 84.[27] An η^1:η^3-vinylcarbene complex of

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[22] (a) Hofmann, P.; Hämmerle, M. *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 908. (b) Hofmann, P.; Hämmerle, M.; Unfried, G. *New J. Chem.* 1991, *15*, 769.

[23] 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.

[24] Fischer, H.; Mulheimer, J.; Märkl, R.; Dötz, K. H. *Chem. Ber.* 1982, *115*, 1355.

[25] Casey, C. P.; Cesa, M. C. *Organometallics* 1982, *1*, 87.

[26] Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* 1980, *113*, 1449.

[27] (a) Anderson, B. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* 1990, *112*, 8615. (b) Chelain, E.; Goumont, R.; Hamon, L.; Parlier, A.; Rudler, M.; Rudler, H.; Daran, J. C.; Vaissermann, J. *J. Am. Chem. Soc.* 1992, *114*, 8088.

[28] Casey, C. P. *React. Intermed.* 1981, *2*, 135.

tungsten similar to **82** but with a cyclopentadienyl ligand has been structurally characterized.[23]

Effects of the Metal on the Product Distribution

The effects of the metal on furan formation are revealed by the data in Tables 1 and 2. Furans are products of the reactions of arylcarbene complexes with both 3-hexyne and 1-pentyne (Tables 1 and 2) and have been previously observed for chromium.[15b] A greater proportion of furan products is observed for all three metals in reactions with terminal alkynes versus internal alkynes. The observation that can be made in this study is that tungsten and molybdenum complexes give greater proportions of furan products than does chromium. This was found to be true for 3-hexyne as well as for 1-pentyne. The fact that terminal acetylenes give higher proportions of furans than do internal acetylenes can be accounted for in Scheme 4 by a consideration of the vinylcarbene-complexed intermediates **82-*E*** and **82-*Z***. Apparently for both classes of alkynes there is a preference for the formation of **82-*E***, as only a minor part of the reaction flux goes through **82-*Z*** to the furan product. The source of this preference for the *E* isomer of **82** is not known but could be due to an electronic preference for the methoxy group to be exo (as in **82-*E***), a steric preference for the phenyl group to be endo (as in **82-*E***), or a combination of both. In any event, the steric preference for the phenyl to be endo would be expected to be largest when R_S is non-hydrogen and smallest when R_S is hydrogen. Therefore, the greatest reaction flux through **82-*Z*** and thus to furan product would be expected to occur with a terminal acetylene (R_S = H). What cannot be determined at this point is whether this distribution between **82-*E*** and **82-*Z*** is determined by a kinetically controlled carbon–carbon bond formation from **80** or by an equilibration of **82** to the thermodynamically more stable *E* isomer.[22b] If it is assumed that for all three metals, as has been shown for a chromium carbene complex,[15b] that the furan product is formed via the *Z* isomer of a vinylcarbene-complexed intermediate such as **82**, then the fact that chromium gives much less furan products than do either molybdenum or tungsten may be the result of either a greater kinetic perference for **82-*E*** for chromium versus molybdenum or tungsten or an equal kinetic pref erence for **82-*E*** for all three metals and an equilibration mechanism for molybdenum or tungsten that is faster than that for chromium. Such an equilibration mechanism may involve a solvent-induced formation of the metallacyclobutene **81** or the reversible formation of **82** from **80**.[22b] With regard to the former possibility, it was observed for the reactions of the tunsten complex **7** with both 3-hexyne and 1-pentyne (and for molybdenum complex **26** with 1-pentyne) that there is a substantially greater amount of furan product in THF than in benzene. The reactions in acetonitrile for the tungsten complex suffer from a dramatic loss in mass balance, and thus no conclusions should be drawn from these reactions. The fact that the cyclopentenedione product **92** (**43** in Table 2) is observed together with the furan product in benzene but in THF solvent only the furan product is observed is consistent with the mechanisms in Scheme 4. Both products have been proposed to be derived from the vinylketene complex **84-*Z***, the furan via a solvent-assisted formation of the 2-metallacyclopentenone **83** and the cyclopentenedione via a reaction with alkyne to give the 3-metallacyclopentenone **91**.[15b,17]

The two most prominent products found in the reactions in the present study are the phenol products and the indene (cyclopentadiene) products which, as indicated in Scheme 4, must be derived from the *E* isomers of the vinylcarbene- and vinylketene-complexed intermediates **82** and **84**. The results of the present study provide a wealth of new information regarding the factors affecting the distribution between these two classes of products, which can be summarized by the following five generalizations: (1) a greater proportion of phenol versus indene (or cyclopentadiene) products is observed for alkenyl complexes than for aryl complexes, (2) phenol over indene (cyclopentadiene) formation is favored in the order chromium > tungsten > molybdenum, (3) phenol formation is favored in less coordinating and/or less polar solvents, (4) phenol formation is favored at higher concentrations of alkyne, (5) a greater proportion of phenol versus indene (or cyclopentadiene) products is observed for 1-pentyne than for 3-hexyne.

The observation that alkenyl complexes give a greater proportion of phenol over indene (cyclopentadiene) products than do aryl complexes can be accounted by either one or more of the three possibilities outlined in Scheme 6. If the CO-insertion step from **82-*E*** to **84-*E*** is reversible, then the formation of the η^6 complex **106-*E*** should be more favorable for alkenyl complexes, since for aryl complexes this transformation would require disruption of an aromatic ring.[9a] An alternate explanation is that if the cyclization of the vinylcarbene-complexed intermediate **82-*E*** to intermediate **102** is reversible, then greater proportions of indene (cyclopentadiene) product would be expected for aryl versus alkenyl complexes if the 1,5-sigmatropic hydrogen shift to give **85** is more facile for an aryl complex than for an alkenyl complex, which may be expected since aromaticity would be restored for an aryl complex but not for an alkenyl complex. A third possibility is that there is a simultaneous CO insertion/coordination from **82-*E*** to give directly **106-*E*** which would be expected to be more facile for an alkenyl complex than for an aryl complex, where aromaticity would be disrupted. The degree to which aryl complexes are more prone to give five-membered-ring products is revealed in the reaction of the chromium complex **56** with 3-hexyne in acetonitrile (Table 3, entry 6) which represents the only example of the isolation of a cyclopentadiene product from the reaction of an chromium alkenylcarbene complex.[6]

The present study reveals for the first time the effect of the metal on the distribution between phenol and indene (cyclopentadiene). The order of selectivity for the CO-insertion phenol product is chromium > tungsten > molybdenum. This trend does not correlate with the metal–CO bond strengths in the metal hexacarbonyls.[29] It does hold for chromium ($\Delta H_{\text{Cr–CO}}$ = 36.8 kcal/mol)[29] versus tungsten ($\Delta H_{\text{W–CO}}$ = 46.0 kcal/mol),[29] as has previously been suggested,[8] since the product distribution is further shifted to the CO-inserted product (phenol) over the non-CO-inserted product (indene or cyclopentadiene) for chromium, which has a weaker metal–CO bond strength than does tungsten. However, this correlation does not hold for molybdenum, which, like chromium, has a metal–CO bond strength ($\Delta H_{\text{Mo–CO}}$ = 40.5 kcal/mol)[29] that is much weaker than for tungsten but which gives less CO-inserted products than tungsten. This difference in

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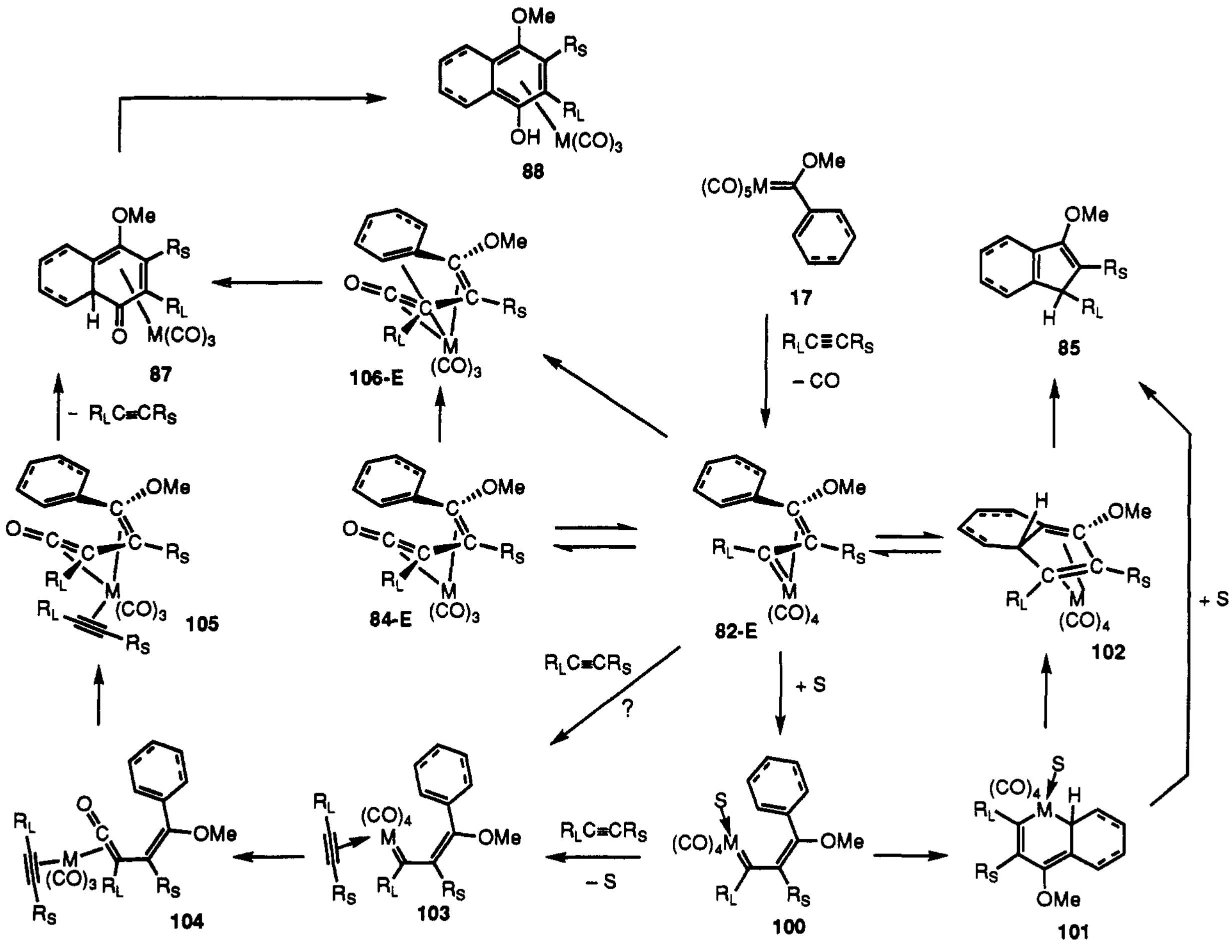
[29] Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905.

Scheme 6



molybdenum may be related to the well-established propensity of molybdenum to undergo ligand substitution ($\Delta H^{\ddagger}_{\mathrm{Mo}}$ = 31.7 kcal/mol) with greater rates than either chromium ($\Delta H^{\ddagger}_{\mathrm{Cr}}$ = 40.2 kcal/mol) or tungsten ($\Delta H^{\ddagger}_{\mathrm{W}}$ = 39.9 kcal/mol) in phosphine substitution on the metal hexacarbonyls.[30] These differences could be manifested in their effects on the partition between the various reaction paths leading from the vinylcarbene-complexed intermediate **82-*E*** in Scheme 6. In the presence of a coordinating solvent, the molybdenum complexes would be the most susceptible to the displacement of the double bond in complex **82-*E*** by solvent and, as will be discussed below, this should lead to an increased proportion of indene (cyclopentadiene) products. This implies that in the absence of a strongly coordinating solvent molybdenum complexes may give as much (or more based on metal–CO bond energy) phenol products as do tungsten complexes. In fact, in all of the data presently available for noncoordinating solvents such as benzene or heptane, the distributions between phenol and indene (cyclopentadiene) products are similar for molybdenum and tungsten and are in favor of phenol products. Moreover, in the reactions of the cyclohexenyl complexes **57** and **58** with 3-hexyne (Table 3), it can be seen that in heptane as solvent (but not in THF) the partition is slightly more in favor of the phenol product for molybdenum than it is for tungsten.

The effect of solvent on the distribution between phenol and indene (cyclopentadiene) products was studied extensively in this work. The general trend observed for all of the reactions in the present work is that reflected in the reactions of the molybdenum dihydropyranylcarbene complex **65** with 3-hexyne (Tables 5 and 6). It is clear from the data in Table 5 that for those solvents of poor coordinating ability more phenol products are observed than for solvents of higher coordinating ability. To account for these solvent effects, it is proposed that coordinating solvents will either displace the double bond in **82-*E*** (Scheme 6) to generate the solvated intermediate **100** or that the solvent will intercept the unsaturated metal center after a dissociative loss of the double bond in **82-*E***. Recent calculations suggest that the unsaturated complex resulting from dechelation of the double bond in **82-*E*** is not significantly different in energy from **82-*E***.[22] By the interconversion indicated by **100** → **101** → **102**, the solvent can function to enhance the formation of the intermediate **102** and thus the formation of the indene (cyclopentadiene) products. An alternate explanation of the effect of coordinating solvents is that they could serve in ligand displacements of the metal from the intermediate **102**, thus driving the reaction to the five-membered-ring products. This explanation is not consistent with the fact that, although alkynes can affect the distribution between phenol and indene (cyclopentadiene) products, they do so in the opposite sense. The higher the concentration of the alkyne, the greater the proportion of the phenol product that is formed, which is not the expectation if the alkyne were serving to simply displace the ligand from the metal in **102**.

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[30] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; pp 249–251.

In all of the reactions of carbene complexes with alkynes that have been examined to date in different solvents, the observation is that those solvents that are more polar and/or coordinating give a shift in the distribution between phenol and indene (cyclopentadiene) products in favor of the latter. There are only two exceptions to this statement. One was observed for the reaction of the chromium complex **17** with diphenylacetylene, and it has not been explained why this is an exception, but it is known that it is not due to steric effects.[31] The other exception is from the present work and was observed in the reaction of the molybdenum complex **26** with 3-hexyne in acetonitrile (Table 1, entries 13 and 14). As can be seen from the data in Tables 1 and 2, arylcarbene complexes of molybdenum have a very high propensity to give indene products in THF and benzene as solvents; however, in acetonitrile the phenol **28** to our surprise was the major product. This effect is not seen for the other metals or for 1-pentyne, nor is it seen for alkenyl complexes of molybdenum. The reaction of complex **65** with 3-hexyne was examined in a variety of solvents, and it is clear from the data in Table 5 that distribution is shifted away from the phenol product with increasing coordinating ability of the solvent. This is nicely confirmed by the data in Table 7, where the shift in the product distribution toward the five-membered ring correlates with the number of equivalents of added acetonitrile in both benzene and THF as solvent. The reason that the reaction of the molybdenum arylcarbene complex **26** with 3-hexyne is an exception to the solvent trends seen in this and all previous work cannot be readily identified at this point.

It has been previously observed that the concentration of the alkyne in the reactions of chromium carbene complexes with alkynes can have an effect on the distribution between phenol and indene products, where higher concentrations of alkyne lead to greater proportions of phenol product, and this has been termed the allochemical effect.[3,49] What is revealed in the present work is that molybdenum is much more sensitive to the allochemical effect than either chromium or tungsten. The previous reports of the allochemical effect for chromium were only with aryl complexes and then largely for those with ortho substituents that could chelate to the metal (i.e. complex **18**, Scheme 3) or with bulky acetylenes.[3] As can be seen from the data in Tables 1 and 2, molybdenum arylcarbene complexes have such a high propensity to give indene products even at high concentrations that the presence of an allochemical effect does not readily reveal itself. However, in the reactions of the molybdenum alkenyl complexes one can definitely see the effects of concentration on the product distribution under conditions where chromium and tungsten show no effect. For example, in Table 4 the reactions of the molybdenum complex **65** with 3-hexyne were examined under conditions where both the concentration of the carbene complex and the concentration of the alkyne were varied, and as was found for chromium, the distribution between the phenol and indene (cyclopentadiene) products is dependent on the concentration of the alkyne and not on the concentration of the carbene complex. The explanation that has been previously suggested to account for this effect is incorporated into Scheme 6 and is consistent with all of the data in the present work.[3] The vinylcarbene complex intermediate **82-*E*** is intercepted by a molecule of alkyne to give the alkyne complex **103** by direct associative displacement of the double bond, by a solvent-assisted process (via **100**), or by an unassisted dissociative process (not shown). Our hypothesis is that the coordination of the alkyne in intermediate **103** leads to a CO insertion that is more rapid than the same insertion in the vinylcarbene-complexed intermediate **82-*E***. The reason for this is that an alkyne can be either a 2e$^-$ or 4e$^-$ donor and during the insertion of CO in **103** the alkyne can switch from a 2e$^-$ donor to a 4e$^-$ donor such that the product **104** is saturated at the metal, a situation that would not be possible for the CO insertion in intermediate **82-*E***. The data from the present work bring to light another aspect of the allochemical effect that was not previously appreciated: that the effect is greatly reduced or nonexistent when the reaction is carried out in a noncoordinating solvent.[3] This aspect can be most clearly seen in the reaction of the molybdenum cyclohexenyl complex **57** with 3-hexyne (Table 3). The ratio of phenol to cyclopentenone is independent of concentration in hexane but not in THF. This suggests solvent is required to displace the double bond in **82-*E*** before the alkyne can coordinate to the metal. Finally, with regard to the observation that the terminal alkyne 1-pentyne gives more phenol products than the internal alkyne 3-hexyne, this can be explained by the allochemical mechanism shown in Scheme 6. For steric reasons, terminal acetylenes should be more able to intercept the solvated carbene-complexed intermediate **100** and thus lead to greater proportions of the phenol product and, as also observed, this would be expected to be increasingly important as the concentration of the alkyne is increased.

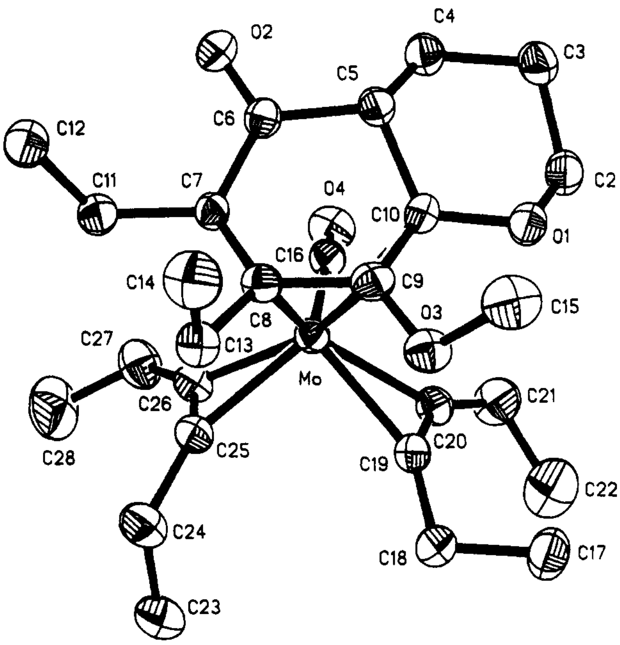

Figure 1. Structure of the bis-(3-hexyne)molybdenum dienone complex **107**.

Isolation and Characterization of a Nontautomerized Cyclohexadienone Intermediate

In addition to the organic products discussed above, the reactions of the molybdenum carbene complex **64** with 3-hexyne give rise to a few colored, presumably organometallic bands upon elution from silica gel. Two of these appear to be stable enough to be isolated, and one was obtained in sufficient quantities to be characterized.

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[31] For a discussion, see ref 3.

Table 8. Crystal Data for 107 and Summary of Intensity Data Collection and Structure Refinement

compd	107
color	red
fw	524.6
space group	$P2_1/c$
temp, °C	22
cell constants	
a, Å	19.088(4)
b, Å	10.101(1)
c, Å	14.578(3)
α, deg	90.0
β, deg	109.917(13)
γ, deg	90.0
cell vol, Å^3	2642.51(74)
formula units/unit cell	4
D_{calcd}, g cm^{-3}	1.3185
μ_{calcd}, cm^{-1}	43.43
diffractometer/scan	P2$_1$ four-circle diffractometer
radiation, graphite monochromator	CuKα (λ = 1.5418)
max cryst dimens, mm	0.3 × 0.2 × 0.3
check reflns	820; 242; 115
no. of reflns measd	4088
2θ range, deg	$0 \leq 2\theta \leq 57$
no. of Rflns obsd ($F_o \geq 5\sigma(F_o)$)	2405
no. of params refined	290
GOF	1.3583
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.0598
R_w	0.0788

Single-crystal X-ray diffraction has established the structure of this compound as the unique *bis*(3-hexyne)(η^4-cyclohexadienone)molybdenum carbonyl complex **107** (Figure 1). It is obtained in 3–5% yield under a variety of the reaction conditions discussed above, but especially with higher reaction concentrations and with THF as solvent. The red-purple crystalline complex is reasonably stable to air, water, and silica gel chromatography and persists at room temperature either as a solid or in solution for several days. It does decompose upon oxidizing with $(FeCl_3)_2(DMF)_3$[32] or upon heating in degassed THF at 60–70 °C for several hours with the free phenol **59** being liberated in 78% and 84% yield, respectively. As far as can be determined, only one other example exists of a transition metal complexed to a cyclohexadienone in which aromatization of the organic fragment by tautomerization is possible.[33]

Complex **107** is crystallographically similar to the *tris*(alkyne)metal carbonyls investigated by Tate, King, Bau, and others,[34–36] with one alkyne being replaced by the dienone ligand. The crystal data, fractional coordinates, and selected bond distances for **107** can be found in Tables 8–10. We consider **107** to be an 18-electron complex with the alkyne ligands acting as "three-electron donors" by the empirical definition of Templeton.[35] That is, a total of six electrons are involved in bonding from the two alkynes to the metal. This is supported by the intermediate length of the M–C(alkyne) bonds (2.08–2.11 Å) and also by the intermediate ^{13}C NMR chemical shifts of the alkyne carbons (162 and 180 ppm). Only two alkyne resonances are observed in the ^{13}C NMR. This was determined by labeling the starting carbene complex (made from molybdenum hexacarbonyl with 25% ^{13}CO incorporation), performing the reaction, and isolating the labeled cyclohexadienone complex (Scheme 7). Three signals are enhanced in the ^{13}C NMR spectrum of the labeled complex, and these are assigned to the metal carbonyl, the ketone carbon, and the sp^2 ring carbon bearing the methoxy group (starred in Scheme 7). Four signals appear as triplets (singlets flanked by a ^{13}C–^{13}C doublet), and these are assigned the remaining cyclohexadienone ring (indicated by arrows in Scheme 7). All

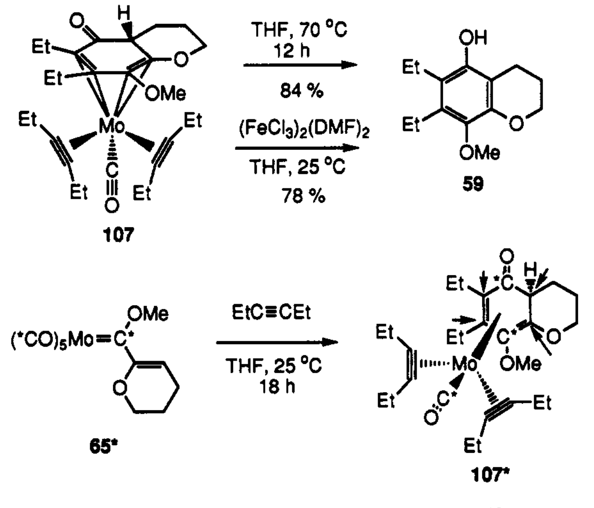
Table 9. Final Fractional Coordinates for 107

atom	x	y	z	B, Å^2
Mo	0.24342(4)	−0.0009(1)	0.2612(1)	3.6(1)
O1	0.1111(4)	0.0960(7)	0.0531(5)	4.7(2)
O2	0.2802(4)	0.3903(7)	0.2749(5)	5.5(3)
O3	0.2345(4)	−0.0348(7)	0.0331(5)	4.7(2)
O4	0.1582(4)	0.1405(8)	0.3837(5)	6.3(3)
C2	0.0527(6)	0.1552(11)	0.0764(8)	5.3(4)
C3	0.0569(6)	0.3048(12)	0.0840(8)	5.5(4)
C4	0.1304(6)	0.3430(11)	0.1622(8)	5.3(4)
C5	0.1961(5)	0.2771(10)	0.1401(7)	4.1(3)
C6	0.2672(5)	0.2892(10)	0.2255(7)	4.0(3)
C7	0.3191(5)	0.1800(9)	0.2459(7)	3.7(3)
C8	0.3132(5)	0.0793(10)	0.1698(7)	3.9(3)
C9	0.2423(6)	0.0584(11)	0.1040(7)	4.3(3)
C10	0.1818(5)	0.1319(10)	0.1143(7)	4.1(3)
C11	0.3920(6)	0.2019(11)	0.3290(8)	5.1(4)
C12	0.4456(6)	0.2993(12)	0.3067(9)	6.1(4)
C13	0.3805(6)	0.0200(10)	0.1531(8)	5.1(4)
C14	0.4003(7)	0.0957(13)	0.0758(9)	6.7(5)
C15	0.1991(8)	0.0078(12)	−0.0641(9)	6.6(5)
C16	0.1874(6)	0.0985(10)	0.3339(7)	4.6(3)
C17	0.1484(7)	−0.3180(13)	0.0465(9)	6.4(4)
C18	0.2112(6)	−0.2897(11)	0.1378(9)	5.7(4)
C19	0.1952(6)	−0.1750(10)	0.1926(7)	4.6(3)
C20	0.1494(5)	−0.1263(11)	0.2301(7)	4.5(3)
C21	0.0772(7)	−0.1429(14)	0.2450(10)	7.3(5)
C22	0.0446(8)	−0.2779(19)	0.2246(13)	9.9(7)
C23	0.3829(8)	−0.3362(14)	0.3854(11)	8.4(6)
C24	0.3948(7)	−0.2046(13)	0.3440(10)	6.9(5)
C25	0.3368(5)	−0.1035(10)	0.3451(7)	4.5(3)
C26	0.3115(6)	−0.0417(12)	0.4043(8)	5.0(4)
C27	0.3266(8)	−0.0060(13)	0.5093(10)	7.0(5)
C28	0.3953(10)	−0.0476(21)	0.5790(11)	10.9(7)

Table 10. Selected Bond Distances (Å) for 107

Mo–C7	2.386(10)	Mo–C25	2.065(9)
Mo–C8	2.327(11)	Mo–C26	2.088(10)
Mo–C9	2.363(11)	C7–C8	1.481(14)
Mo–C10	2.461(9)	C8–C9	1.383(12)
Mo–C16	2.010(12)	C9–C10	1.425(16)
Mo–C19	2.078(10)	C19–C20	1.277(17)
Mo–C20	2.116(10)	C25–C26	1.285(18)

Scheme 7



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but two of the ^{13}C signals downfield from 60 ppm are thereby accounted for. Since there is no symmetry element by which the two alkyne ligands of **107** can interconvert, observation of only two ^{13}C NMR signals probably indicates that, at least in solution, rotation about the metal–alkyne bond is occurring, a fact also implied by the broadness of some of the methylene signals in the ^1H NMR. However, no coalescence of the ^1H NMR signals was observed with increased temperature before the complex decomposed (~75 °C). The analogous tungsten complex **108** is apparently also produced from the corresponding reaction of complex **66** with 3-hexyne (Table 4). A small amount of a red compound is isolated by chromatography, and the ^1H NMR spectrum is consistent with that from the molybdenum reaction, but this product was not rigorously characterized. The organometallic complex **109** was also isolated in reasonable yields (10–20%) from the reaction of (cyclohexenylmethoxycarbene)tungsten complex **58** with 1-pentyne (Table 7). This complex appears to contain two coordinated alkyne ligands (by ^1H NMR) and does possess a terminal CO band in the IR spectrum; it also quantitatively liberates the quinone upon oxidation. This compound has not been completely characterized, but the structure analogous to **107** seems reasonable from the spectral data.

The formation of the bis(3-hexyne)molybdenum cyclohexadienone complex **107** is consistent with the mechanism presented in Scheme 6 to acocunt for the allochemical effect. However, this complex cannot be an actual intermediate in phenol formation because although it can be thermally converted to the phenol **59**, the thermal requirement is greater than that for the overall benzannulation of the molybdenum complex **64** with 3-hexyne. Perhaps intermediates of the type **105** with a single alkyne ligand would not be as thermally robust. Thus, while the isolation of complex **107** cannot be taken as proof of the proposed mechanism for the allochemical effect, it does demonstrate that a molecule of the substrate alkyne can coordinate to the metal center in this reaction after the first molecule of the alkyne substrate is covalently incorporated. The isolation of **107** is also significant, since it is the first time that the long-proposed ultimate intermediate of the benzannulation of a group 6 carbene complex and an alkyne has been isolated. This lends support to the longstanding mechanistic proposal that the penultimate step in the benzannulation mechanism is an electrocyclic ring closure of a vinylketene-complexed intermediate.

Experimental Section

Tetrahydrofuran (THF), ether, and benzene were distilled from benzophenone ketyl under nitrogen. Acetonitrile (CH_3CN), trimethylacetonitrile ($(CH_3)_3CN$), and benzonitrile (PhCN) were distilled from CaH_2 under nitrogen. 3-Hexyne and 1-pentyne were filtered through a short column of basic alumina prior to use. Chromatographic purifications were performed on EM Science silica gel (230–400 mesh). Elemental analyses were done by Galbraith Laboratories in Knoxville, TN. GC analyses were obtained on a Varian Star-3600 GC instrument. Oxidation with CAN refers to a 0.5 M solution of ceric(IV) ammonium nitrate in 0.1 N aqueous nitric acid. An oxidative workup with ferric(III) chloride–DMF complex involved treatment with an excess of this reagent[32] as a THF solution. The phenylcarbene complexes 7, 17, and 26 were prepared by the literature procedure[37] with methyl triflate as alkylated agent. Carbene complexes **56**,[9a] **58**,[3] and **64**[9a] were prepared as described in the literature.

General Procedure for Reactions of 3-Hexyne with Phenylcarbene Complexes Illustrated for the Chromium Complex 17. In THF: Oxidation of the Naphthol Product 28. A 0.1 M solution of the chromium carbene complex **17** (156.1 mg, 0.500 mmol) in THF (5 mL) was introduced into a 25-mL Kontes single-necked pear-shaped flask filled with argon and equipped with a threaded Teflon stopcock, and then 107.4 μL of 3-hexyne (0.95 mmol, 1.9 equiv) was added. The reaction mixture was deoxygenated by the freeze–thaw method (three cycles), and then the flask was sealed under 1 atm of argon at room temperature. The reaction was performed at 80 °C, and its progress was monitored by TLC analysis (1/1/20 $Et_2O/CH_2Cl_2/$hexane or 5% EtOAc is petroleum ether, visualization by UV, phosphomolybdic acid (PMA), or $KMnO_4$), which revealed that the reaction was complete after 47 h. The reaction mixture was concentrated under reduced pressure to provide a brown oil. A small sample of the crude reaction mixture was taken up in CH_2Cl_2, and the solution was filtered through a pipet-size silica gel column and concentrated. A ^1H NMR of this sample was recorded, with accurate integrations taken over the methoxy region (2.75–4.25 ppm). The possible primary products of interest are **27A**, **27B**, **28**, **29**, and **30**, and all have been fully characterized and reported previously. The characteristic methoxy absorptions for the possible products are as follows: indene **27A** (δ 3.86),[9a] indene **27B** (δ 2.99),[9a] naphthol **28** (δ 3.88),[9a,38] furan **29** (δ 3.93),[39] and cyclobutenone **30** (δ 3.37).[9a] In this reaction and all other reactions (in Table 1) that involved 3-hexyne, only the major product(s) was isolated and the yields for all other minor products were calculated from the isolated yield of the major product from the integrated ^1H NMR of the crude reaction mixture.

The rest of the crude reaction mixture from above was dissolved in 10 mL of CH_2Cl_2, and then 20 mL of 0.5 M aqueous ceric(IV) ammonium nitrate (CAN) (20 equiv) was added. The two-phase mixture was stirred vigorously for 1 h in the air at room temperature. The organic layer was separated, diluted with 10 mL of CH_2Cl_2, washed with 2 × 25 mL of H_2O and 2 × 25 mL of saturated aqueous NaCl, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. After further drying under high-vacuum pump (0.01 mmHg/25 °C), a bright yellow oil was obtained (127.4 mg). Separation of the products by column chromatography on silica gel (gradient elution from 0 to 5% EtOAc in petroleum ether) provided 96.4 mg (90%) of the naphthoquinone **34** as a yellow solid: R_f 0.39 (5% EtOAc in petroleum ether); yellow prisms from ethyl acetate and petroleum ether; mp 70–71 °C (lit.[9a,40] mp 67–69 °C). A second major compound (9.6 mg, 7.4%) was isolated and identified as the monoketal **35**: yellow oil, R_f 0.13 (5% EtOAc in petroleum ether); ^1H NMR ($CDCl_3$) δ 1.14 (t, 3H, J = 7.4 Hz), 1.26 (t, 3H, J = 7.3 Hz), 2.50 (q, 2H, J = 7.4 Hz), 2.59 (q, 2H, J = 7.3 Hz), 2.88 (s, 6H), 7.45 (t, 1H, J = 7.2 Hz), 7.60 (t, 1H, J = 7.9 Hz), 7.65 (d, 1H, J = 7.1 Hz), 8.06 (d, 1H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.4, 14.3, 19.7, 20.3, 51.4, 98.6, 126.2, 126.3, 129.2, 132.9, 133.2, 139.3, 144.2, 153.1, 183.4; IR (neat, cm^{-1}) 2972 m, 2937 m, 2876 w, 2829 w, 1658 s, 1601 m, 1456 m, 1375 w, 1349 w, 1312 w, 1282 s, 1260 m, 1223 w, 1073 s, 865 w, 770 m, 724 w; mass spectrum (EI; m/z (% relative intensity)) 260 (100) M$^+$, 245 (36), 231 (96), 214 (89), 199 (46), 185 (24), 171 (27), 157 (18), 141 (15), 128 (28), 115 (21), 105 (38), 91 (12), 77 (35); m/z calcd for $C_{16}H_{20}O_3$ 260.1412, measd 260.1449. Two minor fractions were also isolated from this reaction. These were identified as the α,β-unsaturated lactone **37** (<0.6 mg, <0.5%) and the keto ester **39** (<0.6 mg, <0.5%) by comparison of their ^1H NMR spectra with those of

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authentic samples that were isolated and characterized from the reaction of the tungsten complex **7**. In addition the indene **27B** was detected (1.3%) in the ^{1}H NMR spectrum of the crude reaction mixture. Indene **27A** and cyclobutenone **30** were not detected either in the ^{1}H NMR spectrum of the crude reaction mixture or during the isolation process. The yield of the furan product **29** was judged to be less than 1% on the basis of the maximum combined yield of **37** and **39**, which, as will be described for the reaction of the tungsten complex **7**, are the oxidation products of the furan **29**.

Monoacetals of the type **35** have been obtained from related reactions that have employed an oxidative workup with 0.5 M ceric(IV) ammonium nitrate in anhydrous MeOH[6d] but have never been reported from oxidations in an aqueous medium. The monoketal **35** was found to slowly hydrolyze to the naphthoquinone **34** in air at room temperature with an approximate half-life of 8 days. Control experiments were performed to demonstrate that CAN treatment of the methoxynaphthol **28** provided exclusively a mixture of the naphthoquinone **34** and a small amount of the monoketal **35** (4–10 mol %). Therefore, a combined yield (97.4%) of **34** and **35** should reflect the yield of methoxynaphthol **28** in these reactions.

A 0.005 M solution of the carbene complex **17** (156 mg, 0.500 mmol) in THF (100 mL) containing 1.9 equiv of 3-hexyne was subjected to the same reaction conditions (34 h) described above. After an oxidative workup with CAN, isolation of the two major products gave 93.0 mg (87%) of the naphthoquinone **34** and 12.5 mg (9.6%) of the monoketal **35**. The ^{1}H NMR spectrum of the crude reaction mixture prior to oxidation revealed the presence of indene **27B** (1.7%) and the furan **29** (1.3%) and the absence of the indene **27A** and the cyclobutenone **30**.

In Benzene. A 0.1 M solution of the carbene complex **17** (156 mg, 0.500 mmol) in benzene (5 mL) containing 1.9 equiv of 3-hexyne was subjected to the reaction conditions (46 h) described in the general procedure. Prior to oxidation with CAN, the ^{1}H NMR spectrum of the crude reaction mixture revealed the presence of the naphthol **28** and a compound tentatively identified as the chromium tricarbonyl complex **36** in a ratio of 6:1 that was consistent over several runs. Attempts to isolate pure complex **36** failed because it decomposed quickly to the naphthol **28**. Complex **36**: R_f 0.06 (5% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$) δ 1.17 (t, 6H, J = 7.8 Hz), 2.69 (q, 4H, J = 7.8 Hz), 3.97 (s, 3H), 5.05 (brs, 1H), 5.45 (t, 1H, J = 5.5 Hz), 5.53 (t, 1H, J = 3.1 Hz), 6.38 (d, 1H, J = 5.6 Hz), 6.49 (d, 1H, J = 4.1 Hz). After an oxidative workup with CAN the products were separated on silica gel to the quinone **34** (98.1 mg, 92%) and the quinone monoacetal **35** (5.8 mg, 4.5%). A screen of all of the rest of the fractions collected from the column permitted an assignment of a maximum of 1% combined yield of **37** and **39** (and hence a maximum of 1% yield of the furan **29**). An examination of the ^{1}H NMR of the crude reaction mixture prior to oxidation showed an upper limit of 0.7% for the combined yield of indenes **27A** and **27B**, and no cyclobutenone **30** could be detected.

A 0.005 M solution of the carbene complex **17** (156 mg, 0.500 mmol) in benzene (100 mL) containing 1.9 equiv of 3-hexyne was subjected to the reaction conditions (64 h) described in the general procedure. The ^{1}H NMR spectrum of the crude reaction mixture prior to oxidation indicated a 1.5/1 ratio of **28**/**36** as the major products and the absence of indene **27B** and cyclobutenone **30**. After an oxidative workup with CAN the products were separated on silica gel to the quinone **34** (98.8 mg, 92%) and the quinone monoacetal **35** (4.8 mg, 3.7%). A fraction representing a maximum combined yield of 0.9% for **37** and **39** was also obtained from the column (and hence a maximum of 1% yield of the furan **29**). A mixture of the two compounds (0.6 mg, <0.6%) was obtained that were identified as the indenone **31** and indanone **32** by comparison of their ^{1}H NMR spectra with those of authentic samples obtained from the reaction of the tungsten complex **7**.

In Acetonitrile. A 0.1 M solution of the carbene complex **17** (156 mg, 0.500 mmol) in acetonitrile (5 mL) containing 1.9 equiv of 3-hexyne was subjected to the reaction conditions (20 h) described in the general procedure. No oxidative workup with CAN was employed. The indenes **27A** and **27B** were isolated by silica gel chromatography (1/1/40 mixture of ether/CH_2Cl_2/hexane, R_f 0.41 and 0.31, respectively) as colorless oils in a total of 25% yield (13/12 ratio). The yields of phenol **28** (32%), the furan **29** (<2%), and the cyclobutenone **30** (7%) were determined from the ^{1}H NMR spectrum of the crude reaction mixture. The reaction in acetonitrile at 0.005 M provided 23.3 mg (65%, isolated) of a 38/27 mixture of indenes **27A** and **27B**, and by ^{1}H NMR quinone **28** (12%), furan **29** (1%), and cyclobutenone **30** (11%) were identified. For all reactions in acetonitrile, (CH_3CN)$Cr(CO)_5$ was observed in 30–75% yield as determined by ^{1}H NMR.

Reaction of the Molybdenum Carbene Complex 26 with 3-Hexyne. In THF. A 0.1 M solution of the molybdenum carbene complex **26** (178.1 mg, 0.500 mmol) in THF (5 mL) containing 1.9 equiv of 3-hexyne was subjected to the reaction conditions (24 h) described in the general procedure for the chromium complex **17**. An oxidative workup with CAN was not employed. A 66/1 mixture of the indenex **27A** and **27B** was isolated in 67% yield (67.6 mg) by chromatography on silica gel (1/1/40 ether/CH_2Cl_2/hexane). The yields of the naphthol **28** and the furan **29** were determined to be 9% and 5%, respectively, from the ^{1}H NMR spectrum of the crude reaction mixture, in which the cyclobutenone **30** could not be detected. The reaction at 0.005 M was carried out in a similar manner and on the same scale to give a 71% yield of the indene **27A** (isolated), a 3% yield of **28** (^{1}H NMR), and a 2% yield of **29** (^{1}H NMR).

In Benzene. The reaction at 0.1 M was carried out in a similar manner and on the same scale as the reaction in THF to give a 74% yield of the indene **27A** (isolated), a 6% yield of **28** (^{1}H NMR), and a 15% yield of **29** (^{1}H NMR). The same reaction at 0.005 M gave a 66% yield of the indene **27A** (isolated), a 5% yield of **28** (^{1}H NMR), and an 8% yield of **29** (^{1}H NMR). Neither indene **27B** nor the cyclobutenone **30** were observed in either of these reactions. In the reaction at 0.005 M a 30% yield of a yellow compound was observed, which was identified as (η^6-C_6H_6)$Mo(CO)_3$ on the basis of the fact that it exhibited a singlet in the ^{1}H NMR at δ 5.52 ppm.

In Acetonitrile. The reaction at 0.1 M was carried out in a similar manner and on the same scale as the reaction in THF. After an oxidative workup with CAN, the two major products were isolated by chromatography on silica gel (2% EtOAc in petroleum ether) to give the quinone **34** (36%) and the quinone monoacetal **35** (3%). The other products from this reaction were quantified from the ^{1}H NMR spectrum of the crude reaction mixture prior to oxidation and found to be the indene **27A** (6%), the indene **27B** (<1%), the furan **29** (6%), and the cyclobutenone **30** (16%). The same reaction at 0.005 M gave a 63% yield of the quinone **34** (isolated), a 4% yield of the quinone monoacetal **35** (isolated), a 5% yield of **27A** (^{1}H NMR), a 6% yield of **29** (^{1}H NMR), and a 3% yield of **30** (^{1}H NMR). The ^{1}H NMR spectrum of the crude reaction mixture prior to oxidation looked much cleaner for the reaction at 0.0005 M (with the methoxynaphthol **28** as the major product). For all reactions in CH_3CN, a 30–70% yield of (CH_3CN)$Mo(CO)_5$ was observed in the ^{1}H NMR spectrum of the crude reaction mixture prior to oxidation.

In 2,2-Dimethylpropionitrile, Benzonitrile, and *o*-Methylbenzonitrile. A 0.005 M solution of the molybdenum carbene complex **26** (22.3 mg, 0.0625 mmol) in *o*-toluonitrile (12.5 mL) containing 1.9 equiv of 3-hexyne was subjected to the reaction conditions (50 h) described in the general procedure for the chromium complex **17**. *o*-Toluonitrile was removed under high vacuum (0.01 mmHg, 25 °C). After an oxidative workup with CAN, the major product was isolated by chromatography on silica gel to give the quinone **34** (68%). The other products from this reaction were quantified from the ^{1}H NMR spectrum of the crude reaction mixture prior to oxidation and found to be the indene **27A** (3%), the indene **27B** (<1%), the furan **29** (<0.5%), and the cyclobutenone **30** (23%). In this reaction (o-MeC_6H_4CN)$Mo(CO)_5$ was observed by ^{1}H NMR in >90% yield. The reaction in benzonitrile at 0.005 M gave a 31% yield of quinone **34** (isolated), a 3% yield of indene **27A** (^{1}H NMR), a 2% yield of indene **27B** (^{1}H NMR), a 1% yield of furan **29** (^{1}H NMR), and a 5% yield of the cyclobutenone **30** (^{1}H NMR). The reaction in 2,2-dimethylpropionitrile at 0.005 M gave a 26% yield of quinone **34** (isolated), a 4% yield of indene **27A** (^{1}H NMR), a 4% yield of furan **29** (^{1}H NMR), and a 2% yield of the cyclobutenone **30** (^{1}H NMR).

Reaction of the Tungsten Carbene Complex 7 with 3-Hexyne. In THF: Oxidation of the Furan Product 29. A 0.1 M solution of the carbene complex **7** (456 mg, 1.03 mmol) in THF (10.3 mL) containing 1.9 equiv of 3-hexyne was subjected to the reaction conditions (42 h) described in the general procedure for the reaction of the chromium complex **17**. At the halfway point of the reaction, another 1.9 equiv of the alkyne was added to ensure completion of the reaction. No oxidative workup with CAN was employed. The major product was isolated in pure form by chromatography on silica gel and identified as the indene **27A** (92.6 mg, 46%). From the ^{1}H NMR spectrum of the crude reaction mixture the yields of the minor products were calculated: indene **27B** (7%), naphthol **28** (6%), and furan **29** (33%). The cyclobutenone **30** could not be detected.

A 0.005 M solution of the carbene complex **7** (235 mg 0.529 mmol) in THF (106 mL) containing 1.9 equiv of 3-hexyne was subjected to the reaction conditions (75 h) described in the general procedure for the reaction of the chromium complex **17**. At the halfway point of the reaction, another 1.9 equiv of the alkyne was added to ensure completion of the reaction. No oxidative workup with CAN was employed. In this reaction the indene products were isolated by silica gel chromatography as a 51:6 mixture of **27A** and **27B** in a total of 57% yield (60.5 mg). The ^{1}H NMR spectrum of the crude reaction mixture indicated the presence of naphthol **28** (8%) and the absence of the cyclobutenone **30**. Also isolated from the silica gel column was a 17/9 mixture of two compounds identified as the lactone **37** and the keto ester **39** in a total yield of 26% (30.8 mg). Spectral data for **37**: colorless oil, R_f 0.22 (10% EtOAc in petroleum ether); ^{1}H NMR (CDCl$_3$) δ 0.99 (t, 3H, J = 7.5 Hz), 1.16 (t, 3H, J = 7.5 Hz), 2.01 (m, 1H), 2.35 (m, 3H), 5.66 (s, 1H), 7.15 (m, 2H), 7.34 (m, 3H); ^{13}C NMR (CDCl$_3$) δ 12.5, 13.1, 16.9, 19.6, 83.4, 126.8, 128.0, 128.8, 129.1, 134.9, 163.9, 174.4; IR (neat; cm^{-1}) 2971 m, 2936 m, 2877 w, 1751 s, 1670 m, 1456 m, 1308 w, 1104 m, 1085 m, 1003 m, 950 w, 778 w, 7 52 w, 700 s; mass spectrum (*m/z* (% relative intensity)) 216 (24) M$^+$, 187 (100), 181 (9), 171 (11), 159 (11), 153 (4), 141 (17), 128 (22), 117 (25), 111 (22), 105 (27), 91 (8), 83 (59); *m/z* calcd for $C_{14}H_{16}O_2$ 216.1150, measd 216.1159. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: 77.13; H, 7.40. Spectral data for **39**: colorless oil, R_f 0.31 (10% EtOAc in petroleum ether); ^{1}H NMR (CDCl$_3$) δ 1.06 (t, 3H, J = 7.6 Hz), 1.16 (t, 3H, J = 7.4 Hz), 2.45 (q, 2H, J = 7.6 Hz), 2.49 (q, 2H, J = 7.4 Hz), 3.39 (s, 3H), 7.40 (t, 2H, J = 7.5 Hz), 7.49 (t, 1H, J = 7.2 Hz), 7.80 (d, 2H, J = 7.9 Hz); ^{13}C NMR (CDCl$_3$) δ 12.4, 13.8, 21.4, 24.7, 51.6, 128.4, 128.6, 132.5, 132.9, 136.1, 151.4, 167.3, 198.4; IR (neat; cm^{-1}) 2980 s, 1740 s, 1670 s, 1600 m, 1580 m, 1450 m, 1320 m, 1250 s, 700 m; mass spectrum (*m/z* (% relative intensity)) 246 (5) M$^+$, 214 (28), 199 (6), 169 (11), 105 (93), 77 (34), 69 (100); *m/z* calcd for $C_{15}H_{18}O_3$ 246.1256, measd 246.1247.

It was suspected that the lactone **37** and the keto ester **39** were secondary products of the reaction and that they were derived from the furan **29** by hydrolysis and oxidation, respectively. The furan **29** is very sensitive but can be isolated in pure form by chromatography on deoxygenated silica gel that also has been pretreated with triethylamine.[39] Spectral data for furan **29**: colorless oil, R_f 0.54 (1/1/20, ether/CH$_2$Cl$_2$/hexane); ^{1}H NMR (CDCl$_3$) δ 1.15 (t, 3 H, J = 7.6 Hz), 1.22 (t, 3 H, J = 7.6 Hz), 2.32 (q, 2 H, J = 7.6 Hz), 2.60 (q, 2 H, J = 7.6 Hz), 3.93 (s, 3 H), 7.33–7.39 (m, 3 H), 7.50–7.53 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 12.4, 13.8, 21.5, 24.7, 51.5, 128.5, 128.6, 132.6, 132.8, 136.3, 151.3, 167.3, 198.3; IR (neat; cm^{-1}) 3030 m, 2980 s, 1720 m, 1 650 m, 1520 m, 1430 m, 1075 m, 1025 m, 730 s, 700 s; mass spectrum (EI; *m/z* (relative intensity)) 230 M$^+$ (24), 215 (44), 199 (7), 169 (12), 105 (100); *m/z* calcd for $C_{15}H_{18}O_2$ 230.1306, measd 230.1310. Control experiments were done to show that the oxidative workup with the 0.5 M ceric ammonium nitrate solution in 0.1 M aqueous nitric acid employed in this work consistently gave a 2/1 mixture of the hydrolysis product **37** and the oxidation product **39**. Hence, in those reactions employing an oxidative workup the yield of the furan can be reliably taken as the combined yield of **37** and **39**.

In Benzene: Oxidation of the Indene Products 27A and 27B. A 0.1 M solution of the carbene complex **7** (145 mg, 0.327 mmol) in benzene (3.3 mL) containing 1.9 equiv of 3-hexyne was subjeced to the reaction conditions (42 h) described in the general procedure for the reaction of the chromium complex **17**. At the halfway point of the reaction, another 1.9 equiv of the alkyne was added to ensure completion of the reaction. The ^{1}H NMR spectrum of the crude reaction mixture prior to oxidation indicated that it contained a mixture of **27A**, **31**, **32**, and **33** in ratios that varied with a particular run. The yields of naphthol **28** (3%) and furan **29** (6%) were constant and were determined by ^{1}H NMR relative to the isolated yield of indenone **31**. The indene **27B** and cyclobutenone **30** were not detected in any of the runs. Attempts were made to isolate the (indene)tungsten tricarbonyl complex **33** in pure form but were met with failure due to its rapid decomposition to **27A** and **32**. Spectral data for **33**: R_f 0.08 (5% EtOAc in petroleum ether); ^{1}H NMR (CDCl$_3$) δ 1.08 (t, 3H, J = 7.5 Hz), 1.20 (m, 3H), 1.25 (m, 1H), 1.99 (m, 1H), 2.26 (hex, 1H, J = 7.2 Hz), 2.58 (hex, 1H, J = 7.2 Hz), 3.09 (m, 1H), 3.79 (s, 3H), 5.09 (t, 1H, J = 5.5 Hz), 5.55 (t, 1H, J = 5.0 Hz), 5.60 (d, 1H, J = 5.8 Hz), 5.97 (d, 1H, J = 5.8 Hz). After an oxidative workup of the crude reaction mixture with CAN the major products were purified by column chromatography on silica gel (gradient elution from 0 to 5% EtOAc in petroleum ether) and identified as the indanone **32** (25.7 mg, 42%) and the indenone **31** (27.0 mg, 44%). Spectral data for indenone **31**: bright yellow oil, R_f 0.19 (1/1/20 ether/CH$_2$Cl$_2$/hexane); R_f 0.37 (5% EtOAc in petroleum ether); ^{1}H NMR (CDCl$_3$) δ 1.07 (t, 3H, J = 7.5 Hz), 1.22 (t, 3H, J = 7.6 Hz), 2.27 (q, 2H, J = 7.5 Hz), 2.54 (q, 2H, J = 7.6 Hz), 7.00 (d, 1H, J = 7.3 Hz), 7.11 (t, 1H, J = 7.4 Hz), 7.27 (t, 1H, J = 7.8 Hz), 7.33 (d, 1H, J = 6.9 Hz); ^{13}C NMR (CDCl$_3$) δ 12.5, 14.1, 15.9, 19.3, 118.8, 121.7, 127.9, 131.1, 133.1, 135.5, 145.3, 158.6, 198.4; IR (neat; cm^{-1}) 2969 m, 2934 m, 2831 w, 1706 s, 1624 w, 1608 w, 1592 w, 1456 m, 762 w, 723 m; mass spectrum (EI; *m/z* (relative intensity)) 186 (60) M$^+$, 171 (39), 157 (35), 149 (100), 129 (32), 115 (22), 105 (29), 97 (22), 91 (34), 83 (34); *m/z* calcd for $C_{13}H_{14}O$ 186.1045, measd 186.1054. Spectral data for indanone **32**: colorless oil, R_f 0.14 (1/1/20 ether/CH$_2$Cl$_2$/hexane); R_f 0.34 (5% EtOAc in petroleum ether); ^{1}H NMR (CDCl$_3$) δ 0.96 (t, 3H, J = 7.4 Hz), 1.00 (t, 3H, J = 7.4 Hz), 1.71 (m, 2H), 188 (m, 2H), 2.32 (m, 1H), 3.04 (quintet, 1H, J = 3.8 Hz), 7.36 (t, 1H, J = 7.4 Hz), 7.48 (d, 1H, J = 7.4 Hz), 7.60 (t, 1H, J = 8.0 Hz), 7.72 (d, 1H, J = 7.5 Hz); ^{13}C NMR (CDCl$_3$) δ 11.4, 11.5, 24.9, 28.5, 45.3 , 54.2, 123.6, 125.6, 127.4, 134.6, 136.5, 157.7, 209.1; IR (neat; cm^{-1}) 2963 s, 2933 s, 2860 m, 2875 w, 1711 s, 1606 m, 1462 m, 1287 w, 750 m; mass spectrum (EI; *m/z* (relative intensity)) 188 (13) M$^+$, 179 (5), 173 (6), 160 (100), 145 (41), 131 (38), 123 (14), 111 (28), 105 (11), 97 (41), 91 (23), 83 (41); *m/z* calcd for $C_{13}H_{16}O$ 188.1201, measd 188.1181.

Control experiments showed that CAN oxidation of the isolated indene mixture did not affect indene **27B** but transformed indene **27A** to a mixture (<1/6) of indenone **31**, the oxidative product, and indanone **32**, the hydrolysis product. Oxidation of purified **27A** with CAN also resulted in a <1/6 mixture of **31** and **32**. Oxidation of the indanone **32** with CAN at room temperature under single-phase (THF/CAN) or two-phase conditions (CH$_2$Cl$_2$/CAN) provided no indenone **31**, and **32** was recovered quantitatively. Only with SeO$_2$ in the presence of acetic acid in refluxing *t*-BuOH for 13 h was it possible to find conditions under which **32** could be oxidized to **31**.[41] It was clear from these experiments that CAN oxidation did not affect indene **27B** and led to the preferential hydrolysis of **27A** to the indanone **32** rather than oxidation to the indenone **31**. Moreover, direct hydrolysis of **27A** under the standard procedure for hydrolysis of enol ethers[42]

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(41) Bernstein, S.; Littell, R. *J. Am. Chem. Soc.* **1960**, *82*, 1235.

(42) (a) Coulsen, D. R. *Tetrahedron Lett.* **1964**, *3323*. (b) Fife, T. H. *J. Am. Chem. Soc.* **1965**, *87*, 1084.

quantitatively yielded a mixture of the indanone **32** and an unknown compound in a 4/1 ratio. The unknown minor product was not fully characterized but was shown to form **32** quantitatively when treated with aqueous 6 N HCl at room temperature. The minor unknown product has the following spectral data: R_f 0.34 (5% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$) δ 0.81 (t, 3H, J = 7.4 Hz), 1.11 (t, 3H, J = 7.5 Hz), 1.40 (m, 1H), 1.55 (m, 1H), 2.61 (m, 1H), 3.40 (dd, 1H, J = 7.2, 12.7 Hz), aromatic protons appeared as a multiplet. This hydrolysis experiment showed that the indanone **32** is not oxidized to the indenone **31** either in air under acidic conditions or with CAN under acidic conditions. Finally and most interestingly, CAN oxidation of the indene mixture in the original crude reaction mixture quantitatively gave the recovered indene **27B** and a mixture of **31** and **32** with an average ratio of 1/1.5. One explanation for the increase in the amount of indenone **31** product relative to the controlled oxidation of **27A** is that the oxidation of indene **27A** may be occurring, partially at least, via its metal complex. These experiments do reveal that the combined yield of **31** and **32** after CAN treatment should reflect the overall yield of **27A**.

A 0.005 M solution of the carbene complex **7** (235 mg, 0.529 mmol) in benzene (106 mL) containing 1.9 equiv of 3-hexyne was subjected to the reaction conditions (73 h) described in the general procedure for the reaction of the chromium complex **17**. At the halfway point of the reaction, another 1.9 equiv of the alkyne was added to ensure completion of the reaction. Again a variable mixture of **27A**, **31**, **32**, and **33** was observed in the crude reaction mixture by ^{1}H NMR prior to the oxidative workup. The yields of naphthol **28** (2%) and furan **29** (1%) were determined by ^{1}H NMR relative to the isolated yield of indenone **31**, and the indene **27B** and cyclobutenone **30** were not detected. After an oxidative workup, the indanone **32** (36.2 mg, 36%) and the indenone **31** (30.4 mg, 31%) were isolated by silica gel chromatography.

In Acetonitrile. A 0.005 M solution of the carbene complex **7** (145 mg, 0.327 mmol) in acetonitrile (65.4 mL) containing 1.9 equiv of 3-hexyne was subjected to the reaction conditions (62 h) described in the general procedure for the reaction of the chromium complex **17**. At the halfway point of the reaction, another 1.9 equiv of the alkyne was added to ensure completion of the reaction. The ^{1}H NMR spectrum of the crude reaction mixture indicated a major product with a singlet at δ 2.33. This compound was isolated with an average yield of 43% via column chromatography (40% CH_2Cl_2 in hexane) and was identified as $(CH_3CN)W(CO)_5$: R_f 0.37 (40% CH_2Cl_2 in hexane); ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 3.95 ($(CH_3CN)W(CO)_5$), 123.2 ($(CH_3CN)W(CO)_5$), 196.5, 199.7; IR (neat; cm^{-1}) 2973 w, 2969 w, 2935 w, 2927 w, 2075 m, 1909 s, 1885 s; mass spectrum (m/z (% relative intensity)) 365 (61) M^+, 337 (9) $M^+ - 1CO$, 309 (63) $M^+ - 2CO$, 281 (100) $M^+ - 3CO$, 253 (66) $M^+ - 4CO$, 225 (74) $M^+ - 5CO$, 184 (14) $M^+ - 5CO - CH_3CN$. This complex was more stable in methylene chloride and CH_3CN than in $CDCl_3$ or benzene but decomposed readily in air with a half-life of <1 h. It has a much longer lifetime under Ar at −10 °C. Carbonyl complexes with more than one CH_3CN ligand were also observed but were not isolated. All other products from this reaction were generated in low yields. From the average of several runs this reaction produces the indenes **27A** and **27B** (5/2 ratio) in 7% yield and the methoxynaphthol **28** in 4% yield. From the ^{1}H NMR spectrum of the crude reaction mixture the other products that could be quantitated are the furan **29** (2%), the lactone **38** (3%), and methyl benzoate (3%). It was interesting to note that lactone **38** was only observed in other reactions in CH_3CN in Table 1 where the cyclobutenone **30** was formed. Presumably **30** was oxidized by CAN to provide **38**.[5d]

General Procedure for the GC Analysis of the Reactions of 1-Pentyne with Phenylcarbene Complexes 17, 26, and 7. The following procedure was developed and utilized for analysis of all of the reactions of the phenyl complexes **17**, **26**, and **7** with 1-pentyne. Unless otherwise specified, the reaction mixture was divided into two parts in a 9/1 ratio by volume and the large portion was used to determine isolated yields and the smaller for GC yields. After addition of triphenylmethane standard to the smaller portion, an alliquot (1–2 mL) was filtered through a pipet-size silica gel column (triethylamine pretreatment of the silica gel was necessary for reactions where the indene **40**, furan **42**, and/or enol ether **51** were major product(s)) and diluted with 1–2 mL of CH_2Cl_2. The filtrate was stirred with a micromagnet to ensure homogeneity and used for analysis. The yields of the products were directly calibrated from the GC trace against the standard and were confirmed in duplicate runs. The analyses were performed on an Alltech 30 M × 0.32 mm SE-54 capillary column. The GC parameters were as follows: H_2 (41 psi); air (54 psi); He (72 psi); pressure (12.1 psi); flow (2.0 mL/min); velocity (36.0 cm/s); split ratio (49); initial column temp (100 °C); initial hold time (2 min); final column temp (225 °C); ramp rate (10 °C/min). Each of the reaction products were purified (≥90% by GC) prior to the determination of their response factor against triphenylmethane. The retention times in minutes and the response factors (in parentheses) for all possible primary and secondary (oxidized and hydrolyzed) products are as follows: triphenylmethane 14.62 (1.00); **40**, 8.83 (1.09); **41**, 14.02 (2.29); **42**, 11.31 (1.46); **43**, 17.23 (1.46); **44**, 14.52 (1.30); **45**, not determined; **46**, 9.08 (1.55); **47**, 11.32 (1.37); **47a**, 13.35 (1.31); **48**, not determined; **49**, 11.94 (1.45); **50**, 11.96 (1.92); **51**, 11.54 (2.20); **52**, not determined; **53a**/**53b**, 11.39/11.53; **54** and **55**, not determined. The column was baked until an injection of solvent gave a solvent integrated area of >99.85% for the normal run time. Isolated yields were not determined for each product from each reaction in Table 2 (isolated yields in parentheses), but a comparison of GC and isolated yields was made at least once for most products.

General Procedure for Reactions of 1-Pentyne with Phenylcarbene Complexes Illustrated for the Chromium Complex 17. In THF. To a 0.1 M solution of the chromium phenylcarbene complex **17** (312.1 mg, 1.00 mmol) in 10.0 mL of THF in a 25-mL single-necked pear-shaped flask, in which the 14/20 joint had been replaced by a high-vacuum threaded Teflon stopcock, and under an argon atmosphere was added 186.3 μL of 1-pentyne (1.90 mmol, 1.9 equiv). The reaction mixture was then deoxygenated by the freeze–thaw method, and the flask was closed under 1 atm of argon at room temperature. The flask was heated at 80 °C, and the progress of the reaction was monitored by TLC (1/1 20 ether/CH_2Cl_2/hexanes or 5% EtOAc in petroleum ether). The reaction was complete in 24 h, and then the flask was opened under a stream of argon and 17.8 mg of triphenylmethane was added as the GC internal standard. In order to ensure the homogeneity of the crude reaction mixture, 5–10 mL of CH_2Cl_2 was usually added after the addition of triphenylmethane. After the mixture was stirred under Ar at room temperature for 15 min, a small aliquot was concentrated, taken up in CH_2Cl_2, filtered through a pipet-size silica gel column, and concentrated. A crude proton NMR spectrum of this sample was recorded, with accurate integrations taken in the methoxy region (2.75–4.25 ppm). The crude reaction mixture was then divided into parts A, B, and C in a volume ratio of 2/1/1.

Part A of the crude reaction mixture was stirred with a 0.5 M solution of ceric ammonium nitrate in 0.1 M HNO_3. The organic layer was separated and stripped of solvent, and seven products were separated from the residue by gradient elution (0–5% EtOAc in petroleum ether) from a silica gel column. The major product isolated (R_f 0.28; 5% EtOAc in petroleum ether) was the quinone **47** (73.2 mg, 73%), which was obtained as yellow prisms from methylene chloride/hexane; mp 37–38 °C (lit.[43] mp 37–39 °C). Quinone **47** was characterized by its ^{1}H NMR and IR spectra, which matched those in the literature,[9a,43] and by its ^{13}C NMR spectrum ($CDCl_3$): δ 13.8, 21.2, 31.5, 125.9, 126.5, 132.0, 132.2, 133.5, 134.7, 151.6, 185.2 (2 aryl C's were not located and presumably overlap). A minor product was obtained as a yellow oil (3.6 mg, 3%; R_f 0.14, 5% EtOAc in petroleum ether) and identified as the quinone **47a**, in which the propyl group of the quinone **47** is hydroxylated at the α-position. This side product

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[43] Mikhailov, B. M.; Ter-Sarkisyan, G. S.; Nikolaneva, N. A. *Zh. Obshch. Khim.* 1971, *41*, 172.

has been previously seen in CAN oxidations of **47**,[9a] and thus the total yield of **47** is 76%. A second minor product (1.8 mg, 2%) was isolated (R_f 0.16, 5% EtOAc in petroleum ether) and identified as the indanone **46** by comparison of its spectra with those of the product characterized from this same reaction at 0.005 M (*vide infra*). A third minor product (6.8 mg, 6%) was isolated (R_f 0.11, 5% EtOAc in petroleum ether) and identified as the keto ester **49** (from furan **42**) by comparison of its spectra with those of the product characterized from the reaction of the molybdenum complex **26**. A fourth minor product (0.6 mg, <0.5%) was isolated (R_f 0.38, 5% EtOAc in petroleum ether) and identified as the two-alkene phenol **44** by comparison of its spectra with those of the product characterized from the reaction of the molybdenum complex **26**. Two other minor products were detected, both of which appeared to have incorporated at least 3 equiv of 1-pentyne but whose structures could not be unambiguously assigned. Unknown I (2.6 mg): R_f 0.33 (5% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$) δ 0.85 (m, 9H), 1.00 (t, 4H, J = 7.1 Hz), 1.38–1.59 (m, 14H), 1.74–2.11 (m, 11 H), 2.71 (br s, 2H), 5.52 (s, 1H), 6.90 (s, 1H); IR (neat; cm^{-1}) 2960 s, 2932 s, 2907 w, 2873 m, 1775 s, 1700 s, 1457 w; mass spectrum (m/z (% relative intensity)) 300 (24) M$^+$, 257 (100), 215 (9), 187 (5), 175 (6), 164 (16), 145 (7), 129 (8), 117 (7), 105 (8). Unknown II (1.7 mg): R_f 0.39 (5% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$) δ 0.83 (t, 3H, J = 6.8 Hz), 0.88 (t, 3H, J = 7.3 Hz), 0.95 (t, 3H, J = 7.3 Hz). 0.99 (t, 3H, J = 7.2 Hz), 1.16 (t, 2H, J = 8.9 Hz), 1.27–1.56 (m, 8H), 1.67–1.83 (m, 5H), 2.11 (br s, 2H), 2.63 (brs, 1H), 5.93 (d, 1H, J = 6.8 Hz), 6.08 (d, 1H, J = 6.8 Hz), 6.91 (s, 1H); IR (neat; cm^{-1}) 2959 s, 2933 s, 2872 m, 1773 s, 1700 s, 1457 w; mass spectrum (m/z (% relative intensity)) 300 (40) M$^+$, 257 (100), 229 (6), 215 (9), 164 (7), 129 (6), 105 (5).

Part B of the crude reaction mixture was subjected to direct column chromatography without CAN oxidation. Chromatographic separation on silica gel (gradient elution from 0 to 4% EtOAc in petroleum ether) provided the naphthol **41** as the major product as a colorless waxy semisolid (35.6 mg, 66%). Spectral data for naphthol **41**: R_f 0.22 (5% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$) δ 1.01 (t, 3H, J = 7.3 Hz), 1.71 (sext, 2H, J = 7.4 Hz), 2.71 (t, 2H, J = 7.6 Hz), 3.93 (s, 3H), 4.70 (br s, 1H), 6.54 (s, 1H), 7.41 (t, 1H, J = 7.2 Hz), 7.45 (t, 1H, J = 7.1 Hz), 8.03 (d, 1H, J = 8.3 Hz), 8.12 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0, 23.4, 32.5, 55.7, 106.2, 120.9, 121.3, 121.8, 124.7, 124.9, 125.6, 125.9, 141.7, 149.4; IR (neat; cm^{-1}) 3441 br, w, 2959 s, 2931 m, 2871 w, 1685 w, 1598 m, 1461 s, 1383 s, 1270 m, 1231 m, 1195 w, 1167 w, 1127 s, 1099 s, 764 s; mass spectrum (m/z (% relative intensity)) 216 (66) M$^+$, 187 (41), 164 (20), 132 (49), 105 (25), 78 (100); m/z calcd for $C_{14}H_{16}O_2$ 216.1150, measd 216.1144. A second pure compound (4.0 mg, 4%) was also collected and determined to be the ether **55**. Spectral data for **55**: yellow oil, R_f 0.29, 5% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$) δ 0.49 (t, 3H, J = 7.3 Hz), 0.92 (m, 2H), 1.00 (t, 3H, J = 7.3 Hz), 1.12 (t, 3 H, J = 7.3 Hz), 1.15 (m, 2H), 1.61 (m, 2H), 1.90 (m, 3H), 1.99 (m, 3H), 2.89 (d, 1H, J = 6.0 Hz), 2.99 (dt, 1H, J = 6.0, 13.7 Hz), 3.93 (s, 3H), 6.58 (s, 1H), 6.93 (s, 1H), 7.36 (t, 1H, J = 7.6 Hz), 7.43 (t, 1H, J = 7.5 Hz), 8.03 (d, 1H, J = 8.3 Hz), 8.10 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 12.6, 13.0, 14.6, 17.7, 20.5, 21.0, 26.0, 39.6, 41.2, 54.9, 55.8, 86.6, 101.9, 120.7, 121.9, 124.8, 125.4, 126.1, 127.1, 142.4, 148.4, 150.5, 153.1, 155.4, 207.4; IR (neat; cm^{-1}) 2960 s, 2932 m, 2873 w, 1707 s, 1459 s, 1384 s, 1221 w, 1105 w, 766 m; mass spectrum (m/z (% relative intensity)) 380 (37) M$^+$, 215 (100), 199 (16), 164 (14); m/z calcd for $C_{25}H_{32}O_3$ 380.2351, measd 380.2359. Ether **55** could be have arisen from the Michael addition of phenol **41** to a cyclopentadienone,[44] and if so, the total yield of **41** would be 70%. The two unknown products isolated from part A were also isolated from part B in similar yields. No indene **40** or furan **42** was isolated from part B but were identified in both parts A and B. The known ketene-trapped product **48** was detected in the crude ^{1}H NMR spectrum of part B (<1%).[9a] The indene **45** was not found in this or any other reaction of the phenyl complexes **7**, **17**, and **26** with 1-pentyne. The unoxidized crude reaction mixtures were screened for **45** by ^{1}H NMR by examination of the methoxy region. For those reactions producing ≥20% yields of indene **40**, a limit of 1% yield of **45** can be set on the basis of unassigned methoxy groups in the region δ 2.80–3.25.

Part C of the crude reaction mixture which contained the internal standard triphenylmethane as described above was analyzed by capillary GC according to the procedure outlined below. From the GC analysis the following yields were obtained: **40**, 2%; **41**, 84%; **42**, 10%; **44**, 0.5%. No secondary products were observed in GC traces, except the indanone **46**, which did appear in some runs.

The reaction was repeated at 0.005 M in carbene complex **17** (78.0 mg, 0.250 mmol) with 46.6 µL of 1-pentyne (0.47 mmol, 1.9 equiv) in 50 mL of THF according to the procedure described above (50 h). The following yields were determined by GC analysis: **40**, 12%; **41**, 60%; **42**, 7%; **44**, 0.5%. From the crude ^{1}H NMR a 1.6% yield of **48** was observed. The indene **40** was isolated by column chromatography on silica gel (gradient elution from 0 to 5% EtOAc in petroleum ether). Spectral data for **40**: colorless oil, R_f 0.47 (5% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3H, J = 7.2 Hz), 1.41 (m, 3H), 1.89 (m, 1H), 3.38 (m, 1H), 3.82 (s, 3H), 5.28 (d, 1H, J = 2.3 Hz), 7.23 (m, 2H), 7.34 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.4, 21.0, 34.9, 45.5, 56.6, 103.0, 117.9, 122.8, 125.5, 126.2, 127.4, 134.6, 147.4; IR (neat; cm^{-1}) 2957 s, 2931 s, 2871 m, 1619 s, 1601 s, 1578 m, 1460 m, 1372 s, 1132 s, 758 s, 740 s; mass spectrum (m/z (% relative intensity)) 188 (46) M$^+$, 159 (100), 146 (53), 131 (19), 115 (23), 105 (34), 91 (23), 77 (25); m/z calcd for $C_{13}H_{16}O$ 188.1201, measd 188.1193. Indene **40** was very sensitive to hydrolysis to **46** but could be isolated if silica gel column was packed with dry triethylamine and allowed to sit for 30–45 min before the column was "rinsed" with petroleum ether. The solvents used were purged with Ar prior to the preparation of the gradient solvent mixtures, and a few drops of the amine were added to each gradient prior to use. The indene **40** was isolated in amounts sufficient for characterization, but not without substantial hydrolysis to the indanone **46**. Control experiments were conducted to show that the hydrolysis of **40** quantitatively produced the indanone **46**. Spectra data for indanone **46**: ^{1}H NMR ($CDCl_3$) δ 0.97 (t, 3H, J = 6.6 Hz), 1.44 (m, 3H), 1.88 (m, 1H), 2.35 (dd, 1H, J = 1.4, 18.5 Hz), 2.84 (dd, 1H, J = 7.8, 18.5 Hz), 3.35 (m, 1H), 7.33 (t, 1H, J = 7.4 Hz), 7.46 (d, 1H, J = 7.5 Hz), 7.55 (t, 1H, J = 7.4 Hz), 7.69 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 20.8, 38.1, 38.3, 43.1, 123.5, 125.6, 127.4, 134.6, 136.7, 159.0, 206.6; IR (neat; cm^{-1}) 2958 m, 2918 m, 2872 w, 1714 s, 1604 w, 1464 w, 1282 w, 759 m; mass spectrum (m/z (% relative intensity)) 174 (37) M$^+$, 132 (100), 105 (42), 91 (8), 77 (37); m/z calcd for $C_{12}H_{14}O$ 174.1045, measd 174.1047.

In Benzene. A 0.005 M solution of the chromium carbene complex **17** (312.1 mg, 1.00 mmol) in benzene (10 mL) containing 1.9 equiv of 1-pentyne was heated at 80 °C for 36 h. The reaction mixture was analyzed according to the procedures discussed above for the reaction in THF. It was then diluted with CH_2Cl_2 to assure homogeneity and divided into two parts in a 9/1 ratio by volume. Triphenylmethane was added to the smaller portion for GC analysis, from which the following products were quantified: **40**, 1%; **41**, 64%; **42**, 4%; **43**, 10%; **44**, 1%. The products of the reaction were separated from the larger portion by column chromatography on silica gel (gradient elution 0–8% EtOAc in petroleum ether) without an oxidative workup with CAN. The major fraction (139.1 mg) isolated cleanly consisted of two major products, the naphthol **41** and cyclopentendione **43** with a ratio of 7.55/1 in 60% and 8% yields, respectively calculated from ^{1}H NMR. These compounds could not be separated, since they coeluted (both have R_f 0.22 in 5% EtOAc in petroleum ether). Hence, the mixture of **41** and **43** (7.55/1) was oxidized with CAN. The postoxidation ^{1}H NMR spectrum showed two clean products: the quinone **47** and cyclopentenedione **43** with a ratio of 7.43/1. The mass recovery was quantitative. This experiment provided 2-fold information: the oxidation of naphthol **41** provides exclusively the quinone **47** (with occasionally a

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(44) Yamashita, A.; Timko, J. M.; Watt, W. *Tetrahedron Lett.* 1988, *29*, 2513.

minor trace of the α-hydroxylated quinone **47a**), and CAN oxidation does not give **43**. The cyclopentenedione **43** could be separated from the quinone **47** (R_f 0.28 in 5% EtOAc in petroleum ether) cleanly via preparative TLC (5% EtOAc in petroleum ether, 0.25-mm plate, one elution). The cyclopentenedione **43** has been previously reported from this reaction,[9a,17a] but its structure and stereochemistry have not been unambiguously assigned. Spectral data for **43**: ^{1}H NMR (CDCl$_3$) δ 0.89 (t, 3H, *J* = 7.3 Hz), 1.06 (t, 3H, *J* = 7.4 Hz), 1.26 (m, 2H), 1.70 (m, 2H), 1.84 (t, 2H, *J* = 8.5 Hz), 2.52 (t, 2H, *J* = 7.8 Hz), 3.19 (s, 3H), 4.99 (s, 1H), 6.93 (s, 1H), 7.30–7.33 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 13.82, 14.34, 17.79, 20.39, 27.57, 37.25, 54.99, 56.91, 111.29, 127.03, 128.31, 128.73, 133.97, 142.05, 156.48, 164.38, 205.27, 206.13; IR (neat; cm^{-1}) 3059 w, 2961 m, 2932 m, 2880 m, 1743 w, 1700 s, 1648 m, 1614 w, 1450 m, 1327 m, 1227 m, 1085 m, 671 w, 670 m; mass spectrum (*m/z* (% relative intensity)) 312 (100) M$^+$ 281 (12), 269 (13), 252 (8), 223 (18), 115 (22), 105 (58), 91 (17), 77 (44). The stereochemistry about the enol ether double bond of **43** was determined by an NOE experiment. Upon irradiation of **43** (in C$_6$D$_6$ in a sealed NMR tube) at the vinyl singlet at 5.13 ppm a 4.5% NOE enhancement was observed at 7.20 ppm, corresponding to the ortho phenyl proton multiplet and implying the *Z* configuration. The benzene solution was then irradiated in a Rayonet apparatus for 48 h, at which time a second set of proton resonances was observed (1/3 ratio relative to **43**). Irradiation of the new vinyl singlet at 4.7 ppm resulted in 3.4% NOE enhancement of the methoxy resonance at 3.30 ppm; a corresponding 5.8% NOE at 4.7 ppm was observed upon irradiation at 3.3 ppm. The NMR tube was then opened up, and the new compound was isolated as a pale yellow oil by chromatography and identified as the *E* double-bond isomer of **43** (thus confirming the *Z* configuration **43**) on the basis of the following spectral data: ^{1}H NMR (CDCl$_3$) δ 0.81 (t, 3H, *J* = 7.1 Hz), 0.87 (t, 3H, *J* = 7.3 Hz), 0.9–1.1 (m, 2H), 1.2–1.4 (m, 2H), 1.78 (t, 2H, *J* = 8.4 Hz), 1.85–1.95 (m, 1H), 2.0–2.2 (m, 1H), 3.68 (s, 3H), 4.66 (s, 1H), 6.35 (t, 1H, *J* = 1.5 Hz), 6.96 (dd, 2H, J_1 = 7.9 Hz, J_2 = 1.5 Hz), 7.15–7.25 (m, 3H); ^{13}C NMR (CDCl$_3$) δ 13.9, 14.3, 17.9, 19.9, 27.2, 39.8, 53.7, 55.4, 99.3, 127.9, 128.7, 129.9, 135.8, 142.4, 159.1, 164.4, 206.5, 207.5; IR (neat; cm^{-1} 3060 w, 2970 s, 2934 m, 2874 m, 1785 w, 1742 w, 1700 s, 1647 m, 1613 w, 1603 w, 1465 m, 1380 m, 1216 s, 1127 m, 767 m, 702 m.

This reaction in benzene was also performed at 0.005 M in carbene complex in the same manner (70 h). The following products were identified and quantified by GC analysis: **40**, 1%; **41**, 59%; **42**, 8%; **43**, 5%; **44**, 3%. The yield of the cyclopentenedione **43** was confirmed by isolation (6%).

In Acetonitrile. The reaction of the chromium complex **17** (312.1 mg, 1.00 mmol) was carried out at 0.1 M in acetonitrile (10 mL) with 1.9 equiv of 1-pentyne by the procedure described above (80 °C, 38 h). GC analysis provided the following results: **40**, 9%; **41**, 48%; **42**, 7%; **44**, 2%. From the ^{1}H NMR spectrum of the crude reaction mixture it was determined that the ketene trapping product **48** was formed in 24% yield. The presence of the known lactone **52**[7] in 0.5% yield was based on the presence of a methoxy absorption at δ 3.28 in the ^{1}H NMR spectrum of the crude reaction mixture. The lactone **52** has been isolated previously[9a] but only after the CAN oxidation (presumably the oxidative product of the cyclobutenone **54**). Since cyclobutenone products are predominately observed in acetonitrile solvent, this reaction mixture was carefully screened for the cyclobutenone **54**.[9a] Column chromatography on silica gel (gradient elution from 0 to 5% EtOAc in petroleum ether) provided 10 or more fractions in which 4–5 fractions contained the pure products indicated in Table 2. All fractions were screened by IR for absorptions in the range 1740–1770 cm^{-1}. Only one fraction had any significant absorption in that range (1759 cm^{-1}), and it was found to be a mixture of the naphthol **41** and a minor product (0.5%) which was tentatively assigned as the lactone **52** based on the basis of the methoxy absorption at δ 3.28 and the fact that a carbonyl stretch at 1760 cm^{-1} has been reported for this compound.[9a] Thus, no significant amount of cyclobutenone **54** was formed in this reaction. The ^{1}H NMR spectrum of the crude reaction mixture also revealed the presence of (CH$_3$CN)Cr(CO)$_5$ in yields ranging from 50 to 90% for all reactions in acetonitrile.

This reaction in acetonitrile was also performed at 0.005 M in carbene complex in the same manner (50 h). The following products were identified and quantified by GC analysis: **40**, 2%; **46**, 1%; **41**, 75%; **42**, 1%; **44**, 5%. From the ^{1}H NMR spectrum of the crude reaction mixture a 1.4% yield of **48** and a 3% yield of **52** were observed. This reaction was also screened for the cyclobutenone **54** as described above, but no substantial amount could be detected.

Reaction of the Molybdenum Complex 26 with 1-Pentyne. In THF: Oxidation of Furan Product 42. The reaction of the molybdenum carbene complex **26** (356.1 mg, 1.00 mmol) with 1.9 equiv of 1-pentyne was carried out at 0.1 M in THF (10 mL) according to the procedure described for the same reaction for the chromium complex **17** (25 h). The crude reaction mixture was divided into two equal parts by volume. To the first part was added triphenylmethane as internal standard, and analysis by GC gave the following results: **40**, 19%; **46**, 2%; **42**, 25%; **44**, 20%. In addition, a 5% yield of phenol **41** and a 20% yield of enol ether **51** were calculated from the ^{1}H NMR spectrum of the crude reaction mixture.

The second part of the crude reaction mixture was utilized for the determination of the isolated yields of the products from this reaction. The crude residue was directly loaded onto a chromatography column that had been prepared from silica gel pretreated with triethylamine, and the products were eluted with a solvent gradient that varied from pure hexane to a 1/1/5 mixture of ether/CH$_2$Cl$_2$/hexane. The furan **42** was isolated in 20% yield (21.5 mg) as a colorless oil. Spectral data for **42**: R_f 0.46 (5% EtOAc in petroleum ether); ^{1}H NMR (CDCl$_3$) δ 0.94 (t, 3H, *J* = 7.3 Hz), 1.04 (sext, 2H, *J* = 7.3 Hz), 2.27 (t, 2H, *J* = 7.4 Hz), 3.94 (s, 3H), 6.40 (s, 1H), 7.12 (t, 1H, *J* = 7.4 Hz), 7.28 (t, 2H, *J* = 7.6 Hz), 7.49 (d, 2H, *J* = 7.7 Hz); IR (neat; cm^{-1}) 2959 s, 2932 s, 2871 m, 1647 s, 1603 s, 1582 w, 1557 s, 1449 w, 1391 s, 1265 s, 1213 s, 991 s, 758 s; mass spectrum (*m/z* (relative intensity)) 216 (100) M$^+$, 185 (55), 173 (97), 142 (26), 139 (17), 95 (90). The furan **42** was sensitive to air oxidation to the keto ester **49**, which was isolated in 2% yield (2.3 mg) from this reaction. Due to its instability, the furan **42** was fully characterized by conversion to the keto ester **49** by ceric ammonium nitrate. This oxidation cleanly produced **49** with no detectable formation of hydrolyzed products analogous to **37** observed for furan **29** (Table 1). Spectral data for **49**: colorless oil, R_f 0.11 (5% EtOAc in petroleum ether; ^{1}H NMR (CDCl$_3$) δ 1.01 (t, 3H, *J* = 7.3 Hz), 1.62 (sext, 2H, *J* = 7.5 Hz), 2.44 (t, 2H, *J* = 7.8 Hz), 3.64 (s, 3H), 6.70 (s, 1H), 7.42 (t, 2H, *J* = 7.6 Hz), 7.52 (t, 1H, *J* = 7.3 Hz), 7.87 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR (CDCl$_3$) δ 13.6, 20.8, 36.1, 52.1, 128.0, 128.5, 128.6, 133.2, 136.8, 146.4, 169.0, 191.2; IR (neat; cm^{-1}) 2962 m, 2934 m, 2873 w, 1732 s, 1668 s, 1615 m, 1580 w, 1449 m, 1381 w, 1266 s, 1212 s, 1137 m, 1017 w, 784 w, 701 s; mass spectrum (*m/z* (% relative intensity)) 232 (59) M$^+$, 201 (27), 155 (57), 105 (100), 77 (87); *m/z* calcd for C$_{14}$H$_{16}$O$_3$ 232.1099, measd 232.1090. A small fraction was isolated which was identified as the naphthol **41** (4%, 4.1 mg). A significant side product isolated from this reaction is the phenol **44** (19.1 mg, 15%). This type of side product has been observed before and is most prevalent for reactions with terminal alkynes.[1g,15b] Spectral data for **44**: colorless oil, R_f 0.38 (5% EtOAc in petroleium ether); ^{1}H NMR (CDCl$_3$) δ 0.94 (t, 3H, *J* = 7.3 Hz), 0.99 (t, 3H, *J* = 7.4 Hz), 1.62 (q, 2H, *J* = 7.8 Hz), 1.67 (q, 2H, *J* = 7.8 Hz), 2.51 (t, 2H, *J* = 7.7 Hz), 2.62 (t, 2H, *J* = 7.7 Hz), 5.04 (br s, 1H), 6.84 (d, 1H, *J* = 1.3 Hz), 6.90 (d, 1H, *J* = 1.3 Hz), 7.36 (m, 2H), 7.43 (m, 3H); ^{13}C NMR (CDCl$_3$) δ 13.9, 14.2, 23.0, 24.9, 32.5, 37.8, 127.5, 127.6, 128.1, 128.8, 129.17, 129.22, 129.8, 134.2, 137.7, 148.1; IR (neat; cm^{-1}) 3561 br s, 3017 w, 2958 s, 2930 s, 2870 s, 1600 w, 1496 w, 1471 s, 1443 s, 1378 w, 1324 s, 1259 w, 1219 s, 1108 s, 1074 w, 769 s, 751 m, 703 s; mass spectrum (*m/z* (% relative intensity)) 254 (59) M$^+$, 225 (100), 105 (13), 77 (10); *m/z* calcd for C$_{18}$H$_{22}$O 254.1670, measd 254.1671.[11] The final two products isolated from this reaction were the enol ether **51** and the keto ester **50** in ratios that varied from run to run. It was initially thought that the keto ester **50** resulted from the hydrolysis of furan **42**, but control experiments revealed that the furan **42** was converted exclusively to the keto ester **49** either by silica gel or by 0.5 M ceric ammonium nitrate in 0.1 M HNO_3. This control experiment revealed that the enol ether **51** is also not derived from the furan **42**. It is likely that enol ether **51** is the result of trapping a vinylketene intermediate with methanol that was generated during the course of the reaction from a source that has not been identified. This type of process does have precedent.[15b] When this same reaction is run in methanol solvent, the furan product is exclusively replaced by the enol ether **51**.[15b] Control experiments reveal that hydrolysis of **51** gives rise to the keto ester **50** as the major product; however, there was substantial loss in this reaction, and since other minor unassigned products result from the hydrolysis of **51**, the yield of **51** was most accurately taken form the ^{1}H NMR spectrum of the crude reaction mixture, which indicates the absence of **50**. Spectral data for enol ether **51**: colorless oil, R_f 0.42 (10% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3H, J = 7.3 Hz), 1.36 (m, 2H), 1.55 (m, 1H), 1.78 (m, 1H), 3.49 (s, CH_3O–vinyl, 3H), 3.67 (m, α-C*H*–COOMe, 1H), 3.68 (s, –COOCH_3, 3H), 5.22 (d, *vinyl proton*, 1H, J = 9.6 Hz), 7.33 (m, 3H), 7.43 (dd, 2H, J = 1.6, 7.9 Hz); ^{1}H NMR (C_6D_6) 3.26 (s, CH_3O–vinyl, 3H), 3.37 (s, –COOCH_3, 3H), 3.97 (dt, α-C *H*–COOMe, 1H, J = 7.4, 9.7 Hz), 5.44 (d, *vinyl proton*, 1H, J = 9.7 Hz); IR (neat; cm^{-1}) 2957 s, 2930 s, 2872 m, 1737 s, 1651 w, 1609 w, 1485 w, 1449 w, 1210 w, 1193 w, 1164 w, 1072 w, 770 w; mass spectrum (*m/z* (% relative intensity)) 248 (33) M$^+$, 225 (85), 216 (15), 205 (20), 189 (100), 171 (11), 159 (14), 147 (35), 145 (66), 129 (19), 115 (19), 105 (92), 91 (39), 83 (21), 77 (15); *m/z* calcd for $C_{15}H_{20}O_3$ 248.1412, measd 248.1380. Spectral data for keto ester **50**: colorless oil, R_f 0.28 (10% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3H, J = 7.3 Hz), 1.37 (sext, 2H, J = 7.6 Hz), 1.57 (m, 1H), 1.66 (m, 1H), 3.04 (m, 2H), 3.44 (dd, 1H, J = 10.3, 18.8 Hz), 3.68 (s, 3H), 7.42 (t, 2H, J = 6.8 Hz), 7.52 (t, 1H, J = 7.3 Hz), 7.92 (d, 2H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 13.9, 20.4, 34.3, 40.1, 40.5, 51.8, 128.0, 128.6, 133.2, 136.6, 176.1, 198.3 ; IR (neat; cm^{-1}) 2958 m, 2931 m, 2874 w, 1734 s, 1685 s, 1598 w, 1449 m, 1349 w, 1215 m, 1167 s, 1002 w, 757 m; mass spectrum (*m/z* (% relative intensity)) 234 (5) M$^+$, 120 (36), 105 (100), 87 (6), 77 (62); *m/z* calcd for $C_{14}H_{18}O_3$ 234.1256, measd 234.1255. The regiochemistry of the incorporation of the propyl group in **50** and **51** follows from the presence of the vinyl proton δ 5.22 for **51**. The stereochemistry of the vinyl group was established by comparison of the chemical shifts of the vinyl protons with the calculated values (for the *Z* isomer, calcd $\delta_{\text{vinyl H}}$ 5.21, whereas for the *E* isomer, calcd $\delta_{\text{vinyl H}}$ 4.96 ppm)[45] and the values for related compounds[15b] and also by NOE experiments. NOE studies on **51** in C_6D_6 revealed that the irradiation of the vinyl proton (δ 5.44) produced no enhancement of the methoxy protons (δ 3.26) of the enol ether. However, irradiation of the α-proton (δ 3.97) to the ester group gave a 15% enhancement of the methoxy signal at δ 3.26. Irradiation of the methoxy protons of the enol ether (δ 3.26) only produced and enhancement (percentage not determined) of the α-proton signal at δ 3.97.

This reaction in THF was also performed at 0.005 M in carbene complex in the same manner (60 h). The following products were identified and quantified by GC analysis: **40**, 27%; **42**, 27%; **44**, 6%. From the ^{1}H NMR spectrum of the crude reaction mixture a 12% yield of the naphthol 41 and an 11% yield of the enol ether 51 were observed.

In Benzene. The reaction of 178.0 mg of the molybdenum complex **26** (0.500 mmol) with 93.2 μL of 1-pentyne (0.95 mmol, 1.9 equiv) was carried out at 0.1 M in **26** in benzene (5 mL) according to the procedure described for the reaction for the chromium complex **17** with 1-pentyne in THF (36 h). The reaction mixture was divided into two parts in a 9/1 ratio by volume. The smaller fraction was analyzed by GC after addition of triphenylmethane standard, which gave the following results: **40**, 62%; **42**, 2%; **43**, 1.3%; **44**, 21%. From the ^{1}H NMR spectrum of the crude reaction mixture the presence of a 4% yield of naphthol **41** and a 2.5% yield of enol ether **51** was determined. The larger fraction was loaded onto a silica gel column (gradient elution from 0 to 5% EtOAc in petroleum ether) and gave a 51% isolated yield of the indene **40** (43.4 mg), a 29% isolated yield of the two-alkyne phenol **44** (33 mg), a 3% isolated yield of the furan **42**, a 2% isolated yield of the indanone **46**, and a 1.8% isolated yield of the cyclopentenedione **43**. The same reaction in benzene was repeated at 0.005 M, and GC analysis gave the following results: **40**, 47%; **46**, 33%; **42**, 3%; **43**, 3%; **44**, 6%. The ^{1}H NMR spectrum of the crude reaction mixture run at 0.005 M revealed the presence of **41** (3%) and **51** (1%).

In Acetonitrile. The reaction of the molybdenum complex **26** (44.5 mg, 0.125 mmol) with 1.9 equiv of 1-pentyne was carried out at 0.005 M in **26** in acetonitrile (25 mL) according to the procedure described for the reaction for the chromium complex **17** with 1-pentyne in THF (60 h). The products that were quantitated by GC analysis were as follows: **40**, 2.5%; **46**, 0.5%; **41**, 9%; **42**, 2%; **44**, 2%. Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that four addition products were formed in this reaction: **48**, 1%; **51**, 1%, **52**, 2%, **53a** + **53b** (1.3/1, 27% total). All reactions in acetonitrile gave (CH_3CN)-$Mo(CO)_5$ in yields ranging from 30 to 75%, as indicated by the ^{1}H NMR spectrum of the crude reaction mixture. A portion of the crude reaction mixture was eluted through a silica gel column to isolate the major products of this reaction (solvent gradient 0–5% EtOAc in petroleum ether). Analysis of all of the fractions by IR did not reveal the presence of the cyclobutenone **54**. The two major products isolated were identified as the diastereomeric lactones **53a** and **53b** (stereochemistry not assigned), which were not detected in the same reaction of the chromium complex **17**. Spectral data for **53a**: colorless oil, R_f 0.27 (5% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, J = 7.1 Hz), 1.36 (m, 3H), 1.86 (m, 1H), 1.86 (dd, 1H, J = 11.1, 12.9 Hz), 2.71 (dd, 1H, J = 8.3, 12.9 Hz), 2.98 (m, 1 H), 3.10 (s, 3H), 7.38 (m, 3H), 7.42 (m, 2H) (1D-COSY and NOE experiments confirmed the proton assignments); ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_3CH_2–), 20.4, 32.2, 39.8 (–*C*HCOOMe), 43.5, 51.4 (–(Ph)CO CH_3), 108.0, 125.5 (aromatic carbon), 128.7 (aromatic carbon), 128.8 (aromatic carbon), 138.5, 178.4 (an APT experiment showed the following carbon resonances were inverted: 13.7 (CH_3CH_2–), 39.8 (–*C*-HCOOMe), 51.4 (–(Ph)COCH_3), 125.5 (three phenyl carbons), 128.7 (aromatic carbon), 128.8 (aromatic carbon)); IR (neat; cm^{-1}) 2960 w, 2949 w, 2935 w, 2929 w, 1786 s, 1450 w, 1178 w, 1148 w, 1100 w, 1028 w, 959 m, 906 w; mass spectrum (*m/z* (% relative intensity)) 234 (52) M$^+$, 216 (70), 202 (36), 188 (25), 177 (78), 164 (19), 148 (17), 120 (100), 91 (63); *m/z* calcd for $C_{14}H_{18}O_3$ 234.1256, measd 234.1248. Spectral data for **53b**: colorless oil, R_f 0.26 (5% EtOAc in petroleum ether); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3H, J = 7.3 Hz), 1.37 (m, 2H), 1.59 (m, 1H), 1.86 (m, 1H), 2.32 (dd, 1H, J = 6.5, 13.0 Hz), 2.45 (dd, 1H, J = 9.3, 13.0 Hz), 2.56 (m, 1H), 3.11 (s, 3H), 7.39 (m, 5H) (1D-COSY and NOE experiments confirmed the proton assignments); ^{13}C NMR ($CDCl_3$) δ 14.3 (CH_3CH_2–), 20.7, 33.4, 40.3 (–*C*HCOOMe), 42.4, 51.9 (–(Ph)-CO*C*H 3), 109.2, 125.6 (aromatic carbon), 128.7 (aromatic carbon), 128.8 (aromatic carbon), 138.9, 178.4 (an APT experiment showed the following carbon resonances were inverted: 14.3 (CH_3CH_2–), 40.3 (–*C*HCOOMe), 51.9 (–(Ph)COCH_3), 125.6 (three phenyl carbons), 128.7 (aromatic carbon), 128.8 (aromatic carbon)); IR (neat; cm^{-1}) 2960 w, 2940 w, 2873 w, 1784 s, 1450 w, 1321 w, 1308 w, 1268 w, 1224 w, 1182 m, 1136 w, 1079 w, 1041 m, 1026 m, 983 w, 957 m, 895 w; mass spectrum (*m/z* (% relative intensity)) 234 (52) M$^+$, 216 (70), 202 (36), 188 (25), 177 (78), 164 (19), 148 (17), 120 (100), 91 (63); *m/z* calcd for $C_{14}H_{18}O_3$ 234.1256, measd 234.1248. The regiochemistry of alkyne incorporation in **53a** and **53b** was confirmed by the following chemical correlation with keto ester **50**, which was undertaken since NOE experiments were inconclusive. A mixture of **53a** and **53b** (1.3/1, 2.3 mg) was treated with 0.1 M aqueous NaOH in THF, and then after 4 h the THF was removed and the residue was neutralized with 6 N HCl (added dropwise until pH 1–2). The aqueous solution was then extracted with CH_2Cl_2, and the organic layer was washed with H_2O and brine and dried (Na_2SO_4). The ^{1}H NMR spectrum

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[45] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991; p 215.

indicated an equal consumption of both isomers, but hydrolysis did not go to completion. The crude keto acid was esterified by sequential treatment with oxalyl chloride and then methanol in the presence of triethylamine. Elution of the products on preparative TLC (5% EtOAc in petroleum ether) gave a fraction containing the unreacted lactone isomers **53a** and **53b** and the keto ester **50** in a 4/3/1 ratio. The keto ester **50** is formed as a single regioisomer from the mixture of **53a** and **53b**, thus allowing the assignment of the regiochemistry of alkyne incorporation in **53** as indicated in Chart 2, since the regiochemistry of **50** was determined by chemical correlation with **51**.

This same reaction was also carried out in acetonitrile at 0.1 M in carbene complex (26 h). The products that were quantitated by GC analysis were as follows: **40**, 8%; **46**, 2%; **41**, 5%; **42**, 3%; **44**, 4%. Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed that five addition products were formed in the reaction: **48**, 25%, **51**, 30%, **52**, 3%; **53a** + **53b** (0.5% total). A portion of the reaction mixture was chromatographed on silica gel as described above, and a screen of all of the fractions by IR did not reveal any cyclobutenone **54**.

In Methanol. The reaction of the molybdenum complex **26** (44.5 mg, 0.125 mmol) with 1.9 equiv of 1-pentyne was carried out at 0.1 M in **26** in methanol (1.25 mL) according to the procedure described for the reaction of the chromium complex **17** with 1-pentyne in THF (27 h). The products that were quantitated by GC analysis were as follows: **40**, 15%; **46**, 4%; **41**, 2%; **42**, 0.2%; **44**, 25%. Analysis of the ^{1}H NMR spectrum of the crude reaction mixture with triphenylmethane as internal standard showed that enol ether **51** was produced in 41% yield.

Reaction of the Tungsten Complex 7 with 1-Pentyne. In THF. The reaction of the tungsten complex **7** (444.0 mg, 1.00 mmol) with 1.9 equiv of 1-pentyne was carried out at 0.1 M in **26** in THF (10 mL) according to the procedure described for the reaction for the chromium complex **17** with 1-pentyne in THF. This reaction took 8 days due to the fact that polymerization of 1-pentyne competed with the benzannulation reaction.[8] The addition of 1.9 equiv of 1-pentyne every 12 h was required to drive the reaction to completion (a total of 28 equiv of alkyne was added). The products that were quantitated by GC analysis were as follows: **40**, 5%; **46**, 1%; **41**, 6%; **42**, 37%; **44**, 10%. Analysis of the ^{1}H NMR spectrum of the crude reaction mixture showed that enol ether **51** was produced in 18% yield. Isolation of the major products required elution on silica gel (pretreated with Et_3N) with a gradient solvent system (0–10% EtOAc in petroleum ether). The first to elute was a colored band that was tentatively identified as poly-1-pentyne in 59% yield. Also isolated was a 6% yield (11.6 mg) of the naphthol **41** and a 31% yield of the furan **42** (60.2 mg).

This reaction was repeated in THF at 0.005 M in **7**, and in this case only one addition portion (1.9 equiv) of alkyne was added at the halfway point. The reaction was complete in 48 h, and virtually no polyacetylene was formed. GC analysis gave the following results: **40**, 7%; **46**, 2%; **41**, 10%; **42**, 38%; **44**, 7%. From the crude ^{1}H NMR spectrum a 20% yield of enol ether **51** and a 4% yield of **52** were observed.

In Benzene. The reaction of the tungsten complex **7** (222.0 mg, 0.500 mmol) with 1.9 equiv of 1-pentyne was carried out at 0.1 M in **26** in benzene (5 mL) according to the procedure for the reaction in THF. This reaction took 10 days, due to the fact that polymerization of 1-pentyne competed with the benzannulation reaction.[8] The addition of 1.9 equiv of 1-pentyne every 12 h was required to drive the reaction to completion (a total of 38 equiv of alkyne was added). The products that were quantitated by GC analysis were as follows: **40**, 46%; **46**, 11%; **41**, 7%; **42**, 12%; **43**, 1.2%, **44**, 19%. Analysis of the ^{1}H NMR spectrum of the crude reaction mixture showed that enol ether **51** was produced in 2% yield. Column chromatography (gradient elution from 0 to 5% EtOAc in petroleum ether) on silica gel gave poly-1-pentyne in 76% yield, the indene **40** in 11% yield (9.1 mg), the furan **42** in 13% yield (13.0 mg), the phenol **44** in 15% yield (29.2 mg), and the indanone **46** in 38% yield (29.6 mg).

This reaction was repeated in benzene at 0.005 M in **7**, and in this case only one additional portion (1.9 equiv) of alkyne was added at the halfway point. The reaction was complete in 70 h, and virtually no polyacetylene was formed. GC analysis gave the following results: **40**, 53%; **46**, 7%; **41**, 6%; **42**, 5%; **44**, 14%. From the crude ^{1}H NMR spectrum a 1% yield of enol ether **51** was observed.

In Acetonitrile. The reaction of the tungsten complex **7** (44.4 mg, 0.100 mmol) with 1.9 equiv of 1-pentyne was carried out at 0.005 M in **7** in acetonitrile (20 mL) according to the procedure for the reaction in THF. The reaction was complete in 30 h, and an additional 1.9 equiv of alkyne was added at the halfway point. No significant amount of polyacetylene was formed. GC analysis gave the following: **40**, 6%; **46**, 3%; **41**, 10%; **42**, 5%; **44**, 1%. The ^{1}H NMR spectrum of the crude reaction mixture the showed the presence of ketene trapping product **48** (<0.5%), the enol ether **51** (5%), and the lactone **52** (2%).

Synthesis of Cyclopentenylcarbene Complexes 77–79. These complexes were prepared by a procedure similar to that reported for the corresponding ethoxy complexes.[46] Bromocyclopentene[47] (1.25 g, 8.47 mmol) was dissolved in 15 mL of THF at 0 °C. A 1.7 M solution of *t*-BuLi (9.9 mL, 16.9 mmol) in pentane was added dropwise via syringe, and the mixture was stirred for 10 min. The solution was warmed to room temperature for 10 min and transferred via cannula to a vigorously stirred slurry of molybdenum hexacarbonyl (4.46 g, 16.9 mmol) in 25 mL of THF. The resulting red-brown solution was stirred at room temperature for 2 h. Solvent was removed by rotary evaporator and then by high vacuum for 1 h. The brown oily solid was dissolved in 50 mL of argon-purged H_2O, and any solids were removed by filtration through Celite. To this was added 40 mL of argon-purged CH_2Cl_2 and then 2.5 g (16.9 mmol) of $(CH_3)_3O^+BF_4^-$. The two-phase mixture was stirred for 30 min, and then the reaction was quenched with 25 mL of saturated aqueous $NaHCO_3$. The layers were separated, and the aqueous phase was reextracted with 25 mL of CH_2Cl_2 and 25 mL of hexane. The combined organic layers were washed with H_2O and brine and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the residue was chromatographed on silica gel with a 1/100 mixture of ether and hexane. The red band was collected to give 2.14 g (73%) of the molybdenum complex **78**. Molybdenum carbene complexes, but not those of chromium and tungsten, cannot be stored as oils. The molybdenum complexes are crystallized from pentane or hexane immediately following chromatography. Solvent removal by rotary evaporation gives an oil which decomposes rapidly, and in some cases vigorously, even at temperatures below 0 °C. Therefore, for the molybdenum complexes, after chromatography the solvent volume was reduced to 5–10 mL by rotary evaporation, and crystallization was induced by immersing the solution in a dry-ice/acetone bath for several hours. Molybdenum complex **78**: red solid, mp 30–31 °C; ^{1}H NMR ($CDCl_3$) δ 1.93 (pentet, 2H, $J = 7.6$ Hz), 2.50–2.53 (m, 2H), 2.60–2.64 (m, 2H), 4.68 (s, 3H), 7.23–7.30 (m, 1H); ^{13}C NMR (C_6D_6) δ 23.02 (t), 31.32 (t), 34.78 (t), 67.84 (q), 158.98 (d), 159.72 (s), 206.92 (s), 213.58 (s), 327.16 (s); IR (neat; cm^{-1}) 2955 w, 2066 m, 1983 m, 1919 s, 1585 w, 1445 w, 1252 w, 1228 m, 986 w; mass spectrum (*m/z* (% relative intensity)) 348 (^{98}Mo, 5) M$^+$, 320 (^{98}Mo, 37) 292 (^{98}Mo, 36), 264 (^{98}Mo, 52), 236 (^{98}Mo, 72), 208 (^{98}Mo, 80), 206 (^{98}Mo, 100), 176 (^{98}Mo, 83), 163 (^{98}Mo, 63), 98 (^{98}Mo, 37), 79 (53), 67 (83). Chromium complex **77**: 70% yield; red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.91 (quintet, 2 H, $J = 7$ Hz), 2.52 (br s, 2 H), 2.62 (br s, 2 H), 4.74 (s, 3 H), 7.17 (br s, 1 H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 23.3, 32.4, 35.0, 67.0, 154.8, 159.4, 217.8, 224.4, 337.2; IR (neat; cm^{-1}) 2948 m, 2057 s, 1916 s, 1593 w, 1452 w, 1253 m, 1223 m; mass spectrum (*m/z* (% relative intensity)) 302 (8) M$^+$, 274 (35), 246 (19), 218 (32), 190 (57), 162 (100), 132 (53), 119 (47); *m/z* calcd for $C_{12}H_{10}O_6Cr$ 301.9882, measd 301.9867. Tungsten complex **79**: 61% yield, red solid, mp 36–37 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.93 (quintet, 2 H, $J = 8$ Hz),

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[46] Fischer, E. O.; Wagner, W. R.; Kreissl, F. R.; Neugebauer, D. *Chem. Ber.* **1979**, *112*, 1320.

[47] Fuillaumet, F.; Lammel, V.; Cludert, G.; Caubere, P. *Tetrahedron* **1974**, *30*, 1289.

2.55–2.51 (m, 4 H), 4.56 (s, 3 H), 7.24 (s, 1 H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 23.4, 31.8, 35.2, 69.7, 158.9, 161.4, 198.5, 203.8, 310.8; IR (neat cm^{-1}) 2956 w, 2065 m, 1909 s, 1593 w, 1437 m, 1225 m; mass spectrum (*m/z* (% relative intensity)) 434 (^{184}W, 32) M$^+$, 406 (^{184}W, 20), 378 (^{184}W, 33), 350 (^{1} 8^{4}W, 22), 322 (^{184}W, 91), 292 (^{184}W, 65), 292 (^{1}18^{4}W, 100), 277 (^{184}W, 37), 299 (^{184}W, 61). **Synthesis of (Cyclcohexenylmethoxymethylene)pentacarbonylmolybdenum (57).** This complex was prepared from bromocyclohexene[47] and molybdenum hexacarbonyl according to the procedure described above for the cyclopentenyl complex **78**. Spectral data for **57**: ^{1}H NMR ($CDCl_3$) δ 1.63 (m, 4H), 2.21 (m, 2H), 2.38 (m, 2H), 4.69 (s, 3H), 7.07 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.5, 22.0, 24.8, 27.1, 68.5, 144.5, 154.9, 206.3, 213.4, 336.7; IR (CH_2Cl_2; cm^{-1}) 3040 s, 2955 s, 2060 s, 1940 s, 1620 w, 890 s; mass spectrum (*m/z* (% relative intensity)) 362 (^{98}Mo, 5) M$^+$, 334 (^{98}Mo, 30), 306 (^{98}Mo, 40), 278 (^{96}Mo, 35), 266 (^{98}Mo, 20), 250 (^{98}Mo, 50), 222 (^{96}Mo , 100), 220 (^{98}Mo, 83).

Synthesis of ((Dihydro-2-pyranyl)methoxymethylene)-pentacarbonylmolybdenum and -tungsten Complexes 65 and 66. To a solution of 5,6-dihydro-4*H*-pyran (1.3 mL, 15 mmol) in THF (0.7 mL) under argon at −78 °C was added a 1.7 M solution of *t*-BuLi (9.7 mL, 16.5 mmol) in pentane over a period of several minutes. The solution turned cloudy and was stirred at −78 °C for 15 min and then warmed to 0 °C for an additional 15 min. The vinyllithium was solubilized by the addition of 5 mL of THF, and the resulting clear orange solution was added via cannula to a vigorously stirred slurry of $Mo(CO)_6$ (3.17 g, 12 mmol) in 20 mL of THF. The orange-brown mixture was stirred at room temperature for 45 min, and then the solvent was evaporated. The alkylation with trimethyloxonium tetrafluoroborate was performed as described for the cyclopentenyl complex **78**. After purification by column chromatography on silica gel the product was crystallized from hexane to give the molybdenum complex **65** in 60% yield (2.6 g, two crops). The yield of this particular complex is, however, highly variable with ~40% yield being typical. The analogous tungsten complex **66** was obtained in 53% yield by the same procedure. Spectral data for **65**: red solid, mp 42–43 °C; ^{1}H NMR ($CDCl_3$) δ 1.85 (m, 2H), 2.20 (m, 2H), 4.18 (t, 2H, *J* = 5 Hz), 4.69 (s, 3H), 5.66 (t, 1H, *J* = 4.5 Hz); ^{13}C NMR ($CDCl_3$) δ 20.99 (t), 21.47 (t), 66.28 (t), 68.19 (q), 103.79 (d), 161.20 (s), 206.29 (s), 214.44 (s), 324.65 (s); IR ($CDCl_3$) 2069 s, 1993 s, 1950 s, 1598 w, 1446 w, 1243 m, 1001 w, 602 w; mass spectrum (*m/z*) 264 ($Mo(CO)_6$), 252 (carbene ligand dimer). Spectral data for **66**: red solid, mp 47–48 °C; ^{1}H NMR ($CDCl_3$) δ 1.85 (m, 2H), 2.11 (m, 2H), 4.17 (t, 2H, *J* = 5 Hz), 4.60 (s, 3H), 5.77 (t, 1H, *J* = 4.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.17, 21.47, 66.40, 69.07, 104.21, 162.68, 197.58, 204.62, 307.71; IR ($CDCl_3$; cm^{-1}) 2954 m, 2937 m, 2876 m, 2070 s, 1986 s, 1956 s, 1597 m, 1445 m, 1426 w, 1348 w, 1294 w, 1241 s, 1212 m, 1200 m, 1181 m, 1147 m, 1061 m, 1005 m; mass spectrum (*m/z* (% relative intensity) 450 M$^+$ (^{184}W, 5), 422 (^{184}W, 45), 394 (^{184}W, 25), 366 (^{184}W, 30), 338 (^{184}W, 40), 310 (^{184}W, 45), 265 (^{184}W, 5), 239 (^{184}W, 5). Anal. Calcd for $C_{12}H_{10}O_7W$: C, 32.02; H, 2.23. Found: C, 31.82; H, 2.18.

General Procedure for the Reaction of AlkenylCarbene Complexes with Alkynes: Illustrated for the Reaction of the Molybdenum Cyclohexenyl Complex 57 with 3-Hexyne. A 0.005 M solution of the carbene complex **57** (0.180 g, 0.5 mmol) and 3-hexyne (0.115 mL, 1.0 mmol) in 100 mL of THF was deoxygenated by the freeze–thaw method (−196 to +25 °C, three cycles) in a single-necked flask that had the 14/20 joint replaced by a high-vacuum threaded Teflon stopcock. The flask was backfilled with 1 atm of argon and the stopcock closed at 25 °C. The reaction mixture was stirred at 25 °C for 36 h and then at 50 °C for 8 h, at which time TLC indicated that the starting complex **57** had been completely consumed. The solvent volume was reduced to approximately 10 mL by rotary evaporator, and then 30 mg of *p*-toluenesulfonic acid hydrate (0.15 mmol, 0.33 equiv) in 2–5 mL of H_2O was added. The hydrolysis reaction was allowed to proceed for 0.5–1.5 h. The reaction mixture was diluted with 50 mL of H_2O, and the organic components were extracted into ether (two to three portions, ~75 mL total volume), washed with saturated aqueous $NaHCO_3$, water, and brine and dried over anhydrous $MgSO_4$. Upon solvent evaporation, the residue was chromatographed on silica gel with a 1/1/20 mixture of ether/CH_2Cl_2/hexanes as eluent, which gave in order of elution the phenol **59** (6.6 mg, 0.028 mmol, 6%) as a white solid and the cyclopentenone **60** (61.5 mg, 0.32 mmol, 64%) as a colorless oil. Spectral data for phenol **59**: mp 47 °C; R_f 0.18; ^{1}H NMR ($CDCl_3$) δ 1.17–1.22 (m, 6H), 1.72–1.75 (m, 2H), 1.81–1.84 (m, 2H), 2.59 (t, 2H, *J* = 6.2 Hz), 2.63–2.67 (m, 4H), 2.74 (t, 2H, *J* = 6.3 Hz), 3.71 (s, 3H), 4.44 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.50, 15.93, 19.48, 19.62, 22.32, 22.49, 23.08, 23.81, 60.64, 121.03, 125.64, 128.73, 132.81, 147.71, 149.66; IR ($CHCl_3$; cm^{-1}) 3450 m, 2920 s, 1445 s, 1415 m, 1330 m, 1240 m, 850 m; mass spectrum (*m/z* (% relative intensity)) 234 (100) M$^+$, 219 (90), 205 (15), 190 (3), 119 (53), 110 (50), 91 (75). Satisfactory analysis was obtained for this compound (C, H). Spectral data for cyclopentenone **60**: R_f 0.14; ^{1}H NMR ($CDCl_3$) δ 0.97 (t, 3 H, *J* = 7.5 Hz), 1.02–1.09 (m, 1 H), 1.12 (t, 3 H, *J* = 7.6 Hz), 1.23 (m, 1 H), 1.33 (m, 1 H), 1.49 (m, 2 H), 1.66 (m, 1 H), 1.88 (m, 1 H), 1.96 (m, 1 H), 2.17 (q, 2 H, *J* = 7.5 Hz), 2.27 (m, 1 H), 2.35 (dd, 1 H, *J* = 12.4, 6.4 Hz), 2.53 (m, 1 H), 2.83 (br q, 1 H, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 11.95, 13.36, 16.17, 21.20, 21.48, 21.62, 22.63, 27.57, 3 9.91, 45.45, 139.31, 176.68, 211.00; IR ($CDCl_3$; cm^{-1}) 2930 s, 1685 s, 1630 s; mass spectrum (*m/z* (% relative intensity) 192 (80) M$^+$, 177 (30), 164 (35), 163 (100), 151 (50), 149 (30), 135 (70), 107 (30), 93 (50), 91 (50), 81 (45), 79 (75), 77 (35), 67 (55), 55 (60), 53 (35), 41 (60); *m/z* calcd for $C_{13}H_{20}O$ 192.1514, found 192.1522. The reactions of the tungsten complex **58** produced a minor product for several of the reactions in Table 3 that only displayed two different ethyl absorptions in the ^{1}H NMR spectrum and was not purified and characterized.

This procedure was utilized for all of the reactions indicated in Table 3. The reactions in Tables 3–7 were screened primarily for the phenol and cyclopentenone products, and no complete effort was made to isolate and identify all of the minor products formed in these reactions. However, the ^{1}H NMR spectrum of each crude reaction mixture was taken, and in those cases where significant side products were formed, they are noted in the tables and in the experimental procedure below. The general observation is that the reactions of the alkenyl complexes produce significantly less side products than the reactions or aryl complexes.

Reactions of the (Dihydropyranyl)carbene Complexes 64–66 with 3-Hexyne. The reaction of the molybdenum carbene complex **65** (0.181 g, 0.5 mmol) and 3-hexyne (0.115 mL, 1.0 mmol) in 100 mL of THF (0.005 M in **65**) was carried out as described above in the general procedure (25 °C, 60 h). After acid hydrolysis, the products were separated from the reaction mixture by chromatography on silica gel with a mixture of ether/CH_2Cl_2/hexanes (gradient elution 1/1/10 to 1/1/4) and were identified as the phenol **67** (9 mg, 0.04 mmol, 8%) and the cyclopentenone **68** (64 mg, 0.33 mmol, 66%). The phenol **67** was characterized by comparison of its spectral data with those in the literature[9a] and by the following data: ^{13}C NMR ($CDCl_3$) δ 14.48, 15.51, 18.83, 19.00, 19.32, 21.56, 60.57, 65.43, 108.42, 119.17, 133.32, 139.63, 145.96, 147.29. Spectral data for cyclopentenone **68**: ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3H, *J* = 7.6 Hz), 1.14 (t, 3H, *J* = 7.7 Hz), 1.14 (m, 1H), 1.58 (m, 2H), 2.20 (m, 3H), 2.31 (m, 1H), 2.53 (m, 1H), 2.84 (m, 1H), 3.58 (m, 1H), 3.78 (m, 1H), 4.10 (d, 1H, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 11.58, 13.04, 15.92, 21.44, 21.88, 26.23, 38.16, 68.83, 76.53, 138.85, 174.63, 205.74; IR (neat; cm^{-1}) 2966 s, 2937 s, 2874 s, 1709 s, 1631 s, 1462 m, 1360 m, 1154 s, 1065 m, 1042 m, 1017 m, 945 m; mass spectrum (*m/z* (% relative intensity)) 194 (30) M$^+$, 166 (30), 165 (30), 164 (15), 151 (50), 138 (100), 137 (25), 123 (15), 109 (20), 84 (45), 81 (15), 79 (15), 77 (15), 67 (25); *m/z* calcd for $C_{12}H_{10}O_2$ 194.1307, measd 194.1350.

This procedure including the acid hydrolysis was employed for all of the reactions of the dihydropyranyl complexes indicated in Tables 4–6. The acid hydrolysis greatly simplifies the product mixture, since if the acid hydrolysis is not employed a number of different products are observed that are apparently derived from the dienyl ether **69**. For example, isolation of the products from the reaction of the molybdenum complex **65** with 3-hexyne in THF (0.05 M) without an acid hydrolysis by loading the crude reaction mixture onto a silica gel column gave the phenol **67** (31%), cyclopentenone **68** (10%), the cyclohexadienone complex **107** (3%), and a compound that is assigned as the dienyl ether **69a** (12%, stereochemistry of double bond not determined). Spectral data for **69a**: R_f 0.6, 1/1/4; ^{1}H NMR (CDCl$_3$) δ 1.02 (t, 3H, J = 7.5 Hz), 1.47 (m, 1H), 1.58 (m, 1H), 1.67 (m, 1H), 1.71 (d, 3H, J = 6.9 Hz), 1.92 (m, 1H), 2.11 (m, 1H), 2.21 (m, 1H), 2.91 (br q, 1H, J = 7.5 Hz), 3.65 (m, 1H), 3.81 (s, 3H), 4.78 (d, 1H, J = 7.4 Hz), 5.12 (q, 1H, J = 5.7 Hz); ^{13}C NMR (CDCl$_3$) δ 12.82, 13.68, 15.97, 21.24, 22.53, 37.00, 56.63, 61.93, 75.30, 108.30, 124.57, 144.14, 155.18; IR (neat; cm^{-1}) 2965 s, 2937 s, 2857 m, 1650 s, 1464 m, 1378 s, 1291 m, 1260 s, 1167 m, 1120 m, 1077 s, 1039 s, 1024 m, 812 m; mass spectrum (m/z (% relative intensity) 208 (50) M$^+$, 178 (10), 177 (100), 151 (10), 138 (15), 135 (20), 91 (15), 85 (55), 83 (85), 79 (10), 77 (10). The same reaction with an acid hydrolysis gave phenol **67** (31%), the cyclopentenone **68** (33%), and a small amount of the cyclohexadienone complex **107**.

The reaction of the tungsten complex **66** with 3-hexyne predominantly gave the phenol **67**, as indicated in Table 4. The crude reaction mixtures from complex **66** were also examined by capillary GC, which indicated the presence of a maximum of 2% cyclopentenone **68**. The reaction of the tungsten complex **66** at high concentration (0.5 M) also produced a small amount (3%) of compound **108**, which was not completely purified and characterized but whose ^{1}H NMR suggests that it is the tungsten analog of the molybdenum cyclohexadienone complex **107**.

The yields of **67** and **68** from the reactions in Table 6 were determined both by isolation and by capillary GC. The GC yields (average of three injections) were determined on the crude reaction mixture with response factors (average of two determinations) for each product that were determined relative to anthracene as an internal standard. GC analysis was performed on a 25 M × 0.32 mm OV-1710 column with a temperature program of 150 °C/5 min ramped at 10 °C/min to 200 °C and held for 20 min. The cyclopentenone **68** (R_t = 6.5 min), anthracene (R_t = 10.0 min), and the phenol **67** (R_t = 14.1 min) were well resolved.

Effect of Concentration on the Reaction of the Molybdenum Dihydropyranyl Complex 65 with 3-Hexyne and the Isolation of the Cyclohexadienone Complex 107. The reaction of molybdenum complex **65** and 3-hexyne was carried out with the procedure described with variations of the concentration of both the carbene complex and the alkyne as indicated in Table 4. When large excesses of alkyne were used, it was necessary to distill the 3-hexyne from either sodium metal or sodium borohydride prior to use to remove small amounts of the peroxide present, which leads to decreased overall yields due to the oxidation of the carbene complex prior to reaction with the alkyne. From the reactions at higher carbene complex concentration (0.05 M and above) three minor colored products were also observed. One was unstable to air, another could not be purified, and a third was obtained as a red crystalline solid and identified as the bis(3-hexyne)(cyclohexadienone)molybdenum carbonyl complex **107** (3–5% yield). Spectral data for **107**: mp 101–104 °C, R_f 0.15, 1/1/14; ^{1}H NMR (CD$_2$Cl$_2$) δ 0.34–0.45 (dt, 1H, J_1 = 14 Hz, J_2 = 7 Hz), 0.72 (t, 3H, J = 7.2 Hz), 1.05 (m, 12H), 1.36 (t, 3H, J = 7.3 Hz), 1.35–1.65 (m, 4H), 2.09–2.15 (m, 1H), 2.30 (dt, 1H, J_1 = 13.2 Hz, J_2 = 7.2 Hz), 2.65 (m, 2H) 2.8–3.5 (br m, 8H), 3.2–3.8 (m, 1H), 3.80 (s, 3H), 3.89 (dt, 1H, J_1 = 13.1 Hz, J_2 = 7.4 Hz); ^{13}C NMR (CDCl$_3$) δ 13.93, 13.97, 14.08, 14.12, 17.65, 22.34, 24.25, 24.47, 25.75, 26.05, 26.36, 42.51, 58.50, 67.65, 76.42, 96.93, 101.25, 130.98, 161.91, 180.29, 196.02, 234.93 (assuming that the two alkyne ligands are freely rotating about the metal alkyne bonds in solution (*vide infra*) but are inequivalent with respect to the cyclohexadienone ligand, the ^{13}C NMR spectrum should have one fewer resonance in the region δ 13–27 than is reported here); IR (neat, NaCl cm^{-1}); 2967 (s), 2933 (s), 2873 (m), 2802 (w), 1993 (s), 1750 (m), 1629 (s), 1453 (m), 1411 (m), 1371 (m), 1356 (m), 1292 (m) 1275 (m), 1253 (m), 1204 (m), 1159 (m), 1087 (s), 1068 (m), 1031 (m), 957 (m); mass spectrum (CI; m/z (% relative intensity)) 527 (^{98}Mo, 15) M + 1, 498 (^{98}Mo, 15), 257 (^{98}Mo, 65), 237 (^{98}Mo, 60), 221 (^{98}Mo, 30); m/z calcd for $C_{27}H_{41}O_4Mo$ 527.2064, found 527.1792. The structure of **107** was confirmed by an X-ray diffraction analysis (vide infra).

In order to assign the coordination alkyne resonances in the ^{13}C NMR spectrum of complex **107**, the labeled complex **107*** was synthesized from ^{13}C-labeled carbene complex **65***. Mo(CO)$_6$ (25% ^{13}CO incorporation) was labeled via the procedure of Shore.[48] The labeled carbene complex **65*** was synthesized as described above for the nonlabeled complex and reacted with 3-hexyne (0.1 M in THF, 2 equiv of alkyne). The ^{13}C NMR spectrum of the labeled complex **107*** showed enhanced signals at δ 130.98, 196.02, and 234.93 ppm, which are thus assigned to the carbon bearing the methoxy group, the ketone carbon, and the carbon monoxide ligand, respectively. The signals at 42.51, 76.42, 96.93, and 101.26 ppm were split into triplets (singlets each flanked by a doublet (J_{CC} ≈ 57 Hz)) and are thus assigned as the tertiary carbon and the three remaining sp^2 ring carbons. The alkyne carbons are then assigned the resonances at 161.91 and 180.29 ppm, which place them within the "three-electron-donor" region as defined by Templeton.[35]

X-ray Data Collection, Structure Determination, and Refinement for 107. A red single crystal of **107** was mounted on a pin and transferred to the goniometer. The space group was determined to be $P2_1/c$. A summary of data collection parameters is given in Table 8. The Mo position was calculated from Patterson synthesis. All other non-hydrogen atoms were located by subsequent difference Fourier maps. Block-diagonal least-squares anisotropic refinement of all non-hydrogen atoms was performed using the local program NEWBLDS (G. VanDuyne, 1987). H atomic positions were generated from assumed geometries 1.02 Å from the attached C and given isotropic temperature factors of 1.2 times that of the C to which they were bonded and were not refined. No correction for decomposition was applied. The Stuart–Walker absorption correction technique was applied: R(before) = 0.066, R(after) = 0.0598. The final values of the positional parameters are given in Table 9, and selected bond distances are given in Table 10. The thermal parameters, least-squares planes, final fractional coordinates for hydrogen, and complete sets of bond distances and bond angles can be found in the supplementary material.

Reaction of the Dihydropyranyl Complexes 64–66 with 1-Pentyne. The reaction of the molybdenum complex **65** (0.181 g, 0.5 mmol) and 1-pentyne (100 mL, 1 mmol) in 100 mL (0.005 M) of THF was carried out according to the general procedure (40 h). The reaction mixture was opened to air, the solvent was removed, and the residue was directly chromatographed on silica gel with a 1/1/10 mixture of ether/CH$_2$Cl$_2$/hexanes to give the phenol **72a** (40.4 mg, 0.182 mmol, 36%), the cyclopentenone **73a** (7.2 mg, 0.04 mmol, 8%), and a compound (4.4 mg, 0.024 mmol, 5%) that was isomeric with **73a** which is tentatively assigned as that with the double bond at the ring junction. Two other organic compounds were isolated, and each was found to isomerize to a mixture of the two (28.5 mg combined). These apparently acyclic compounds were not identified. This reaction was repeated at a carbene complex concentration of 0.05 M and after acid hydrolysis in the workup gave the phenol white solid, mp 80–82 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.98 (t, 3 H, J = 7.4 Hz), 1.62 (pentet, 2 H, J = 7.4 Hz), 2.01 (m, 2 H), 2.49 (t, 2 H, J = 7.5 Hz), 2.67 (t, 2 H, J = 6.7 Hz), 3.81 (s, 3 H), 4.20 (t, 2 H, J = 5.3 Hz), 4.35 (s, 1 H), 6.51 (s, 1 H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 13.9, 19.5, 21.6, 23. 2, 31.9, 56.3, 66.0, 110.6, 110.8, 117.6, 142.0, 144.9; IR (neat; cm^{-1}): 3468 m, 2956 m, 2932 m, 2870 m, 1609 w, 1478 s, 1465 m, 1333 m, 1244 s, 1191 m, 1121 s, 1101 s, 991 m; mass spectrum (m/z (% relative intensity)) 222 (70) M$^+$, 207 (20), 193 (100), 165 (15), 137 (10); m/z calcd for $C_{13}H_{18}O_3$ 222.1256, found 222.1225. Spectral data for cyclopentenone **73a**: ^{1}H NMR

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[48] Bricker, J. C.; Payne, M. W.; Shore, S. G. *Organometallics* **1987**, *6*, 2545.

[49] For examples of the effect of added alkyne on the intramolecular benzannulation of manganese carbene complexes, see: Balzer, B. L.; Cazanoue, M.; Finn, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 8735.

(CDCl$_3$) δ 0.98 (t, 3H, J = 7.4 Hz), 1.15–1.23 (m, 1H), 1.54–1.70 (m, 4H), 2.18–2.42 (m, 3H), 2.79 (dt, 1H, J_1 = 10.0 Hz, J_2 = 3.5 Hz), 3.51–3.58 (m, 1H), 3.76–3.82 (m, 1H), 4.17 (d, 1H, J = 6.4 Hz), 5.93 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 13.89, 19.69, 21.68, 26.92, 33.94, 40.70, 64.21, 77.36, 126.06, 183.06; IR (neat; cm^{-1}): 2957 s, 2933 s, 2071 s, 1716 s, 1633 m, 1605 m, 1457 m, 1 377 m, 1252 m, 1247 m, 1125 m, 1108 w, 1067 m, 800 w cm^{-1}; mass spectrum (m/z (% relative intensity)) 180 (15) M$^+$, 137 (23), 124 (28), 85 (68), 83 (100). The reaction with the tungsten complex **68** as indicated in Table 7 gave exclusively the phenol **72a** but required additional alkyne to go to completion (4–6 equiv). The phenol **72a** could be separated from the polyacetylene that was formed by bulb-to-bulb distillation or by the gradient elution technique described for the reaction of the cyclopentenyl complex **79**.

Reaction of the Cyclohexenyl Complexes 56–58 with 1-Pentyne. The reaction of the cyclohexenyl tungsten **58** (0.224 g, 0.5 mmol) and 1-pentyne (0.100 mL, 1 mmol) in 100 mL of THF (0.005 M) was carried out according to the general procedure. After 48 h at 80 °C the carbene complex was still present, so an additional 0.100 mL of alkyne was added. The starting complex **58** was consumed after an additional 16 h (64 h total). After the solvent was removed, the residue was loaded onto a silica gel column and the gradient elution performed with a 1/1/10 to 1/1/6 mixture of ether/CH$_2$Cl$_2$/hexanes. After the initial brown-red polymer eluted from the column, the phenol **72b** was collected (R_f 0.34 (1/1/10), 89.1 mg, 0.405 mmol, 81%). The brown compound **109** (42.1 mg) was also isolated, which was shown by IR to have a terminal W–CO stretch (2012 cm^{-1}) and which contained more than 1 equiv of alkyne. Oxidation of **109** with Ce(NH$_4$)$_2$(NO$_3$)$_6$ in THF/H$_2$O gave the 2-*n*-propyl-5,6,7,8-tetrahydronaphthoquinone **110**, which had spectral data identical with those that have been reported for this compound.[9a] While this brown compound has not been completely characterized, it is tentatively assigned the structure of the bis(1-pentyne)-(cyclohexadienone)tungsten carbonyl analog of complex **107**. If this assignment is correct, then the complex is formed in 14% yield. The reaction of complex **58** was repeated at a carbene complex concentration of 0.1 M, and the same products (phenol and metal complex) were isolated in 62% and 20% yields, respectively. If this reaction at 0.1 M is followed by an oxidative workup with Ce(NH$_4$)$_2$(NO$_3$)$_6$, the quinone **110** can be isolated in 88% yield. Spectral data for phenol **72b**: white solid, mp 63–64 °C; R_f 0.34 (1/1/4); ^{1}H NMR (CDCl$_3$) δ 0.99 (t, 3 H, J = 7.3 Hz), 1.64 (sextet, 2 H, J = 7.6 Hz), 1.72–1.74 (m, 2 H), 1.77–1.79 (m, 2 H), 2.54 (t, 2 H, J = 7.8 Hz), 2.58–2.63 (m, 4 H), 3.75 (s, 3 H), 4.19 (s, 1 H), 6.48 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.1, 22.4, 23.2 (2-C), 23.4, 32.5, 55.7, 108.9, 124.3, 124.5, 124.6 145.0, 150.9; IR (CDCl$_3$) 3600 s, 2925 s, 1595 s, 1 260 m, 1190 s; mass spectrum (m/z (% relative intensity)) 220 (100) M$^+$, 191 (95); m/z calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1462. The reactions of the chromium and molybdenum complexes **56** and **57** with 1-pentyne indicated in Table 7 were not observed to give any products other than phenol **72b**, went to completion without the addition of extra alkyne, and did not give any apparent formation of polyacetylene.

Reaction of the Cyclopentenyl Complexes 77–79 with 1-Pentyne. Carbene complex **79** (150 mg, 0.346 mmol), 0.07 mL (0.691 mmol) of 1-pentyne, and 69 mL of THF were combined according to the general procedure and heated at 80 °C. An additional 0.07 mL (0.691 mmol) of 1-pentyne was added after 13, 24, and 37 h. After a total of 61 h, the reaction mixture was worked up with *p*-TsOH–H$_2$O according to the general procedure. The crude reaction product was purified by flash chromatography on silica gel, first with a 50/1/1 mixture of hexanes/CH$_2$Cl$_2$/ether as eluent without air pressure to remove orange polyacetylene products and then with 10/1/1 to 4/1/1 solvent mixtures as eluent under mild air pressure to isolate 62 mg (0.301 mmol, 87%) of phenol **72c** (R_f 0.13, 20/1/1) as an off-white solid. The spectral data matched those reported for this compound.[17b] The same reactions of the chromium and molybdenum complexes went to completion with 2 equiv of alkyne, did not produce any detectable polyacetylene, and gave the phenol **72c** in 54 and 80% yields, respectively. The reaction of the chromium complex in hexane has been reported to give **72c** in 51% yield along with a 9% yield of a vinylcyclopentenedione product.[17b]

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Supplementary Material Available: Crystal structure data for **107**, including tables of crystal data and refinement details, atomic parameters, anisotropic thermal parameters, bond distances, and bond angles (7 pages). Ordering information is given on any current masthead page.

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