2166 *J. Am. Chem. Soc.* **1996,** *118,* 2166−2181

Reaction of Fischer Carbene Complexes with 1,3-Butadiynes: A New Strategem for Biaryl Synthesis with Construction of the Biaryl Bond Preceding Synthesis of the Arenes

Jianming Bao, William D. Wulff,* Michael J. Fumo, Eugene B. Grant, Douglas P. Heller, Mark C. Whitcomb, and Siu-Man Yeung

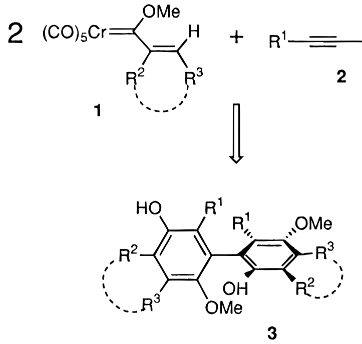
Contribution from the Searle Chemistry Laboratory, Department of Chemistry, University of Chicago, Chicago, Illinois 60637

Received September 12, 1995⊗

Abstract: The first examples of the reactions of Fischer carbene complexes with 1,3-butadiynes are reported. These reactions are of interest since they provide new methods for the synthesis of acetylenic substituted arenes and also for the synthesis of biaryls. The reactions of the complexes $(CO)_5Cr{=}C(OR^1)R^2$ [R^1 = Me, *n*-Bu; R^2 = phenyl, 1-naphthyl, 1-cyclohexenyl] were investigated with the conjugated diynes $R^3C{\equiv}C{-}C{\equiv}CR^3$ [R^3 = *t*-Bu, *i*-Pr, Ph]. All of the carbene complexes will react with 1 equiv of the diyne to give good yields of acetylenic arenes **5**, **19**, and **23**, each with high selectivity for the regioisomer in which the substituent R^3 on the diyne is incorporated adjacent to the phenol function. The reactions of the alkynylarenes **5**, **19**, and **23** with a second equivalent of carbene complexes, **4**, **16**, and **22**, respectively, generate the bis-phenols **26**, **31**, and **33**, with varying amounts of five-membered-ring annulated compounds as side products. These side products are not seen with the cyclohexenyl complex **22** and can be minimized to some extent for the phenyl complex **4a** by proper control of the concentration and the temperature. Attempts to carry out benzannulations of both of the acetylenic functions in the 1,3-diyne concurrently by employing 2 equiv of the carbene complex were not successful, and this is suspected to be due to the presence of a chromium tricarbonyl group on the newly formed arene ring after the first benzannulation, such as in complex **34**. The concurrent double benzannulation of a diyne can be achieved in an intramolecular fashion with the bis-carbene complex **39**. The intramolecular process leads to a reversal in the regiochemistry of the second benzannulation producing the C_2-symmetrical 2,2′-binaphthol **40** from the reaction of complex **39** with the diyne **8** along with the indenylnaphthalene **41**. The reaction of the optically pure bis-carbene complex **44** derived from (2*R*,3*R*)-butane-2,3-diol with diyne **8** gives a single diastereomer of the 2,2′-binaphthol **46**. Chemical correlation with the known 2,2′-binaphthol **51** reveals that the biaryl axis in **46** has an *S*-configuration, which was predicted from an examination of models.

The reaction of Fischer carbene complexes with alkynes is a synthetically important reaction for the preparation of oxygenated benzenes.[1] This methodology has been extended to nonconjugated diynes, with significant study directed to cases where polycyclic systems can be generated.[2] In view of these studies, which have taken place over an extended period of time, it is surprising that the reactions of Fischer carbene complexes with conjugated 1,3-diynes have never been reported.[3] The attractiveness of the potential of this class of reaction is illustrated in Scheme 1, where it can be seen that, if the adjacent benzannulations are carried out independently on each of the alkyne functions with the carbene complex **1**, then a new route to biaryls will result.[4] This approach to biaryl synthesis embodies the reverse of the normal strategy of biaryl synthesis: the biaryl bond is constructed prior to the construction of either of the two aryl rings. We report here the first examples of the reactions of Fischer carbene complexes with conjugated 1,3-diynes and demonstrate that biaryls can be constructed from this reaction with both inter- and intramolecular dispositions of the two carbene complexes. It is further demonstrated in the intramolecular case that high asymmetric induction in the formation of the biaryl can be achieved if a chiral carbene complex is employed.

Scheme 1



⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1996.

[1] For reviews on the synthetic applications of Fischer carbene complexes, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Dötz, K. H., *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Wulff, W. D. In *Advances in Metal−Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (d) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK, 1990; Vol 5. (e) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, UK, 1995; Vol. 12. (f) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, UK, 1995; Vol. 12. (g) Doyle, M. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, UK, 1995; Vol. 12.

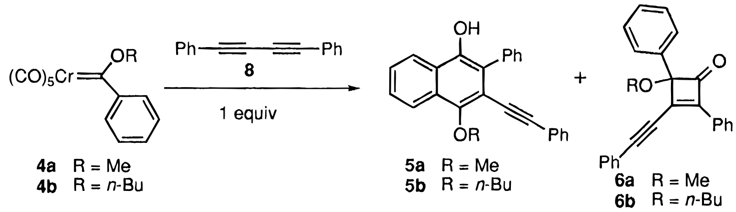
[2] For citations to the literature, see: Bao, J.; Wulff, W. D.; Dragisich, V.; Wenglowsky, S.; Ball, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7616.

[3] (a) Parts of this work have been reported in preliminary form: Wulff, W. D.; Bao, J. *Abstracts of Papers*, 203rd ACS National Meeting, San Francisco, April 5−10, 1992; (b) See also: Chan, K. S.; Mak, C. C. *Tetrahedron* **1994**, *50*, 2003.

[4] For a review of biaryl synthesis, see: Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 977.

0002-7863/96/1518-2166$12.00/0

Table 1. Monobenzannulation of 1,3-Diynes with the Aryl Complexes **4**[a]



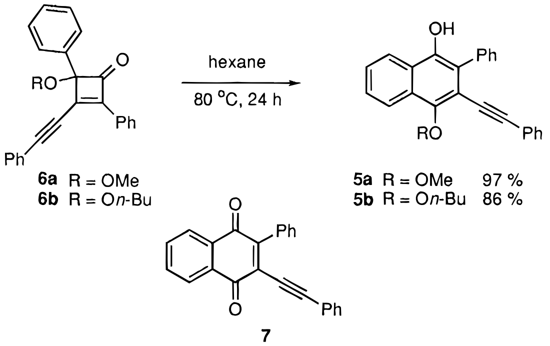
entry	complex	R	solvent	[4a] (M)	temp (°C)	time (h)	yield (%)[b]	
							5	**6**
1	**4a**	Me	THF	0.03	60	24	20	21
2	**4a**	Me	THF	0.03	70	23	44	nd
3	**4a**	Me	THF	0.5	70	24	16	nd
4	**4a**	Me	THF	0.1	105	2	42[c,d]	nd
5	**4a**	Me	THF	0.21	105	3	12[c,e]	nd
6	**4a**	Me	THF	0.21	105	3	nd[c,f]	nd
7	**4b**	*n*-Bu	THF	0.03	50	17	53[c]	21
8	**4b**	*n*-Bu	THF	0.03	70	24	61	nd
9	**4b**	*n*-Bu	benzene	0.03	70	24	31 (40)[g]	nd
10	**4b**	*n*-Bu	hexane	0.03	70	24	25 (31)[g]	nd

[a] All reactions carried out with 1 equiv of **8** under an argon atomosphere. [b] nd, not detected. [c] Isolated as the quinone (**7**) after an oxidative workup with Ce^{IV}. [d] 41% after 24 h. [e] Slow addition of **8** over 1 h. [f] Slow addition of **4a** over 1 h. [g] Yield based on recovered starting material.

Monobenzannulation of 1,3-Diynes. In our very first attempt at reacting a carbene complex and a 1,3-diyne, we examined the reaction of an excess of the phenylcarbene complex **4a** with the diyne **8** (3:1 stoichiometry) and observed the formation of a complex reaction mixture that contained no clear predominate product (the outcome was not significantly different when carried out in the presence of 3 equiv of Bu_3P). While the disposition of this particular reaction was not further pursued, the related reaction of excess complex **22** and diyne **8** was examined in more detail (Scheme 9). More readily interpretable results for the reaction of complex **4** with diyne **8** were obtained with a 1:1 stoichiometry, and the results are summarized in Table 1. The reaction of the phenyl complex **4a** with 1 equiv of the commercially available 1,4-diphenyl-1,3-butadiyne (**8**) gave the acetylenic naphthol **5a** and the cyclobutenone **6a** in nearly equal amounts. Cyclobutenone products have been previously reported from the reactions of carbene complexes, and, while it is thought that in most cases they are not intermediates on the pathway for the formation of the normal phenol product, they will undergo thermal isomerization to phenol products.[5] This was demonstrated for cyclobutenone **6a**, where the phenol **5a** was obtained in 97% yield upon thermolysis in hexane at 80 °C in 24 h (Scheme 2). This is consistent with the fact that the reactions of **4a** with **8** at 70 °C and 105 °C give only the naphthol **5a**, but in the same overall mass balance as the reaction at 60 °C which produced both **5a** and **6a**. An increased mass balance for these reactions could not be obtained with either slow addition of the carbene complex **4a** to the diyne **8** or *vice versa* (entries 5 and 6).

A significantly higher mass balance is observed for the reaction of the (*n*-butyloxy)carbene complex **4b** than for the reaction of the methoxy complex **4a** (Table 1, entry 2 vs entry 8). It is not known if this effect pertains for the reactions of these complexes with simple alkynes. A 74% mass balance can be obtained for the reaction of complex **4b** at 50 °C, where an oxidative workup with ceric ammonium nitrate was employed to give the naphthoquinone **7** in 53% yield and the cyclobutenone **6b** in 21% yield. At 70 °C, the naphthol **5b** (no oxidative workup) is formed to the exclusion of **6b** in 61% yield. For reasons that are not understood at this time, the reaction of complex **4b** with diyne **8** is slower and less efficient for the formation of naphthol **5b** in benzene and hexane solvent as compared to the reactions in THF. Although the effects of solvent on the product distribution from the reactions of carbene complexes with monoalkynes have been observed, the effect of the monoalkyne on the rate has not been examined.[5a,6]

Scheme 2



7

The regiochemistry of alkyne incorporation has been examined for a number of alkynes, and in most situations the regiochemical outcome is determined by the steric difference between the two substituents of the alkyne, giving as the major product the regioisomer in which the larger group is incorporated adjacent to the phenol function.[1c,7] Thus, it would be expected that the structure of the product **5a** from the reaction of complex **4a** and diyne **8** would be that indicated in Table 1, where the phenyl group is adjacent to the hydroxyl group. However, given that electronic factors can reverse the regiochemistry in some instances,[7d] it was deemed necessary to confirm the assignment

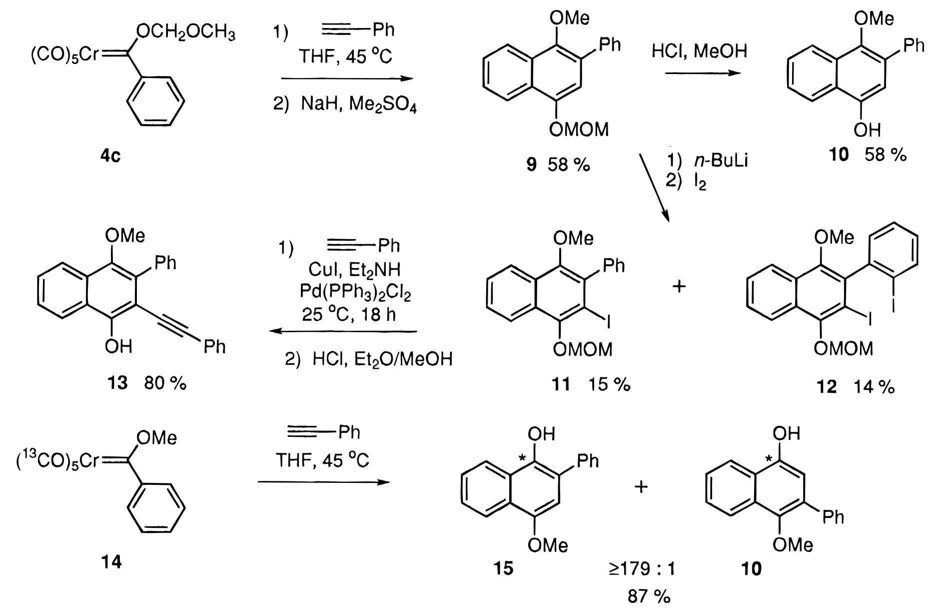
---

(5) (a) 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. (b) Yamashita, A.; Toy, A. *Tetrahedron Lett.* **1986**, *27*, 3471. (c) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177.

(6) (a) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Brandvold, T. A.; Chamberlin, S.; *J. Am. Chem. Soc.* **1991**, *113*, 9293. (b) Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P.; Mitchell, J.; Clardy, J. *Organometallics* **1994**, *13*, 102. (c) Yamashita, A. *Tetrahedron Lett.* **1986**, *27*, 5915. (d) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177.

(7) (a) Yamashita, A.; Toy, A. *Tetrahedron Lett.* **1986**, *27*, 3471. (b) Dötz, K. H.; Muhlemeier, J.; Schubert, U.; Orama, O. *J. Organomet. Chem.* **1983**, *247*, 187. (c) Wulff, W. D.; Tang, P. C.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7677. (d) Chamberlin, S.; Wulff, W. D.; Waters, M. L. *J. Am. Chem. Soc.* **1994**, *116*, 3113.

Scheme 3



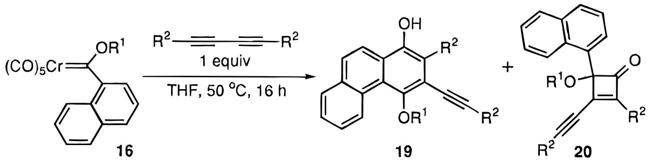
of **5a**, and this was done by the synthesis of the other possible regioisomer **13**, as indicated in Scheme 3.

The benzannulation of the [(methyloxy)methoxy]carbene complex **4c** with phenylacetylene, followed by methylation of the phenol function, gave the naphthalene **9**. The regiochemistry of **9** was determined by cleavage to the 3-phenyl-4-methoxynaphthol (**10**), which was shown not to be the 2-phenyl isomer **15** produced from the reaction of the phenylcarbene complex **14** with phenylacetylene. It has never been unambiguously proven that the benzannulation reaction with phenylacetylene gives the regiochemistry indicated in **15**. Thus, the ^{13}C-labeled carbene complex **14** was prepared, and, upon reaction with phenylacetylene, it was found that the labeled carbon is not directly coupled to any aryl carbon that bears a proton. Since an authentic sample of **10** was in hand, the opportunity was provided to quantify the regioselectivity of the reaction of the phenyl(methoxy)carbene complex with phenylacetylene, which by capillary GC was found to be greater than or equal to 179:1 in favor of **15** over **10**.

The completion of the synthesis of **13** was accomplished by the metalation of the naphthalene **9** directed by the MOM group. Quenching of the resulting aryl lithium with iodine provided a sample of the aryl iodide **11**, which upon coupling with phenylacetylene under the conditions described by Sonogashira[8] and cleavage of the MOM group provided **13**. The spectral data of **13** revealed that this compound is nonidentical with the naphthol **5c** obtained from the reaction of complex **4a** with diyne **8**.

The benzannulations of the naphthylcarbene complex **16** give higher yields of monobenzannulated product with diyne **8** (Table 2) than do those of the phenyl complex **4** (Table 1). As was the case with the phenyl complexes, the benzannulation with the *n*-butyloxy complexes give higher yields than the methoxy complexes. Excellent yields of the alkynylphenanthrol **19c** can be obtained for the reaction of complex **16b** and the diphenylbutadiyne **8**. The reaction of the di-*tert*-butyldiyne **18** with complex **16b** gives mainly the cyclobutenone **20d**, but the diisopropyldiyne **17** gives exclusively the phenanthrol **19e** but in a much reduced yield. The formation of **19e** from 1 equiv of the diyne was accompanied by a 45% recovery of carbene complex **16b**. It is suspected that either polymerization or oligomerization of the diyne is responsible for the incomplete conversion observed for the reaction of diyne **17** with both complexs **16a**,**b**.

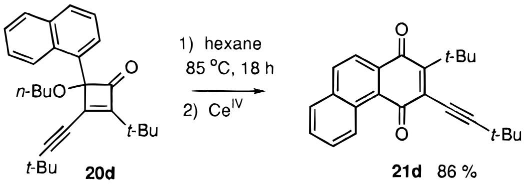
Table 2. Monobenzannulation of 1,3-Diynes with the Naphthyl Complexes **16**[a]



complex	R^1	R^2	alkyne	phenanthrol	cyclobutenone	yield (%) 19	yield (%) 20
16a	Me	Ph	**8**	**19a**		61	
16a	Me	*i*-Pr	**17**	**19b**		41 (53)[b]	
16b	*n*-Bu	Ph	**8**	**19c**		82	
16b	*n*-Bu	Ph	**8**	**19c**	**20c**	86[c]	<2
16b	*n*-Bu	*t*-Bu	**18**	**19d**	**20d**	6[c]	72
16b	*n*-Bu	*i*-Pr	**17**	**19e**		36 (65)[b]	

[a] All reactions carried out at 0.03 M in **16** with 1 equiv of diyne under an argon atmosphere. [b] Based on recovered **16**. [c] Isolated as quinones **21c**,**d** after an oxidative workup with Ce^{IV}.

Scheme 4

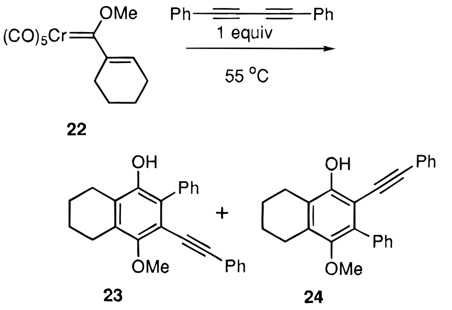


The formations of **19** and **20** were found to occur with the same sense of regiochemical incorporation of the alkyne. This was confirmed by a chemical correlation in which both phenanthrol **19d** and the cyclobutenone **20d** were converted to the quinone **21d**; the former by oxidation with cerium(IV) and the latter by thermolysis and then oxidation, as indicated in Scheme 4. It has been previously observed[5a,b] that the formation of cyclobutenone products is more likely for sterically hindered alkynes and carbene complexes, and this is consistent with the fact that, for the reactions of the naphthyl complex **16b**, significant cyclobutenone formation is seen only with the di-

---

(8) (a) Rossi, R.; Carpita, A.; Bellina, F. *Org. Prepr. Proc. Int.* **1995**, *27*, 129. (b) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

Scheme 5

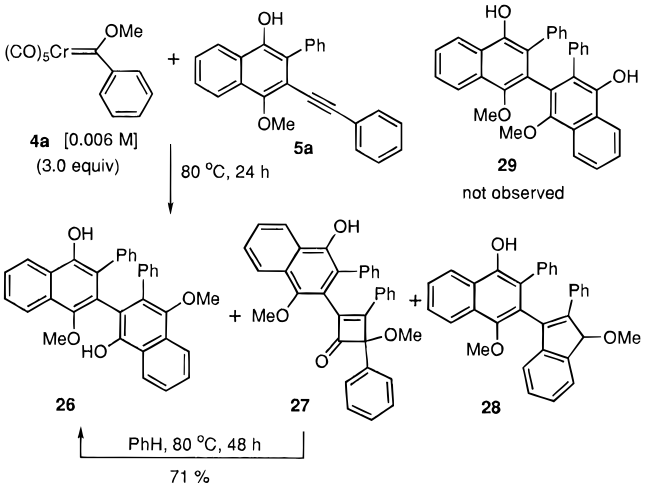


solvent	[22]	Time	Yield 23	Yield 24
benzene	0.05	30 h	44 %	<1.3 %
THF	0.05	20 h	73 %	2.4 %
THF	0.5	20 h	73 %	2.8 %

tert-butyldiyne **18**, and little is seen with the diphenyldiyne **8** and the diisopropyldiyne **17**.

It has been generally observed that alkenyl complexes will give cleaner reaction mixtures in the benzannulation with simple alkynes than do arylcarbene complexes.[6b] This was found to be true for the cyclohexenyl complex **22** and the phenyl complex **4a** in their reactions with the diphenyldiyne **8** (Table 1 and Scheme 5). The reaction of the cyclohexenyl complex gave good yields of the phenol **23**, and no cyclobutenone was detected. The yield of the phenol product was also higher for the cyclohexenyl complex under similar conditions (44% for **4a** vs 73% for **22**). Another difference is that the yield of the phenol **23** is not dependent on the concentration of the reaction, whereas the yield of **5a** fell from 44% to 23% when the concentration was raised from 0.03 to 0.5 M. A similarity in the two complexes is the solvent dependence on efficiency of phenol formation. The yields of the phenol product drop for both complexes when the reaction solvent is changed from THF to benzene. In the case of the aryl complex **4a**, it is not clear whether this is due to a decrease in the rate of the reaction or the formation of undetected side products since significant amounts of carbene complex were recovered in the reaction with benzene (Table 1). For the cyclohexenyl complex **22**, however, it appears that this is due to a solvent-induced change in the product distribution, since the yield of **23** drops by a factor of 2, even though the reaction goes to completion. In the case of the reaction of the cyclohexenyl complex **22** with diyne **8**, we were able to isolate the regioisomeric phenol **24**. Based on the isolated yields for each isomer, the regioselectivity for this reaction is approximately 28:1. Upon oxidation with cerium(IV), both of the phenols **23** and **24** gave the quinone **25**, confirming their regioisomeric relationship.

Scheme 6

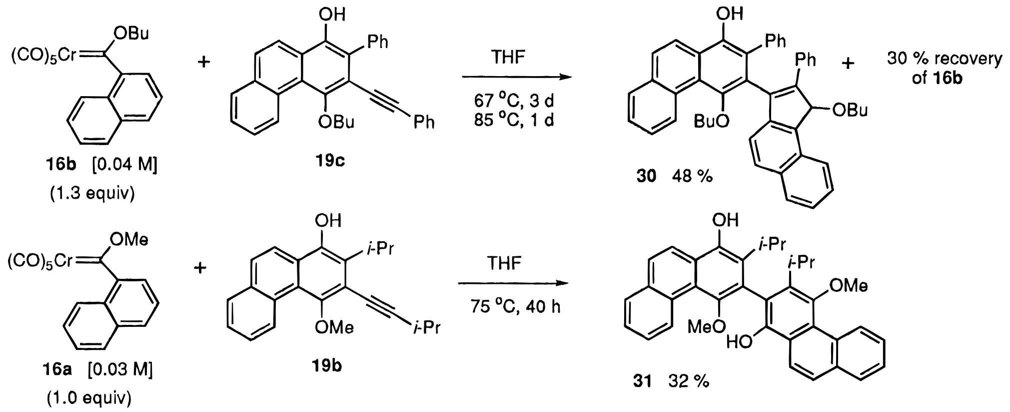


Solvent	[5a]	% Yield 26	% Yield 27	% Yield 28
THF	0.1 M	35	16	11
THF	0.05	17	29	8
THF	0.006	19	32	23
benzene	0.05	16	nd	nd

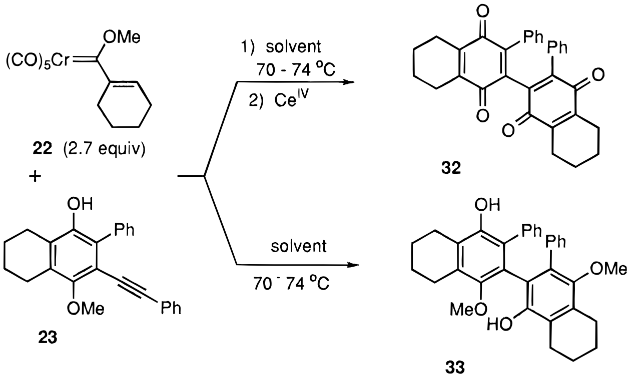
Biaryls from the Sequential Benzannulation of 1,3-Diynes. Benzannulation of the diphenyldiyne **8** with the first equivalent of phenylcarbene complex **4a** produced phenol and cyclobutenone products (Table 1), and benzannulation of the second equivalent gives phenol, cyclobutenone, and indene products, as shown in Scheme 6. A single regioisomer of each of the three products was observed. Since the phenol product obtained was not C_2 symmetric, the regioisomeric structure **29** could be ruled out as the product of the reaction. Formation of the regioisomer **26** is consistent with the general observation that alkynes are incorporated with the largest group of the alkyne into the position adjacent to the phenol function.[7] In this case, while both substituents of the alkyne in **5a** are aryl groups, the naphthyl groups bears two ortho substituents and thus, as expected, is incorporated into the position ortho to the phenol in the last-formed naphthalene ring in **26**. The regiochemistry of cyclobutenone **27** was assigned by its thermal conversion to the phenol **26**. The regiochemistry of the indene **28** was assigned on the assumption that it has the same regiochemistry as the phenol and cyclobutenone. Indene products are well established primary products from the reactions of carbene complexes with alkynes, and their formation is favored with polar solvents, increased electron density on the carbene complex, decreased concentration, and the presence of aryl groups on the alkyne.[6] A slight dependence of the product distribution on the concentration was seen, as indicated in Scheme 6, with the fraction of the indenyl product the highest at the lowest concentration in THF. The one attempt made in benzene as solvent led to a dramatic drop in the mass balance and to less than detectable amounts of **27** and **28**. This observation was not further pursued, although a considerable amount of insoluble material was observed for this reaction. Nonetheless, the biaryl **26** can be obtained in 42−46% overall yield from the reaction shown in Scheme 6, since the cyclobutenone **27** can be thermally converted to the biaryl **26**.The second step of the sequential benzannulation of the (butyloxy)carbene complex **16b** with diphenyldiyne **8** gives the indene product **30** as the only significant product of the reaction, along with a 30% recovery of the phenanthrylacetylene **19c**. This is despite the fact that the first step is highly efficient giving the phenanthrol **19c** in 82% yield from the reaction of complex **16b** with 1 equiv of diyne **8** (Table 2). This reaction of the butyloxy complex **16b** with the 4-(butyloxy)phenanthrol **19c** is to be compared with the reaction of the methoxy complex **4a** with the 4-methoxynaphthol **5a**. The fact that the reaction of **16b** with **19c** gives a greater preference for indene over phenol compared to the reaction of **4a** with **5a** is consistent with observations that increased steric hindrance on the carbene complex and in the alkyne can lead to increased proportions of indene products.[1,5,6] With this in mind, the reaction of the methoxycarbene complex **16a** with the phenanthrylacetylene **19b** was investigated, and it was found that, as expected, this reaction gave an increased preference for phenol products relative to the reaction of **16b** with **19c** (Scheme 7).

The synthesis of biaryls by the sequential double benzannulation of the diyne **8** was more successful with the cyclohexenylcarbene complex **22** than with either the phenylcarbene complex **4a** or the naphthylcarbene complex **16a**. The first step gave the arylacetylene **23** in 73% yield, and the second gave the biaryl **33** in 56% yield. The increased facility of the biaryl synthesis from the cyclohexenyl complex **22** compared to the

Scheme 7

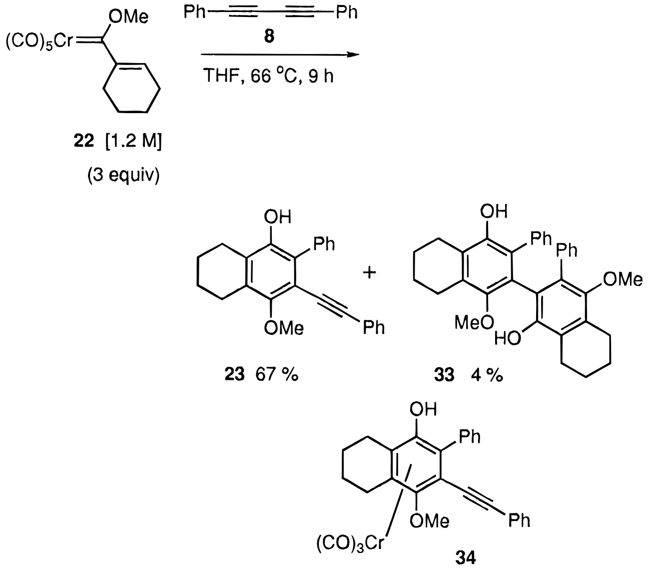


Scheme 8



solvent	[22]	Time	Yield 32	Yield 33
benzene	0.016 M	33 h	16 %	
benzene	0.16 M	34 h	42 %	
benzene	1.7 M	10 h	60 %	
THF	1.7 M	12 h		56 %

Scheme 9

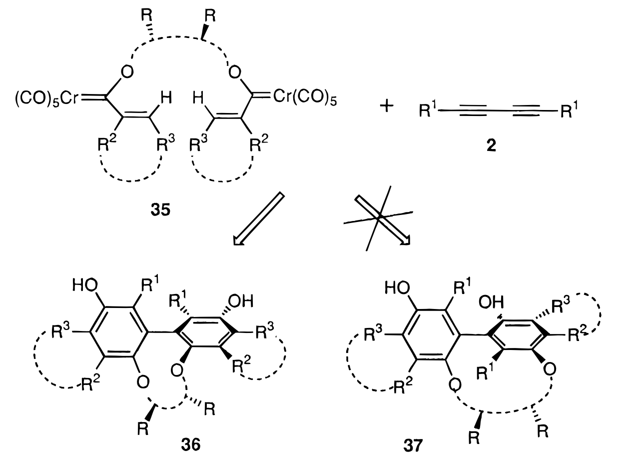


aryl complexes **4a** and **16a** is consistent with the well-established observation that the benzannulations of alkenyl complexes are less likely than those of aryl complexes to give indene or cyclobutenone side products.[6b] The yield of the bis-quinone **32**, obtained upon an oxidative workup, increases with increasing concentration, giving a 60% yield when the reaction is carried out at 1.7 M in carbene complex. In this reaction, there is not a significant solvent effect, since the reactions in THF and benzene give yields that are within experimental error.

In contrast to the finding that the double-benzannulation of diyne **8** with the cyclohexenyl complex **22** can be successfully performed if each benzannulation is carried out separately (Scheme 8), no success has been realized for the one-pot double benzannulation. The reaction of diyne **8** with an excess of carbene complex **22** (3 equiv) in THF at 1.2 M in **22** and at 66 °C in 9 h gave a 67% yield of the monobenzannulated product **23** and a 4% yield of the double benzannulated product **33** (Scheme 9). This reaction cannot be driven further. Upon heating the reaction mixture at 70 °C for 60 h, the yield of the monobenzannulated product **23** drops to 5%, but the yield of the double benzannulated product **33** is still negligible (0.6%). One possible explanation for this is that, prior to workup and exposure to air, the monobenzannulated product exists as the chromium tricarbonyl complex **34**, which is much less reactive to the second benzannulation than the noncomplexed naphthol **23**. This is supported by TLC of the reaction mixture, which, after 4 h at 66 °C, reveals the presence of mainly one yellow compound, which has an R_f value different from that of **23**. In the isolation of **23**, the reaction mixture is stirred in air prior to chromatography; however, if the reaction mixture is opened and directly loaded onto a silica gel column and quickly eluted, a small portion of yellow compound can be obtained. While this material is air sensitive with respect to conversion to **23**, its ^{1}H NMR and IR spectra are consistent with the arene complex **34**. If the unreactivity of the arene complex **34** is the problem, then a solution would involve the *in situ* decomplexation of **34**. While such a solution has not yet been found, this was attempted by carrying out the reaction in the presence of 3 equiv (per Cr) of tri-*n*-butylphosphine, which, after 10 h at 70 °C, gave only a 74% yield of **23** (along with <1.3% of regioisomer **24**) and no detectable amount of the double benzannulated product **33**.

Biaryls from the One-Pot Intramolecular Double Benzannulation of 1,3-Diynes. Given that the inability to realize a one-pot double benzannulation with diyne **8** with either the phenylcarbene complex **4a** or the cyclohexenyl complex **22** was due to the sluggishness in the second benzannulation, consideration was given to strategies involving bis-carbene complexes of the type **35** since the second benzannulation in the reactions of these complexes with diynes would be intramolecular. In addition to providing a possible solution to the one-pot double benzannulation of diynes, this strategy would also serve to expand the scope of these reactions and provide access to symmetrical biaryls of the type **36** and would thus be complementary to the intermolecular version, which as was seen above gives unsymmetrical biaryls (Scheme 6). It is expected that bis-carbene complexes of the type **35** would give the symmetrical biaryl **36** in favor of the unsymmetrical biaryl **37** (Scheme 10). Although meta-cyclophanes containing six atoms in the bridge are known,[9] it is expected that the strain inherent

Scheme 10



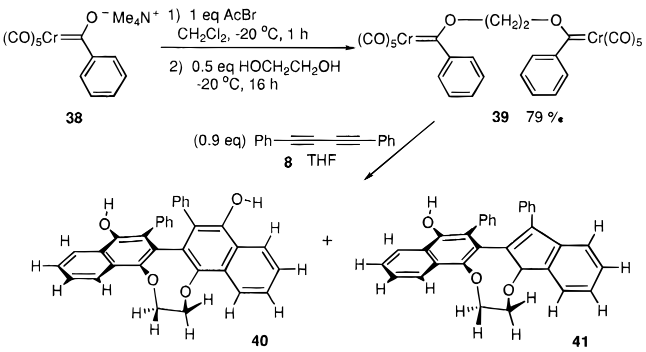
in the meta-cyclophane **37** would be sufficient so as to lead to the predominant production of the symmetric biaryl **36**, which does not contain a meta-cyclophane bridge. Finally, the strategy of employing an intramolecular double benzannulation of a 1,3-diyne with a bis-carbene complex offers an opportunity for an asymmetric synthesis of biaryls with an induction in the stereochemistry of the newly formed biaryl axis from a chiral diol that is used to tether the bis-carbene complex.

The bis-methylene-tethered phenyl-substituted carbene complex **39** was prepared by the Connors method for the preparation of alkoxy complexes from alcohols.[10,15] The mixed anhydride from (hydroxyphenyl)carbene complex and acetic acid was prepared by the treatment of the metal acylate **38** with acetyl bromide. This anhydride was used to doubly acylate ethylene glycol, which gave the bis-carbene complex **39** in 79% yield. The reaction of the bis-carbene complex **39** with 0.9 equiv of the diphenylbutadiyne **8** gave two predominant products, which were identified as the desired 2,2′-binaphthol **40** and the indenylnaphthalene **41**. The latter resulted from the failure of carbon monoxide to insert in one of the annulation steps. Based on the results shown in Table 1 and Scheme 6, it is likely that the naphthalene unit in **41** is constructed in the first annulation followed by the formation of the indene unit in the second. The indenylnaphthalene **41** was obtained as one diastereomer, but the relative stereochemistry was not determined. The data in Scheme 11 reveal that the partition between the binaphthalene **40** and the naphthylindene **41** is dependent on the concentration and the temperature, although the low mass balance observed for these reactions somewhat obscures the significance of these observations. Higher concentration favors **40** over **41**, consistent with the general observations seen for reactions with simple alkynes, where higher concentration favors the incorporation of carbon monoxide-inserted products.[6ab,11] In addition, it can be seen that higher temperature shifts the partition in favor of **41**, which is also consistent with previous studies on simple alkynes which revealed that higher temperatures favor non-CO-inserted products.[6a]

Two bis-carbene complexes derived from substituted glycols were investigated, and the results are summarized in Schemes 12 and 13. Complex **42** was prepared from the *meso*-2,3-butanediol in 51% yield, as indicated in Scheme 12. The reaction of complex **42** with the diphenyldiyne **8** did not give either of the two products seen with the unsubstituted ethylene-tethered complex **39** (Scheme 11). Instead, this reaction produced as the predominant product of the reaction the indenyl-substituted cyclobutenone **43**, which was obtained as a single diastereomer in 22% yield. The relative stereochemistry in **43** was not assigned. It is not known why the presence of the methyl groups in complex **42** causes such a dramatic change in the reaction course. The fact that it is not known if the cyclobutenone or the indene ring is formed in the first annulation step makes it difficult to consider how the presence of the methyl groups may affect the various intermediates that are likely involved in the mechanism of this reaction and thus the product distribution from this reaction.

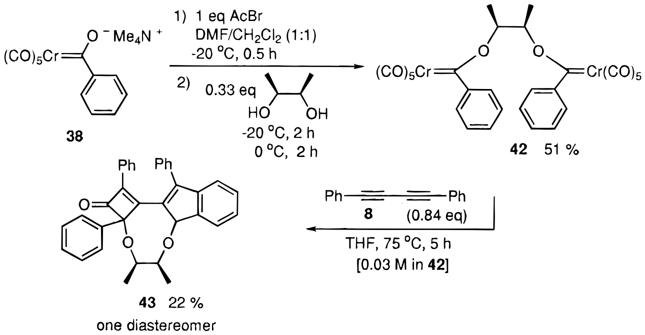
The bis-carbene complex **44** was prepared in optically pure form from (2*R*,3*R*)-butane-2,3-diol to probe the degree to which the stereochemical information present in the chiral diol can be used to induce a specific stereochemistry in the axis of chirality generated when the two arene rings of the 2,2′-binaphthol **46** are generated from the double benzannulation of diyne **8**. The outcome of the reaction of the chiral bis-carbene complex **44** with diyne **8** was quite different from that of its meso diastereomer **42**. In fact, the reaction of complex **44** gave an equal mixture of the 2,2′-binaphthol **46** and the indenyl naphthalene **47**, which is nearly identical to the outcome of the reaction of the unsubstituted tethered complex **39** (Scheme 11). This reaction also produced a 29% yield of the dihydrodioxane **48**, which was found in a control experiment (51%) to result from the thermal decomposition of the starting carbene complex **44**. Such thermal dimerizations of carbene complexes are known for both inter- and intramolecular situations.[12] A single diastereomer of the 2,2′-binaphthol **46** was formed in this reaction as determined by ^{1}H and ^{13}C NMR. As will be shown below, it has been determined that the 2*R*,3*R* configuration in the diol led to the selective formation of the *S*-configuration of

Scheme 11



[39]	Temp	Time	Yield 40	Yield 41
0.005 M	80 °C	16 h	12 %	21 %
0.024 M	80 °C	16 h	23 %	13 %
0.029 M	105 °C	4 h	19 %	25 %
0.16 M	45 °C	16 h	19 %	7 %
0.20 M	105 °C	4 h	7 %	13 %

Scheme 12



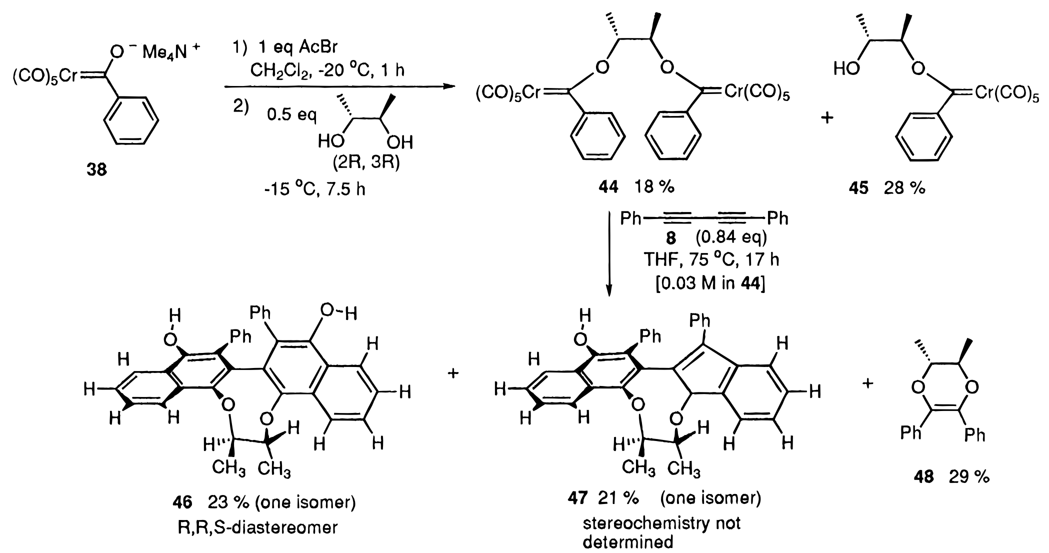
---

(9) (a) Hirano, S.; Hiyama, T.; Fujita, S.; Nozaki, H. *Chem. Lett.* **1972**, 707. (b) For citations to the literature, see: Nishimura, J.; Okada, Y.; Inokuma, S.; Nakamura, Y.; Gao, S. R. *Synlett* **1994**, 884.

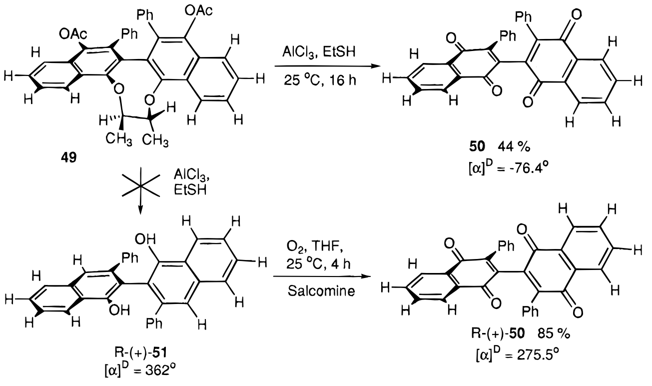
(10) Connor, J. A.; Jones, E. M. *J. Chem. Soc. A* **1971**, 3368.

(11) (a) Harvey, D. F.; Grenzer, E. M.; Gantzel, P. K. *J. Am. Chem. Soc.* **1994**, *116*, 6719. (b) Gross, M. F.; Finn, M. G. *J. Am. Chem. Soc.* **1994**, *116*, 10921.

Scheme 13



Scheme 14



the chiral axis in the 2,2′-binaphthol **46**. The indenylnaphthalene **47** was also obtained as a single diastereomer; however, the relative stereochemistry was not assigned. The reaction of complex **44** with diyne **8** has been attempted only with the conditions indicated in Scheme 13. Further optimization experiments will await the development of improved methods for the synthesis of chiral bis-carbene complexes of the type **44**.

The configuration of the biaryl chiral axis in the 2,2′-binaphthol **46** was determined by chemical correlation with the known optically pure 2,2′-binaphthol **51**[13] via the 2,2′-binaphthoquinone **50**. Oxidation of the optically pure (*R*)-(+)-enantiomer of the binaphthol **51** with salcomine and air gave the bis-naphthoquinone **50**, which had a specific rotation of $[\alpha]^D = 275.5°$. The 2,2′-binaphthol **46** was inadvertently converted to the bis-naphthoquinone **50** as indicated in Scheme 14. The 2,2′-binaphthol **46** was first converted to the bis-acetate **49** by treatment with acetic anhydride, DMAP, and triethylamine in 71% yield. A direct chemical correlation was planned by the conversion of the bis-acetate to the binaphthol **51** with aluminum chloride and ethanethiol, which is known to effect transformations related to that indicated by **49** to **51**.[13] Quite unexpectedly, this reaction led to oxidation to the 2,2′-naphthoquinone **50** in 44% yield. The optical rotation of the naphthoquinone **50** obtained from **49** was $[\alpha]^D = -76.4°$, which represents material that is only 28% optically pure, assuming that no optical activity is lost when **51** is converted to **50**. The 2,2′-binaphthol **46** appears to be a single diastereomer by ^{1}H and ^{13}C NMR, and thus it is thought that the incomplete optical purity is due to partial racemization caused by the treatment with ethanethiol and aluminum chloride. Support for this possibility comes from a control experiment performed on optically pure bis-naphthoquinone **50**. When a sample of **50** ($[\alpha]^D = 275.5°$) was subjected to aluminum chloride and ethanethiol under the reaction conditions, a material was recovered which was not the bis-naphthoquinone **50**. The structure of this compound was not determined but could have been the hydroquinone since, when this material was briefly treated with aqueous ceric ammonium nitrate, the bis-quinone **50** was obtained with a 51% recovery and had an optical rotation of 40.8°, which corresponds to 15% optical purity. Control experiments showed that no loss of optical purity occurs upon treatment of the bis-naphthoquinone **50** with ceric ammonium nitrate. These experiments thus show the (2*R*,3*R*)-diol unit in the bis-carbene complex **44** will induce the formation of an *S*-configuration of the biaryl axis in the 2,2′-binaphthol **46**. The induction in the formation of the biaryl axis in **46** produces exclusively a single compound (*R*,*R*,*S*-configuration) as indicated by ^{1}H and ^{13}C NMR spectroscopy, but since an authentic sample of the (*R*,*R*,*R*)-diastereomer of **46** is not available, a precise quantitation of the degree of induction cannot be determined.

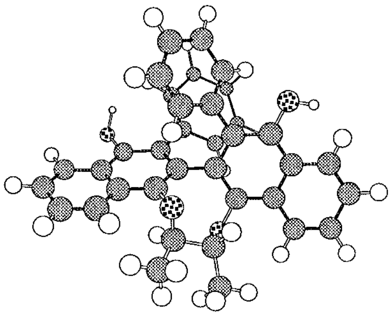
The selective formation of **46** with a chiral axis with the *S*-configuration from the (2*R*,3*R*)-butane-2,3-diol-derived carbene complex **44** was predicted from a consideration of models. The Chem3D model of **46**, which is produced when the *S*-biaryl axis is generated from the carbene complex **44** that is derived from (2*R*,3*R*)-butane-2,3-diol, is shown in Chart 1. This is to be compared with the model of the diastereomer **52**, which would be generated in a situation where the *S*-biaryl axis was generated from a carbene complex analogous to **44** which was derived from (2*S*,3*S*)-butane-2,3-diol. From these models it can be seen that the *S*-biaryl axis should be preferentially formed from the (2*R*,3*R*)-diol auxiliary rather than from a (2*S*,3*S*)-diol auxiliary. In the model of **46**, it can be seen that the methyl groups on the ethylene bridge between the oxygens are directed away from the binaphthyl unit, and this would be a more favorable situation than that for **52**, where the methyl groups

---

(12) Several intermolecular examples have been described since the original report by Fischer: (a) Fischer, E. O.; Heckel, B.; Dötz, K. H.; Muller, J.; Merner, H. J. *J. Organomet. Chem.* **1969**, *16*, P29. For intermolecular examples, see: (b) Huy, H. T.; Lefloch, P.; Louis, J. M.; Fetizon, M. *J. Organomet. Chem.* **1986**, *311*, 79. (c) Macomber, D. W.; Hung, M. H.; Verma, A. G. *Organometallics* **1988**, *7*, 2072.

(13) Bao, J.; Wulff, W. D.; Dominy, J. B.; Fumo, M. J.; Grant, E. B.; Rob, A. C.; Whitcomb, M. C.; Yeung, S.-M.; Ostrander, R. L.; Rheingold, A. L. *J. Am. Chem. Soc.* In press.

Chart 1



46 (S)-biaryl axis from (2R,3R)-butanediol

52 (S)-biaryl axis from (2S,3S)-butanediol

generate close contacts with the bottom periphery of the binaphthol unit.

This work has demonstrated the viability of a new approach to the synthesis of biaryls via the double benzannulation of conjugated 1,3-butadiynes with chromium carbene complexes. In intermolecular reactions of diynes with 2 equiv of carbene complex, the two benzannulations must be carried out sequentially rather than concurrently. The first benzannulation occurs with high regioselectivity and with the formation of few side products for all of the complexes examined, which included phenyl, naphthyl, and cyclohexenyl complexes. The second benzannulation also occurs with high regioselectivity for all complexes. However, the reactions of the phenyl and naphthyl complexes (but not cyclohexenyl) occur with the formation of five-membered-ring non-CO-inserted products as serious side reactions. These side products can be suppressed to a degree by controlling the concentration and the steric bulk of the carbene complex and the diyne. The intramolecular double benzannulation reactions of bis-carbene complexes with diynes allows for the two benzannulations to be performed concurrently. Additional advantages of the intramolecular reactions include the generation of biaryls with symmetry complementary to that possible with the intermolecular reactions and include the fact that this biaryl synthesis can be rendered asymmetric by incorporating a chiral diol in the tether in the bis-carbene complexes. The success obtained in this work in establishing the viability of a new approach to the asymmetric synthesis of biaryls should stimulate the further consideration and investigations of the reaction of carbene complexes with 1,3-butadiynes.

Experimental Section

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Tetrahydrofuran, ether, and benzene were distilled from benzophenone ketyl under nitrogen. Cerium(IV) oxidation employed a 0.5 M solution of ceric ammonium nitrate (CAN) in 0.1 M aqueous nitric acid. Dichloromethane and hexane were distilled from calcium hydride. Proton NMR data were obtained either on a University of Chicago-built DS-1000 500 MHz instrument or on a General Electric QE-300 300 MHz instrument. Carbon-13 spectra were obtained on the QE-300 instrument at 75 MHz. GPC analyses were performed on a Varian Star 3600 instrument. High-resolution mass spectra were recorded on a VG 70-250 instrument. Elemental analyses were done by Galbraith Laboratories in Knoxville, TN. Optical rotations were obtained on a Perkin-Elmer 141 polarimeter at a wavelength of 589 nm (sodium D line) using 1.0 dm cells. Specific rotations, $[\alpha]^{\mathrm{D}}$, are reported in degrees per decimeter at 25 °C, and the concentration (*c*) is given in grams per 100 mL.

Reaction of Phenyl(methoxy)chromium Carbene Complex 4a with 1,4-Diphenyl-1,3-butadiyne (8). A solution of 0.265 g (0.85 mmol) of 1,4-diphenyl-1,3-butadiyne (**8**) and 0.172 g (0.85 mmol) of phenyl(methoxy)chromium carbene complex **4a**[14] in 28.3 mL of THF (0.03 M in **4a**) was introduced into a 100 mL single-necked flask that was modified by the replacement of the 14/20 joint with a threaded high-vacuum stopcock. The resulting solution was deoxygenated by the freeze−pump−thaw method (three cycles) and backfilled with argon, and then the stopcock was closed at 25 °C and the flask placed in a 60 °C oil bath for 24 h. After removal of the solvent, the two products were separated from the crude reaction mixture on silica gel by elution with a 1:1:8 mixture of ether/CH_2Cl_2/hexane and then with a 1:1 mixture of $CHCl_3$/hexane to give **6a** (0.0622 g, 0.18 mmol, 21%) and **5a** (0.0593 g, 0.17 mmol, 20%). Spectral data for **5a**: $R_f = 0.37$ (1:1 $CHCl_3$/hexane); white solid, mp 90−92 °C; ${}^1H$ NMR ($CDCl_3$) δ 4.14 (s, 3 H), 5.42 (s, 1 H), 7.15 (m, 2 H), 7.22 (m, 3 H), 7.48 (m, 1 H), 7.53 (m, 6 H), 8.20 (d, 1 H, $J = 7.6$ Hz), 8.21 (d, 1 H, $J = 7.4$ Hz); ${}^{13}C$ NMR ($CDCl_3$) δ 62.01, 85.68, 97.90, 112.35, 122.12, 122.76, 123.45, 124.99, 126.67, 126.90, 127.66, 127.99, 128.08, 128.17, 128.46, 129.11, 130.89, 131.14, 134.82, 144.23, 152.15; IR (neat) 3538 s, 3057 m, 2929 s, 2846 m, 1586 m, 1492 m, 1443 m, 1369 s, 1296 s, 1211 m, 1144 m, 1064 s, 1028 m, 1003 m, 829 w, 757 s, 690 s cm^{-1}; mass spectrum, *m/z*, (relative intensity) 350 M^+ (100), 335 (45), 318 (12), 307 (45), 289 (22), 276 (35), 202 (23), 138 (16), 105 (14), 97 (15); high-resolution EI MS calcd for $C_{25}H_{18}O_2$ *m/z* 350.1307, measd 350.1303. Anal. Calcd for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18. Found: C, 85.46; H, 5.21. Spectral data for **6a**: $R_f = 0.41$ (1:1:8 CH_2Cl_2/ether/hexane); yellow oil; ${}^1H$ NMR ($CDCl_3$) δ 3.59 (s, 3 H), 7.33−7.51 (m, 9 H), 7.60−7.66 (m, 4 H), 8.14−8.17 (m, 2 H); ${}^{13}C$ NMR ($CDCl_3$) δ 53.76, 81.84, 102.00, 117.08, 121.54, 126.44, 128.02, 128.30, 128.51, 128.55, 128.70, 128.83, 130.52, 130.77, 132.26, 136.48, 150.68, 151.89, 192.93; IR (neat) 3062 w, 3030 w, 2953 w, 2931 w, 2184 m, 1758 s, 1586 w, 1495 m, 1442 m, 1360 m,1222 w, 1145 w, 1099 w, 1051 w, 1026 w, 756m, 689s cm^{-1}; mass spectrum, *m/z* (relative intensity) 350 M^+ (100), 335 (41), 307 (46), 289 (16), 279 (24), 202 (33), 105 (35), 77 (27); high-resolution EI MS calcd for $C_{25}H_{18}O_2$ *m/z* 350.1307, measd 350.1321.

The outcome of this reaction under a variety of conditions is summarized in Table 1. The deoxygenation procedure is not necessary, as indicated by the data in entries 4−6. These reactions were carried out by introduction of the reagents into an argon-flushed flask equipped with a reflux condensor. The regiochemistry of the cyclobutenone was shown by chemical correlation to be the same as that determined for the naphthol **5a**. A solution of the cyclobutenone **6a** (0.039 g, 0.11 mmol) in 15 mL of hexane was heated in a sealed flask at 82 °C for 17 h under nitrogen. After purification by flash chromatography with a 1:1:10 mixture of ether/CH_2Cl_2/hexane, 0.038 g (0.11 mmol, 97%) of naphthol **5a** was isolated.

The reaction of diyne **8** with 3 equiv of carbene complex **4a** in THF (0.06 M in **4a**) at 110 °C for 14 h gave a complex mixture of products in which none was significantly prominent. In light of the formation of complex **34** from the reaction of complex **22** and the resistance of **34** to further reaction with **22**, the reaction of **4a** with diyne **8** was performed in the presence of butylphosphine. A mixture of 0.055 g (0.272 mmol) of 1,4-diphenyl-1,3-butadiyne, 0.255 g (0.817 mmol) of

---

[14] Complex **4a** was prepared as described by the literature procedure with methyl triflate as the alkylating agent. (a) Fischer, E. O.; Maasböl, A. *Chem. Ber*. **1967**, *100*, 2445. (b) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Muller, J.; Fischer, R. D. *J. Organomet. Chem*. **1971**, *28*, 237.

[15] Dumas, S.; Lastra, E.; Hegedus, L. S. *J. Am. Chem. Soc.* **1995**, *117*, 3368.

phenyl(methoxy)chromium carbene complex **4a**, and 0.61 mL (2.45 mmol) of tri-*n*-butylphoshine in 136 mL of THF was deoxygenated and allowed to react at 80 °C for 23 h as described in the procedure above. The resulting solution was degassed three times and was put in an 80 °C oil bath for 23 h. The two major products produced were separated on silica gel by elution with a 1:9 mixture of EtOAc/hexane and then with a 1:1 mixture of CH_2Cl_2/hexane to give **5a** (0.020 g, 0.057 mmol, 21%) and methoxy benzoate (8 mg, 0.059 mmol, 22%).

Preparation of Phenyl(*n*-butyloxy)carbene Complex 4b. To a solution of 1.33 g (3.58 mmol) of the tetramethylammonium metalate **38**[16] in 28 mL of dichloromethane at −20 °C was added 0.265 mL (3.58 mmol) of acetyl bromide under nitrogen. After the mixture was stirred at −20 °C for 1 h, 0.328 mL (3.58 mmol) of butanol was added, and the resulting solution was stirred for an additional 2 h. The red mixture was poured into an aqueous saturated $NaHCO_3$ solution. The organic layer was washed with water and brine and then dried with anhydrous $MgSO_4$. The solvent was removed, and the red residue was loaded onto a silica gel column and eluted with a 1:1:30 mixture of ether/CH_2Cl_2/hexane ($R_f = 0.61$) to give 1.18 g (3.33 mmol, 93%) of complex **4b** as a red oil. Spectral data for **4b**: ^1H NMR ($CDCl_3$) δ 1.01 (t, 3 H, $J = 7.2$ Hz), 1.54−1.59 (m, 2 H), 1.95−2.05 (m, 2 H), 4.81 (s, 2 H), 7.20 (s, 2 H), 7.34−7.37 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 13.62, 19.18, 31.51, 81.02, 122.61, 128.14, 129.99, 153.68, 216.23, 224.27, 349.01; IR (neat) 3037 w, 2964 m, 2938 w, 2877 w, 2061 s, 1948 s, 1932 s, 1462 w, 1441 w, 1382 w, 1272 m, 1234 m, 1207 m, 1168 m, 968 w, 938 w, 908 w, 877 w, 760 w, 656 s, 621 m cm^{-1}; mass spectrum, *m/z*, (relative intensity) 354 M$^+$ (1), 326 (1), 298 (1), 272 (1), 242 (1), 220 (36), 123 (53), 105 (96), 80 (100), 77 (44).

Reaction of Phenyl(*n*-butyloxy)carbene Complex 4b with Diphenyl-1,3-butadiyne (8). The reaction of carbene complex **4b** (0.293 g, 0.83 mmol) and 1,3-butadiyne **8** (0.167 g, 0.83 mmol) in 27 mL of THF was carried as described for the reaction **4a** with **8** at 50 °C for 17 h. The crude reaction mixture was oxidized by stirring with 9.9 mL (0.5 M) of CAN solution for 45 min at 25 °C. The resulting mixture was diluted with ether, and the organic layer was washed with water, aqueous saturated sodium bicarbonate, water and brine. The two products, quinone **7** (0.1465 g, 0.44 mmol, 53% as yellow solid, mp = 140−141 °C, $R_f = 0.18$) and cyclobutenone **6b** (0.0677 g, 0.17 mmol, 21% as yellow oil, $R_f = 0.41$), could be isolated from the concentrate after flash chromatography on silica gel with a 1:1:16 mixture of ether/CH_2Cl_2/hexane. Spectral data for **6b**: ^1H NMR ($CDCl_3$) δ 0.94 (t, 3 H, $J = 7.3$ Hz), 1.44−1.52 (m, 2 H), 1.71 (pentet, 2 H, $J = 6.9$ Hz), 3.72−3.80 (m, 2 H), 7.35−7.50 (m, 9 H), 7.61−7.67 (m, 4 H), 8.16−8.19 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.82, 19.24, 31.98, 65.66, 81.96, 101.62, 116.93, 121.59, 126.41, 127.99, 128.17, 128.44, 128.69, 128.81, 128.96, 130.45, 130.68, 132.21, 136.92, 151.36, 151.49, 193.56; IR (neat) 3082 w, 3061 m, 3032 w, 2958 s, 2932 s, 2872 s, 2184 s, 1760 vs, 1718 w, 1611 m, 1588 m, 1496 s, 1448 s, 1359 s, 1222 m, 1177 s, 1098 m, 1055 m, 1026 m, 938 w, 812 w, 773 m, 756 w, 690 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 392 M$^+$ (7), 336 (11), 335 (12), 308 (8), 275 (10), 220 (15), 203 (17), 202 (76), 129 (22), 105 (100), 77 (52); high-resolution EI MS calcd for $C_{28}H_{24}O_2$ *m/z* 392.1776, measd 392.1796. Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16. Found: C, 86.45; H, 5.94. Spectral data for **7**: ^1H NMR ($CDCl_3$) δ 7.30−7.41 (m, 5 H), 7.50−7.55 (m, 3 H), 7.58−7.64 (m, 2 H), 7.76−7.82 (m, 2 H), 8.16−8.24 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 84.39, 106.25, 122.04, 126.59, 126.93, 127.65, 128.35, 129.48, 129.69, 130.40, 131.78, 132.22, 133.01, 133.77, 134.13, 148.46, 181.78, 183.42 (two carbons not located); IR (neat) 3068 w, 2197 m, 1668 s, 1654 s, 1595 m, 1495 w, 1442 w, 1354 m, 1324 w, 12987 s, 1243 w, 1208 w, 1143 w, 1071 w, 961 w, 841 w, 758 s, 716 s, 690 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 334 M$^+$ (100), 306 (25), 278 (15), 277 (18), 276 (32), 151 (13), 104 (14), 76 (20); high-resolution EI MS calcd for $C_{24}H_{14}O_2$ *m/z* 334.0994, measd 334.0999. Anal. Calcd for $C_{24}H_{14}O_2$: C, 86.21; H, 4.22. Found: C, 85.98; H, 5.14.

The reaction was repeated at 0.03 M in **4b** and heated at 70 °C for 24 h. The crude reaction mixture was directly loaded onto a silica gel column without an oxidative workup with CAN to give a 61% yield of the naphthol **5b** upon elution from silica gel with a 1:1:16 mixture of ether/CH_2Cl_2/hexane. As indicated in Table 1, the reaction under the same conditions in benzene gave a 31% yield of **5b** (40% based on unrecovered **4b**) and in hexane gave a 25% yield of **5b** (40% based on unrecovered **4b**). Spectral data for **5b**: $R_f = 0.29$ (1:15 EtOAc/hexane); white solid, mp 73−74 °C; ^1H NMR ($CDCl_3$) δ 1.06 (t, 3 H, $J = 7.4$ Hz), 1.66−1.74 (m, 2 H), 1.98−2.02 (m, 2 H), 4.31 (t, 2 H, $J = 6.5$ Hz), 5.46 (s, 1 H), 7.14−7.17 (m, 2 H), 7.26−7.28 (m, 3 H), 7.52−7.62 (m, 7 H), 8.18−8.28 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.09, 19.57, 32.68, 74.84, 86.13, 97.63, 112.49, 122.24, 122.69, 123.56, 124.98, 126.61, 126.78, 128.00, 128.18, 128.36, 128.42, 129.09, 130.91, 131.07, 134.93, 144.04, 151.45 (1 aryl C not located); IR (neat) 3544 bs, 3057 w, 2957 s, 2929 s, 2872 m, 1597 w, 1587 m, 1493 m, 1442 m, 1393 m, 1356 m, 1309 m, 1295 s, 1212 m, 1146 m, 1146 m, 1064 s, 1029 m, 972 m, 848 w, 755 s, 703 m, 690 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 392 M$^+$ (100), 336 (90), 318 (14), 307 (42), 289 (17), 276 (16), 231 (12), 202 (23), 105 (10); high-resolution EI MS calcd for $C_{28}H_{24}O_2$ *m/z* 392.1776, measd 392.1809. Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16. Found: C, 85.00; H, 6.18.

The regiochemistry of cyclobutenone **6b** was shown by chemical conversion to be the same as that determined for the naphthol **5b**. The cyclobutenone **6b** (0.0291 g, 0.074 mmol) was dissolved in 10 mL of hexane and heated at 80 °C for 17 h under argon. After removal of the solvent, the residue was loaded onto a silica gel and eluted with a 1:9 mixture of EtOAc/hexane to give 0.0251 g (0.064 mmol, 86%) of **5b** as a white solid. This material was found to be identical by ^1H NMR and TLC to the major product from the reaction of complex **4b** with 1,4-diphenyl-1,3-butadiyne.

Preparation of Phenyl[(methoxymethyl)oxy]carbene Complex 4c. To a solution of chromium hexacarbonyl (5.15 g, 23.3 mmol) in 100 mL of ether at 0 °C was added phenyllithium (25.7 mmol as a 1.8 M solution in a 7:3 mixture of cyclohexane/ether). After 0.5 h, the ice bath was removed, and the solution was allowed to stir for an additional 1 h. To this solution was then added chloromethyl methyl ether (5.32 mL, 70.0 mmol) at 0 °C. The solution was stirred at 0 °C for 1 h and at 25 °C for 10 min and then washed twice with saturated aqueous sodium bicarbonate. After removal of the solvent from the organic layer, the product was purified by flash chromatography with a 1:1:16 mixture of ether/CH_2Cl_2/hexane. Complex **4c** (3.70 g, 0.11 mmol, 46%) was isolated as a red oil. Spectral data for **4c**: $R_f = 0.37$ (1:1:16 ether/CH_2Cl_2/hexane); ^1H NMR ($CDCl_3$) δ 3.71 (s, 3 H), 5.75 (s, 2 H), 7.24−7.27 (m, 2 H), 7.40−7.42 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 58.40, 103.37, 122.43, 128.19, 130.14, 153.41, 215.90, 224.37, 350.62; IR (neat) 3059 w, 3012 w, 2940 w, 2832 w, 2063 s, 1933 s, 1726 w, 1441 w, 1259 w, 1210 w, 1149 m, 1067 m, 930 m, 897 m, 837 w, 762 w, 697 m, 652 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 342 M$^+$ (20), 314 (36), 286 (28), 258 (42), 230 (90), 202 (94), 172 (88), 157 (93), 129 (100), 105 (92), 80 (95); high-resolution EI MS calcd for $C_{14}H_{10}O_7Cr$ *m/z* 341.9832, measd 341.9858.

Reaction of Phenyl[(methoxymethyl)oxy]carbene Complex 4c with Phenylacetylene. A 250 mL single-necked flask equipped with a high-vacuum threaded stopcock was charged with complex **4c** (3.51 g, 10.3 mmol), phenylacetylene (1.13 mL, 10.4 mmol), and 51 mL of THF to give a solution that was 0.2 M in complex **4c**. The solution was deoxygenated by the freeze−thaw method (three cycles) and then backfilled with argon at 25 °C. The flask was sealed at 25 °C and placed in a 48 °C oil bath for 12 h. Upon removal of the solvent and chromatography on silica gel with a 1:15 mixture of EtOAc/hexane, a total of 1.7972 g of an 8:1 mixture of two compounds was obtained, identified as 2-phenylnaphthyl-1,4-hydroquinone 4-methoxymethyl ether **56** and 2-phenylnaphthyl-1,4-hydroquinone 1,4-bis(methoxymethyl) ether **57**. This mixture of compounds was dissolved in 45 mL of THF and reacted with sodium hydride (1.67 g, 42 mmol as a 60% dispersion) and dimethyl sulfate (5.46 mL, 58 mmol) under nitrogen at 0 °C for 2.5 h. The reaction was quenched with saturated aqueous $HaHCO_3$, and the organic layer was washed twice with water and stripped of solvents. The two products were separated by flash chromatography with a 1:1:16 mixture of CH_2Cl_2/ether/hexane to give 1.2988 g (4.41 mmol, 43%) of naphthalene **9** as a white solid and 0.1836 g (0.57 mmol, 5.5%) of the bis-ether **57**. In a separate experiment at 0.1 M in **4c** and with 2 equiv of alkyn, naphthalene **9** was obtained in 58%, yield and none of the bis-ether **57** was detected. Spectral data for **9**: $R_f = 0.47$ (1:9 EtOAc/hexane); mp = 104−105 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.52 (s, 3 H), 3.53 (s, 3 H), 5.35 (s, 2 H), 7.08 (s, 1 H), 7.32 (t, 1 H, $J = 7.6$ Hz), 7.41 (t, 2 H, $J = 7.5$ Hz), 7.47 (t, 1 H, $J = 7.2$ Hz), 7.52

---

(16) Fischer, E. O.; Maasbol, A. *Chem. Ber.* **1967**, *100*, 2445.

(t, 1 H, $J = 7.2$ Hz), 7.65 (d, 2 H, $J = 7.3$ Hz), 8.14 (d, 1 H, $J = 8.4$ Hz), 8.21 (d, 1 H, $J = 8.2$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 56.26, 61.16, 95.25, 110.66, 122.10, 122.39, 125.72, 126.48, 126.65, 127.12, 128.31, 129.22, 129.43, 138.77, 147.72, 149.30 (1 C not located); IR (neat) 3057 w, 2992 w, 2931 w, 2828 w, 1595 m, 1498 w, 1460 w, 1444 w, 1366 s, 1353 m, 1230 w, 1149 s, 1101 m, 1060 s, 989 s, 962 m, 926 w, 760 m, 698 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 294 M$^+$ (100), 280 (17), 264 (26), 249 (98), 235 (36), 206 (58), 189 (90), 178 (85), 165 (18), 152 (27), 115 (28), 105 (88), 76 (87); high-resolution EI MS calcd for $C_{19}H_{18}O_3$ *m/z* 294.1256, measd 294.1285. Spectral data for **56**: $R_f = 0.30$ (1:9 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 3 H), 5.29 (s, 2 H), 5.54 (s, 1 H), 6.98 (s, 1 H), 7.36−7.48 (m, 7 H), 8.17−8.21 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 56.17, 95.60, 110.53, 120.50, 121.73, 122.36, 125.18, 126.01, 126.04, 126.56, 127.85, 129.37, 129.50, 137.58, 142.62, 146.78; IR (neat) 3542 m, 3058 w, 2955 w, 2901 w, 1631 w, 1598 m, 1497 w, 1458 m, 1446 w, 1423 w, 1387 m, 1297 m, 1250 w, 1229 m, 1210 w, 1146 s, 1101 m, 1057 s, 973 s, 920 w, 855 w, 760 s, 703 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 280 M$^+$ (90), 250 (42), 235 (100), 207 (26), 189 (40), 178 (97), 165 (20), 149 (27), 105 (91), 77 (92); high-resolution EI MS calcd for $C_{18}H_{16}O_3$ *m/z* 280.1099, measd 280.1148. Spectral data for **57**: $R_f = 0.42$ (1:1:8 CH_2Cl_2/ether/hexane); ^{1}H NMR ($CDCl_3$) δ 3.19 (s, 3 H), 3.55 (s, 3 H), 4.77 (s, 2 H), 5.38 (s, 2 H), 7.11 (s, 1 H), 7.35−7.67 (m, 7 H), 8.20−8.28 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 56.25, 57.46, 95.05, 99.68, 110.41, 122.05, 122.48, 125.71, 126.31, 126.72, 128.30, 129.49, 129.78, 129.77, 130.36, 139.17, 144.24, 149.50; IR (neat) 3061 w, 2933 w, 2825 w, 1596 m, 1498 w, 1444 w, 1362 s, 1229 w, 1148 s, 1083 w, 1059 s, 970 s, 761 m, 698 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 324 M$^+$ (34), 292 (72), 247 (100), 205 (27), 189 (22), 161 (95), 129 (52), 105 (20), 91 (18), 77 (22); high-resolution EI MS calcd for $C_{20}H_{20}O_4$ *m/z* 324.1362, measd 324.1317.

Preparation of Naphthyl Iodide 11 by Metalation of Naphthalene 9. To a solution of **9** (0.791 g, 2.69 mmol) in 20 mL of ether at −78 °C was added butyllithium (4.03 mmol as a 1.6 M solution in hexane). After 5 min, the solution was allowed warm to 25 °C for 12 h. The solution was cooled to −78 °C, and a solution of iodine (1.36 g, 5.36 mmol) in 25 mL of ether was added via cannula. The reaction mixture was warmed from −78 °C to 25 °C and stirred for 2.5 h and then quenched with saturated aqueous sodium bicarbonate. After removal of solvent from the organic layer, the two major products were purified by flash chromatography on silica gel with a 1:9 mixture of EtOAc/hexane to give 0.1643 g (0.39 mmol, 15%) of the naphthyl iodide **11** and 0.2067 g (0.38 mmol, 14%) of the naphthyl diiodide **12**. In addition, 0.3972 g (1.35 mmol, 50%) of the starting material **9** was recovered. Spectral data for **11**: $R_f = 0.40$ (1:9 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 3.50 (s, 3 H), 3.76 (s, 3 H), 5.22 (s, 2 H), 7.28 (d, 2 H, $J = 7.3$ Hz), 7.38−7.55 (m, 5 H), 8.07 (d, 1 H, $J = 7.7$ Hz), 8.16 (d, 1 H, $J = 7.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 58.34, 61.62, 95.58, 100.45, 122.75, 122.93, 126.93, 126.98, 127.65, 127.87, 128.62, 130.18, 135.33, 140.89, 149.96, 150.70 (1 C not located); mass spectrum, *m/z* (relative intensity) 420 M$^+$ (86), 390 (14), 375 (95), 360 (16), 293 (100), 261 (37), 248 (88), 233 (83), 218 (54), 205 (92), 189 (86), 176 (82), 151 (57), 129 (56); high-resolution EI MS calcd for $C_{19}H_{17}O_3I$ *m/z* 420.0222, measd 420.0258. Spectral data for **12**: $R_f = 0.34$ (1:9 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 3.63 (s, 3 H), 3.74 (s, 3 H), 5.24 (q, 2 H, $J = 7.2$ Hz), 7.09 (t, 1 H, $J = 7.6$ Hz), 7.24 (d, 1 H, $J = 7.5$ Hz), 7.44 (t, 1 H, $J = 7.4$ Hz), 7.54−7.55 (m, 2 H), 7.95 (d, 1 H, $J = 7.4$ Hz), 8.07−8.09 (m, 1 H), 8.19−8.21 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 58.42, 61.76, 95.03, 100.62, 101.63, 122.93, 123.05, 127.01, 127.21, 128.01, 128.62, 129.09, 129.38, 130.87, 137.48, 138.88, 145.84, 149.90, 151.02; IR (neat) 3069 w, 2954 m, 2931 m, 2828 w, 1663 w, 1586 w, 1564 m, 1491 m, 1470 w, 1449 m, 1431 w, 1347 s, 1263 w, 1210 m, 1161 s, 1077 s, 1046 s, 1018 m, 981 s, 929 s, 769 s, 741 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 546 M$^+$ (100), 516 (8), 501 (90), 419 (36), 375 (20), 292 (30), 234 (36), 176 (46), 69 (56); high-resolution EI MS calcd for $C_{19}H_{16}O_3I_2$ *m/z* 545.9189, measd 545.9156.

Coupling of Naphthyl Iodide 11 with Phenylacetylene.[8] A 50 mL flask was charged with iodide **11** (0.152 g, 0.36 mmol), phenylacetylene (0.084 mL, 0.77 mmol), bis(triphenylphosphine)palladium chloride (0.027 g, 0.038 mmol), cuprous iodide (0.0036 g, 0.019 mmol), and diethylamine (1.5 mL). The resulting solution was stirred at 25 °C for 18 h. After the solvent was removed, the product was purified on silica gel with a 1:1:8 mixture of ether/CH_2Cl_2/hexane to give 0.142 g (0.36 mmol) of **58**, the methoxymethyl ether of **13,** as yellow oil in 100% yield. Spectral data for **58**: $R_f = 0.33$ (1:1:8 ether/CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$) δ 3.50 (s, 3 H), 3.71 (s, 3 H), 5.48 (s, 2 H), 7.11−7.12 (m, 2 H), 7.20−7.21 (m, 3 H), 7.39 (t, 1 H, $J = 7.5$ Hz), 7.45 (t, 2 H, $J = 7.4$ Hz), 7.52−7.54 (m, 4 H), 8.10−8.12 (m, 1 H), 8.21−8.23 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 58.12, 61.30, 86.16, 97.98, 100.28, 113.41, 122.63, 122.79, 123.31, 126.72, 127.34, 127.36, 127.70, 128.17, 128.22, 128.77, 128.98, 130.62, 131.08, 132.28, 136.58, 149.62, 152.16; IR (neat) 3058 m, 2993 m, 2932 m, 2828 m, 2250 w, 1948 w, 1597 w, 1583 m, 1492 m, 1442 m, 1411 w, 1351 m, 1308 w, 1209 w, 1159 m, 1062 m, 989 m, 931 m, 774 m, 690 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 394 M$^+$ (60), 375 (33), 362 (42), 347 (100), 334 (24), 305 (45), 293 (54), 276 (48), 262 (88), 248 (32), 219 (42), 189 (52), 134 (27), 105 (37); high-resolution EI MS calcd for $C_{27}H_{22}O_3$ *m/z* 394.1569, measd 394.1571.

To a solution of **58** (0.156 g, 0.40 mmol) in 2 mL of ether was added 10 mL of methanol and 0.1 mL of 6 N aqueous HCl. The solution was stirred at 25 °C for 16 h. Extraction with ether and flash chromatography on silica gel with a 1:15 mixture of EtOAc/hexane gave 0.1021 g (0.29 mmol, 80% for two steps) of **13** as an off-white solid. The phenol **13** has different spectral data than **5a** obtained from the reaction of phenyl(methoxy)chromium carbene **4a** with 1,4-diphenyl-1,3-diyne (**8**). Spectral data for **13**: light yellow solid, mp = 143−144 °C; $R_f = 0.42$ (1:9 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 3.46 (s, 3 H), 6.39 (s, 1 H), 7.21 (br s, 5 H), 7.36 (t, 1 H, $J = 7.3$ Hz), 7.43 (t, 2 H, $J = 7.4$ Hz), 7.48 (t, 1 H, $J = 7.8$ Hz), 7.52 (t, 1 H, $J = 7.1$ Hz), 7.57 (d, 2 H, $J = 7.5$ Hz), 8.07 (d, 1 H, $J = 8.2$ Hz), 8.22 (d, 1 H, $J = 8.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 61.27, 83.49, 100.03, 103.63, 122.37, 122.57, 122.71, 123.44, 126.06, 127.41, 127.72 (2 C), 128.32, 128.43, 129.03, 130.34, 130.45, 131.06, 136.47, 146.57, 150.48 (1 aryl C not located); IR (neat) 3494 m, 3057 w, 2932 w, 2841 w, 1596 w, 1587 w, 1492 m, 1443 m, 1392 w, 1370 m, 1321 m, 1290 w, 1203 w, 1154 w, 1077 s, 1027 w, 988 m, 947 w, 755 s, 690 s, 665 w cm^{-1}; mass spectrum, *m/z* (relative intensity) 350 M$^+$ (8), 332 (96), 317 (42), 287 (100), 273 (36), 259 (16), 245 (16), 229 (14), 213 (22), 73 (94); high-resolution EI MS calcd for $C_{25}H_{18}O_2$ *m/z* 350.1307, measd 350.1264.

Preparation of Naphthol 10 by Hydrolysis of 9. To a solution of **9** (0.147 g, 0.50 mmol) in 20 mL of methanol was added 0.3 mL of 6 N aqueous HCl. The solution was stirred at 25 °C for 36 h. Extraction with ether and flash chromatography with a 1:9 mixture of EtOAc/hexane gave 0.0726 g (0.29 mmol, 58%) of **10** as a semisolid. Naphthol **10** was found to be nonidentical with naphthol **15** obtained from the reaction of carbene complex **4a** with phenylacetylene. Spectral data for **10**: $R_f = 0.20$ (1:9 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 3 H), 5.90 (s, 1 H), 6.75 (s, 1 H), 7.31−7.59 (m, 7 H), 8.15−8.19 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 61.27, 110.60, 121.94, 122.32, 124.79, 125.55, 126.78, 127.10, 128.29, 129.16, 129.22, 129.60, 138.25, 146.53, 147.81; IR (neat) 3350 s, 3062 w, 2934 m, 2842 w, 1628 w, 1597 s, 1499 m, 1445 m, 1392 m, 1371 s, 1311 m, 1256 w, 1294 m, 1167 w, 1071 s, 981 m, 909 m, 855 w, 761 s, 698 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 250 M$^+$(100), 235 (84), 207 (54), 178 (36), 105 (12), 76 (16); high-resolution EI MS calcd for $C_{17}H_{14}O_2$ *m/z* 250.0994, measd 250.0949.

Preparation of the ^{13}C-Enriched Carbene Complex 14 and Its Reaction with Phenylacetylene. A single-necked flask equipped with a high-vacuum threaded stopcock was charged with phenyl(methoxy)chromium carbene complex **4a**[14] (0.270 g, 0.87 mmol) and 20 mL of hexane. The solution was deoxygenated by the freeze−thaw method (two cycles), and the flask was backfilled with an atmosphere of ^{13}C-enriched carbon monoxide (^{13}C, 99%; ^{18}O, 10.5%; Isotec Inc., Miamisburg, OH), which was maintained with a balloon. The complex was then heated at 45 °C in an oil bath for 48 h and then recovered from the reaction mixture by flash chromatography on silica gel with hexane (0.184 g, 0.59 mmol, 68%). The ^{13}C NMR spectrum indicated that ^{13}C was introduced at the carbonyl ligands: trans, 30% enrichment, $\delta = 224.09$ ppm; cis, 24% enrichment, $\delta = 216.11$ ppm.

A solution of the ^{13}C-labeled complex **14** (0.184 g, 0.59 mmol) and phenylacetylene (0.122 mL, 1.11 mmol) in 5.6 mL of THF was deoxygenated as described above (three cycles) and backfilled with ^{13}C-labeled carbon monoxide at 25 °C. The flask was sealed at 25 °C and then heated at 45 °C in an oil bath for 21 h. After removal of the volatiles, the naphthol **15** was isolated by flash chromatography with a 1:15 mixture of EtOAc/hexane in 87% yield (0.1276 g, 0.51 mmol). The ^{13}C NMR spectrum of **15** revealed a 70% enrichment at the carbon at $\delta = 141.42$ ppm, which is consistent with the mass spectrum (74% enhancement) and indicates that additional incorporation of label occurs during the benzannulation reaction. An APT experiment indicated that the labeled carbon was one-bond coupled to two quaternary carbon atoms. Spectral data for **15**: $R_f = 0.45$ (1:5 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 3.97 (s, 3 H), 5.46 (s, 1 H), 6.70 (s, 1 H), 7.51−7.58 (m, 7 H), 8.22−8.25 (m, 2 H); ^{13}C NMR ($CDCl_3$, APT) δ 55.72 (CH_3), 105.48 (CH), 120.18 (d, $J = 72.2$ Hz), 121.74 (CH), 122.17 (CH), 125.16 (d, $J = 68.0$ Hz), 125.79 (CH), 125.85, 126.16 (CH), 127.77 (CH), 129.29 (CH), 129.45 (CH), 137.82, 141.42 (*C), 149.24; IR (neat) 3536 m, 3055 w, 2936 w, 1631 w, 1597 m, 1407 w, 1449 m, 1389 m, 1298 m, 1227 m, 1142 w, 1103 m, 1050 w, 984 w, 810 w, 760 m, 703 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 251 (100), 250 (36); high-resolution EI MS calcd for $C_{17}H_{14}O_2$ *m/z* 250.0994, measd 250.1024.

The regioselectivity of this reaction was determined on a run carried out on the nonlabeled carbene complex with phenylacetylene. The crude reaction mixture was analyzed by capillary GC, which indicated that the ratio of **15** (unlabeled) to **10** is greater than or equal to 179:1. This assignment was aided by an independent synthesis of **10** as described above. The retention times of these two columns were 8.18 min for **15** and 8.50 min for **10** on a 30 m × 0.32 mm SE-54 column at 200 °C for 1 min and then ramped at 10 °/min for 15 min with 1 mL/min helium as carrier gas. The ratio of **15**:**10** of ≥179:1 was judged not to be in error as the result of a selective oxidation of one of the isomers to the naphthoquinone since the GC trace of the crude reaction mixture revealed no trace of the quinone as determined by an authentic sample of the quinone, which had a retention time of 6.66 min.

Reaction of 1-Naphthyl(methoxy)carbene Complex 16a with 1,4-Diphenyl-1,3-diyne (8). The reaction of 0.430 g (1.19 mmol) of freshly prepared carbene complex **16a**[13,17] with 0.190 g (1.19 mmol) of 1,4-diphenyl-1,3-butadiyne (**8**) in 31.3 mL of THF was carried out at 50 °C for 16 h according to the procedure described for the reaction of **4a** with **8.** The solvent was removed, and the residue was loaded onto a silica gel column and eluted with a 1:1:16 mixture of ether/CH_2Cl_2/hexane to give 0.289 g (0.72 mmol, 61%) of **19a** as a white solid. Spectral data for **19a**: $R_f = 0.52$ (1:1:8 ether/CH_2Cl_2/hexane); white solid, mp = 161−162 °C; ^{1}H NMR ($CDCl_3$) δ 4.07 (s, 3 H), 5.46 (s, 1 H), 7.16−7.23 (m, 5 H), 7.48 −7.65 (m, 7 H), 7.74 (d, 1 H, $J = 9.1$ Hz), 7.86 (d, 1 H, $J = 7.5$ Hz), 8.18 (d, 1 H, $J = 9.1$ Hz), 9.61 (d, 1 H, $J = 8.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 60.56, 86.12, 97.82, 115.95, 120.71, 123.53, 123.66, 123.88, 125.25, 126.82, 127.18, 127.80, 128.11, 128.20, 128.50, 128.64, 129.20, 129.37, 130.80, 131.25, 133.18, 134.67, 144.87, 154.30 (1 aryl C not located); IR (neat) 3539 s, 3079 w, 3054 m, 2929 w, 1595 m, 1485 m, 1444 m, 1393 m, 1326 m, 1308 m, 1239 m, 1219 m, 1147 w, 1135 m, 1073 w, 1028 w, 1007 s, 908 m, 825 m, 752 s, 690 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 400 M$^+$ (100), 385 (30), 357 (58), 339 (12), 326 (20), 163 (16); high-resolution EI MS calcd for $C_{29}H_{20}O_2$ *m/z* 400.1463, measd 400.1468. Anal. Calcd for $C_{29}H_{20}O_2$: C, 86.98; H, 5.03. Found: C, 86.55; H, 5.33.

Reaction of 1-Naphthyl(methoxy)carbene Complex 16a with 1,4-Diisopropyl-1,3-diyne (17). The diisopropyl diyne **17** was prepared by the Glasser reaction.[18] To a solution of CuCl (3.84 g, 17.6 mmol) and NH_4Cl (6.73 g, 126 mmol) in 36 mL of water was added a solution of isopropylacetylene (1.2 g, 17.6 mmol) and $CuCl_2$ (0.035 g, 0.14 mmol) in 21 mL of ethanol. After being stirrred at 25 °C in air for16 h, the solution was exacted with ether, and the combined organic layer was washed with saturated aqueous sodium bicarbonate, water, and brine. Distillation at 70 °C and 8 mmHg gave 1,4-diisopropyl-1,3-butadiyne (**17**, 0.50 g, 3.73 mmol, 42%) as a colorless liquid. Spectral data for **17**: ^{1}H NMR ($CDCl_3$) δ 1.17 (d, 12 H, $J = 7.0$ Hz), 2.60 (septet, 2 H, $J = 6.8$ Hz).

The reaction of 0.434 g (1.20 mmol) of freshly prepared carbene complex **16a**[13,17] with 0.241 g (1.80 mmol) of 1,4-diisopropyl-1,3-butadiyne (**17**) in 40 mL of THF was carried out at 50 °C for 24 h according to the procedure described for the reaction of **4a** with **8.** The solvent was removed, and the residue was loaded onto a silica gel column and eluted with a 1:15 mixture of EtOAc/hexane to give 0.1653 g (0.50 mmol, 41%) of **19b** as a yellow oil along with 0.095 g (0.26 mmol, 22%) of complex **16a.** Spectral data for **19b**: $R_f = 0.38$ (1:9 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 1.36 (d, 6 H, $J = 6.9$ Hz), 1.52 (d, 6 H, $J = 7.2$ Hz), 2.95 (heptet, 1 H, $J = 6.9$ Hz), 3.84 (heptet, 1 H, $J = 7.2$ Hz), 3.93 (s, 3 H), 5.29 (s, 1 H), 7.52−7.63 (m, 2 H), 7.67 (d, 1 H, $J = 9.1$ Hz), 7.81 (d, 1 H, $J = 6.7$ Hz), 8.03 (d, 1 H, $J = 9.1$ Hz), 9.56 (d, 1 H, $J = 8.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 20.91, 21.73, 22.92, 29.55, 59.75, 75.58, 104.89, 116.90, 119.57, 122.31, 124.02, 126.34, 126.96, 127.65, 128.23, 129.30, 130.78, 132.57, 145.59, 154.75 (1 aryl C not located); IR (neat) 3440 m, 2966 s, 2930 m, 2871 w, 2218 w, 1582 w, 1484 w, 1445 m, 1390 m, 1361 w, 1310 m, 1276 w, 1247 m, 1202 w, 1127 w, 1080 w, 1015 m, 824 w, 758 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 332 M$^+$ (100), 317 (48), 301 (32), 289 (18), 261 (14), 215 (18), 202 (22), 155 (28), 127 (24); high-resolution EI MS calcd for $C_{23}H_{24}O_2$ *m/z* 332.1776, measd 332.1750.

Preparation of Tetramethylammonium 1-Naphthyl(pentacarbonyl)chromium Acylate 59. A solution of 5.0 mL (35.4 mmol) of 1-bromonaphthalene in 120 mL of ether was cooled to −78 °C and treated with 24.4 mL of a 1.6 M solution of *n*-butyllithium in hexane (39.0 mmol). After 10 min, the cold bath was removed, and the flask was allowed to warm to 25 °C for 0.5 h. The flask was cooled to −10 °C, and 7.93 g (35.4 mmol) of chromium hexacarbonyl was added. The mixture was cooled to −78 °C for 5 min, and then the flask was allowed to warm to room temperature for 20 min. After the ether was removed, the residue was dissolved in water and filtered through Celite. To the filtrate was added 5.54 g (35.4 mmol) of tetramethylammonium bromide. The resulting yellow precipitate was extracted into dichloromethane. Upon addition of hexane, a yellow solid precipitated which was collected and identified as the salt **59** (12.63 g, 30.0 mmol, 83%). Spectral data for **59**: yellow solid, mp = 113−115 °C dec; ^{1}H NMR (CD_3CN) δ 3.05 (s, 12 H), 7.11 (d, 1 H, $J = 7.0$ Hz), 7.36−7.43 (m, 3 H), 7.59 (d, 1 H, $J = 8.1$ Hz), 7.79 (d, 1 H, $J = 8.3$ Hz), 7.92 (d, 1H, $J = 8.2$ Hz); ^{13}C NMR (CD_3CN) δ 56.08, 104.19, 118.90, 125.70, 125.87, 126.08, 126.27, 127.07, 128.60, 134.76, 159.22, 223.18, 228.76, 299.96; IR (neat) 3036 w, 2034 s, 1944 s, 1884 vs, 1588 w, 1532 m, 1484 m, 1450 w, 1386 w, 1201 w, 1155 w, 1065 w, 1011 w, 948 m, 878 w, 860 w, 787 m, 733 w, 686 m, 661 s cm^{-1}. Anal. Calcd for $C_{20}H_{19}O_6NCr$: C, 57.01; H, 4.55. Found: C, 57.40; H, 4.41.

Preparation of 1-Naphthyl(butyloxy)carbene Complex 16b. To a solution of 1.0 g (2.38 mmol) of the tetramethylammonium acylate **59** in 18.8 mL of dichloromethane at −20 °C was added 0.176 mL (2.38 mmol) of acetyl bromide under argon. After the mixture was stirred at −20 °C for 1 h, 0.217 mL (2.38 mmol) of 1-butanol was added, and the resulting solution was stirred for 3.5 h at −20 °C. The red mixture was then poured into a separatory funnel containing aqueous saturated $NaHCO_3$ and hexane. The organic layer was washed with distilled water and brine then dried with anhydrous $MgSO_4$. The volatiles were removed by rotary evaporation, and the product was isolated from the red residue via flash chromatography on silica gel with a 1:1:8 mixture of ether/CH_2Cl_2/hexane to give 0.819 g (2.03 mmol, 85%) of **16b** as a red solid. Spectral data for **16b**: $R_f = 0.32$ (1:1:60 ether/CH_2Cl_2/hexane); mp = 44−45 °C; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3 H, $J = 7.4$ Hz), 1.46−1.53 (m, 2 H), 1.84 (br s, 2H), 4.21 (br s, 2 H), 7.01 (d, 1 H, $J = 7.1$ Hz), 7.40−7.53 (m, 4 H), 7.74 (d, 1 H, $J = 8.2$ Hz), 7.74−7.84 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.51, 18.94, 31.43, 79.90, 118.35, 123.69, 124.13, 124.90, 125.35, 126.56, 127.08, 128.30, 128.71, 133.07, 216.07, 224.81, 356.44; IR (neat) 3061 w, 2963 w, 2936 w, 2876 w, 2063 s, 1989 s, 1929 vs, 1589 w, 1505 w, 1466 w, 1382 w, 1279 m, 1244 m, 1199 m, 1158 m, 1076 m, 1045 m, 925 m, 788 m, 702 m, 650 s, 609 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 404 M$^+$ (4), 376 (10), 348 (10), 320 (12), 292 (27), 264 (100), 196 (27), 179 (64), 167 (64), 155 (22), 137 (20), 128 (27); high-resolution EI MS calcd for $C_{20}H_{16}O_6Cr$ *m/z* 404.0352, measd 404.0334. Anal. Calcd for $C_{20}H_{16}O_6Cr$: C, 59.41; H, 3.99. Found: C, 59.71; H, 4.07.

Reaction of 1-Naphthyl(butyloxy)carbene Complex 16b with 1,4-Diphenyl-1,3-butadiyne (8). The reaction of 0.232 g (0.57 mmol) of freshly prepared carbene complex **16b** and 0.116 g (0.57 mmol) of 1,4-diphenyl-1,3-butadiyne (**8**) was carried out at 50 °C for 16 h according to the procedure described above for the reaction of complex

---

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

(18) Eglinton, G.; McCrae, W. *Adv. Org. Chem.* **1963**, *4*, 225.

4a with **8**. To the crude reaction mixture was then added 18.7 mL of a 0.5 M solution of CAN. After being stirred at 25 °C for 1 h, the resulting mixture was extracted with ether, and the organic layer was washed with water, saturated aqueous sodium bicarbonate, water, and brine. The quinone **21c** (0.189 g, 0.49 mmol, 86%) was isolated after flash chromatography on silica gel with a 1:15 mixture of EtOAc/hexane as a red solid. Spectral data for **21c**: R_f = 0.24 (1:15 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 7.30−7.81 (m, 12 H), 7.93 (d, 1 H, J = 7.5 Hz), 8.19 (d, 1 H, J = 8.6 Hz), 8.25 (d, 1 H, J = 8.6 Hz), 9.61 (d, 1 H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 84.82, 106.08, 122.15, 122.29, 127.34, 127.70, 128.18, 128.39, 128.65, 128.72, 129.45, 129.66, 129.80, 130.19, 130.47, 130.52, 131.68, 132.24, 132.65, 135.34, 136.33, 146.07, 184.38, 184.49; IR (neat) 3072 w, 2199 m, 1658 vs, 1646 s, 1597 w, 1493 w, 1459 w, 1442 w, 1381 w, 1359 w, 1333 w, 1305 s, 1232 m, 1204 w, 1145 m, 1096 s, 1061 m, 1027 w, 985 m, 771 s, 756 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 384 M$^+$ (100), 326 (28), 307 (29), 192 (8), 151 (22), 126 (30); high-resolution EI MS calcd for $C_{28}H_{16}O_2$ *m/z* 384.1151, measd 384.1146.

The reaction was repeated under the conditions described above, but an oxidative workup was not employed. The solvent was removed from the crude reaction mixture, and the residue was loaded onto a silica gel column which was eluted with a 1:15 mixture of ethyl acetate/hexane to give 0.341 g (0.77 mmol, 82%) of phenanthrol **19c** as a yellow oil. Spectral data for **19c**: R_f = 0.27 (1:15 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 1.02 (t, 3 H, J = 7.4 Hz), 1.64−1.69 (m, 2 H), 2.03−2.056 (m, 2 H), 4.13 (t, 2 H, J = 6.6 Hz), 5.43 (s, 1 H), 7.13-7.14 (m, 2 H), 7.21−7.47 (m, 4 H), 7.47−7.64 (m, 6 H), 7.73 (d, 1 H, J = 9.1 Hz), 7.85 (d, 1 H, J = 7.6 Hz), 8.17 (d, 1 H, J = 9.2 Hz), 9.67 (d, 1 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.14, 19.57, 32.68, 73.77, 86.63, 97.59, 116.12, 120.71, 123.61, 123.64, 124.18, 125.39, 126.75, 126.88, 127.89, 128.01, 128.07, 128.19, 128.38, 128.57, 129.17, 129.48, 130.80, 131.17, 133.08, 134.81, 144.70, 153.38; IR (neat) 3541 s, 3052 w, 2957 m, 2932 m, 2871 m, 1596 m, 1484 m, 1412 s, 1379 m, 1325 m, 1309 s, 1242 m, 1220 m 1138 m, 1098 w, 1070 w, 1028 w, 977 w, 908 w, 824 m, 734 s, 701m, 690 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 442 M$^+$ (100), 386 (80), 357 (48), 339 (15), 326 (17); high-resolution EI MS calcd for $C_{32}H_{26}O_2$ *m/z* 442.1933, measd 442.1992.

Reaction of 1-Naphthyl(butyloxy)carbene Complex 16b with 1,4-Di-*tert*-butyl-1,3-butadiyne (18). The di-*tert*-butyl diyne **18** was prepared by the Glasser reaction.[18,19] To a solution of CuCl (10 g, 100 mmol) and NH_4Cl (17 g, 318 mmol) in 150 mL water was added a solution of *tert*-butylacetylene (5 mL, 40.6 mmol) and $CuCl_2$ (0.5 g, 2.0 mmol) in 50 mL of ethanol. After being stirred at 25 °C for 48 h in air, the solution was exacted with ether and was washed with sodium bicarbonate, water, and brine. A total of 1.99 g (12.3 mmol, 60%) of 1,4-di-*tert*-butyl-1,3-butadiyne (**18**) was isolated as a white solid after flash chromatography with a 1:1:30 mixture of CH_2Cl_2/ether/hexane. Spectral data for **18**:[19] ^{1}H NMR ($CDCl_3$) δ 1.23; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.95, 30.58, 63.61, 86.27.

The reaction of 0.276 g (0.64 mmol) of freshly prepared complex **16b** and 0.103 g (0.64 mmol) of 1,4-di-*tert*-butyl-1,3-butadiyne (**18**) in 21 mL of THF was carried out at 53 °C for 16 h according to the procedure described above for the reaction of complex **4a** with diyne **8**. The crude reaction mixture was then stirred with 8.0 mL of a 0.5 M solution of CAN, and after 1 h the resulting mixture was extracted with ether and washed with water, saturated aqueous sodium bicarbonate, water, and brine. The two products of this reaction were separated by flash chromatography on silica gel with a 1:2 mixture of $CHCl_3$/hexane to give the quinone **21d** (0.0139 g, 0.040 mmol, 6%) and the cyclobutenone **20d** (0.1854 g, 0.46 mmol, 72%). Spectral data for **21d**: yellow oil; R_f = 0.33 (1:2 $CHCl_3$/hexane); ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 9 H), 1.57 (s, 9 H), 7.62 (t, 1 H, J = 7.0 Hz), 7.70 (t, 1 H, J = 7.2 Hz), 7.88 (d, 1 H, J = 7.2 Hz), 8.00 (d, 1 H, J = 8.5 Hz), 8.11 (d, 1 H, J = 8.5 Hz), 9.34 (d, 1 H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 29.06, 30.19, 30.37, 36.97, 75.18, 119.40, 121.81, 127.09, 128.00, 128.31, 128.53, 129.21, 129.65, 131.17, 134.37, 134.61, 135.73, 156.74, 184.49, 187.55; IR (neat) 3056 w, 2968 s, 2929 m, 2867 w, 2213 m, 1662 s, 1653 vs, 1595 w, 1554 w, 1461 m, 1304 s, 1283 s, 1266 m, 1249 s, 1209 m, 1167 m, 1118 m, 847 m, 817 m, 764 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 344 M$^+$ (30), 329 (100), 314 (27), 299 (15), 287 (12), 273 (13), 259 (12), 245 (12), 215 (14), 202 (15), 149 (21), 126 (24), 83 (15), 71 (24); high-resolution EI MS calcd for $C_{24}H_{24}O_2$ *m/z* 344.1776, measd 344.1715. Spectral data for **20d**: yellow oil; R_f = 0.26 (1:2 $CHCl_3$/hexane); ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3 H, J = 7.3 Hz), 1.28 (s, 9 H), 1.32 (s, 9 H), 1.30−1.50 (m, 2 H), 1.51−1.66 (m, 2 H), 3.53−3.66 (m, 2 H), 7.38 (t, 1 H, J = 7.4 Hz), 7.40−7.54 (m, 2 H), 7.71 (d, 1 H, J = 7.1 Hz), 7.79 (d, 2 H, J = 8.1 Hz), 8.73 (d, 1 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 13.75, 19.22, 27.61, 29.24, 30.01, 32.02, 33.25, 65.38, 72.69, 101.42, 102.53, 124.74, 124.84, 125.43, 125.49, 125.80, 127.85, 129.24, 131.72, 133.86, 134.24, 154.50, 164.75, 193.61; IR (neat) 3049 w, 2966 s, 2932 m, 2903 m, 2870 s, 2211 m, 1757 vs, 1599 m, 1511 w, 1475 m, 1459 m, 1395 w, 1366 m, 1326 m, 1258 m, 1201 m, 1135 m, 1094 m, 1069 m, 1024 m, 778 s, 700 w cm^{-1}; mass spectrum, *m/z* (relative intensity) 402 M$^+$ (6), 346 (46), 331 (3), 317 (6), 290 (5), 155 (100), 127 (66), 83 (18); high-resolution EI MS calcd for $C_{28}H_{34}O_2$ *m/z* 402.2559, measd 402.2539.

It was shown that the cyclobutenone **20d** had the same regiochemistry of alkyne incorporation as quinone **21d** by chemical correlation. The cyclobutenone **20d** (0.0671 g, 0.17 mmol) was dissolved in 30 mL of hexane, and the resulting solution was deoxygenated (two cycles). The flask was sealed at 25 °C under argon and heated at 85 °C for 18 h. The reaction mixture was oxidized with 1.3 mL of aqueous CAN (0.5 M, 0.65 mmol) in air for 1 h. After flash chromatography on silica gel with a 1:30 mixture of EtOAc/hexane, 0.036 g (0.10 mmol, 64%) of quinone **21d** was isolated as a yellow oil, along with 0.0165 g (0.042 mmol, 25%) of the starting material **20d**.

Reaction of 1-Naphthyl(butyloxy)carbene Complex 16b with 1,4-Diisopropyl-1,3-butadiyne (17). The reaction of carbene complex **16b** (0.370 g, 0.92 mmol) with 1,4-diisopropyl-1,3-diyne (**17**) (0.135 g, 1.01 mmol) in 30.5 mL of THF was carried out at 50 °C for 18 h according to the procedure described above for the reaction of complex **4a** with diyne **8**. A single product observed by TLC was purified by flash chromatography on silica gel with a 1:9 mixture of EtOAc/hexane, which gave 0.1231 g (0.33 mmol, 36%) of the phenanthrol **19e** as an oil, along with 0.165 g (0.41 mmol, 45%) of the starting carbene complex **16b**. Spectral data for **19e**: R_f = 0.37 (1:9 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 1.02 (t, 3 H, J = 7.4 Hz), 1.36 (d, 6 H, J = 6.9 Hz), 1.53 (d, 6 H, J = 7.2 Hz), 1.55−1.61 (m, 2 H), 1.98 (pentet, 2 H, J = 7.4 Hz), 2.94 (m, 1 H), 3.84 (m, 1 H), 3.96 (t, 2 H, J = 6.8 Hz), 5.10 (s, 1 H), 7.51 (t, 1 H, J = 7.1 Hz), 7.56 (t, 1 H, J = 8.0 Hz), 7.65 (d, 1 H, J = 9.1 Hz), 7.79 (d, 1 H, J = 7.7 Hz), 7.99 (d, 1 H, J = 9.1 Hz), 9.58 (d, 1 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.16, 19.43, 20.91, 21.78, 22.97, 29.53, 32.60, 72.85, 75.96, 104.51, 117.04, 119.58, 122.62, 124.00, 126.29, 126.67, 127.53, 127.77, 128.12, 129.45, 130.94, 132.50, 145.45, 153.81; IR (neat) 3470 m, 3051 w, 2962 s, 2932 s, 2871 m, 1948 w, 1635 w, 1589 w, 1462 w, 1412 w, 1359 w, 1309 m, 1245 w, 1195 w, 1081 w, 1001 w, 906 w, 822 w, 757 cm^{-1}; mass spectrum, *m/z* (relative intensity) 374 M$^+$ (100), 317 (96), 301 (33), 289 (18), 275 (16), 261 (16), 215 (12), 202 (14), 155 (27), 127 (20); high-resolution EI MS calcd for $C_{26}H_{30}O_2$ *m/z* 374.2246, measd 374.2238.

Reaction of Cyclohexenyl(methoxy)carbene Complex 22 with 1,4-Diphenyl-1,3-butadiyne (8). The reaction of 0.338 g (1.069 mmol) of carbene complex **22** and 0.256 g (1.069 mmol) of 1,4-diphenyl-1,3-butadiyne (**8**) in 2.1 mL of THF (0.5 M in **22**) was carried out at 55 °C for 20 h according to the procedure described for complex **4a** with **8**. The mixture was diluted with THF (miniumum of 20 mL), and a solution of *p*-toluenesulfonic acid monohydrate (0.3 equiv) in water (25 mL for 0.1 g of carbene complex used) was added. The mixture stirred at 25 °C in air for 1 h. The reaction mixture was diluted with water, and the organic components were extracted into ether which was washed with aqueous $NaHCO_3$, water, and brine and dried over $MgSO_4$. After filtration and removal of the solvents, CH_2Cl_2 and a small amount of silica gel were added, and the resulting solution was stirred at 25 °C in air for 1−2 days until the yellow compound on TLC with R_f = 0.18 (1:1 CH_2Cl_2/hexane) was no longer present. The crude reaction mixture was filtered, stripped of solvent, and loaded onto a silica gel column and eluted with a 1:1 mixture of CH_2Cl_2/hexane to give a 73% yield (0.278 g, 0.784 mmol) of the phenol **23** and a 2.8% yield (10.5 mg, 0.03 mmol) of its regioisomer **24**. The regioisomeric relationship of the phenols **23** and **24** was established by chemical correlation, in which each was shown to be oxidized by

---

(19) Smith, E. H.; Whittall, J. *Organometallics* **1994**, *13*, 5169.

CAN to the quinone **25**. If upon opening to air the reaction mixture is immediately chromatographed on silica gel, a sample of the compound that appears as a yellow spot on TLC with $R_f = 0.18$ can be obtained as an orange solid. While this compound is sensitive to air with respect to oxidation to phenol **23,** the spectral data collected on this compounds allow for a tentative assignment as the chromium tricarbonyl complexed naphthalene **34**. The outcome of the reactions at 0.05 M in THF and benzene is summarized in Scheme 5. Spectral data for **23**: white solid, mp 106.5−107.5 °C; $R_f = 0.30$ (1:1 CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$) δ 1.80 (br s, 4 H), 2.70 (br s, 2 H), 2.78 (br s, 2 H), 3.92 (s, 3 H), 4.90 (s, 1 H), 7.09−7.20 (m, 5 H), 7.39−7.49 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 22.21, 23.74, 23.84, 60.64, 85.56, 95.94, 113.36, 123.66, 126.43, 126.82, 127.82, 128.10, 128.26, 128.99, 130.63, 131.08, 131.45, 134.96, 146.25, 152.70 (1 C not located); IR (neat) 3548 s, 2981 s, 1450 s, 1411 s, 1303 s, 755 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 355 (35), 354 M$^+$ (100), 353 (95), 339 (10), 311 (12), 250 (35), 235 (12). Spectral data for **24**: white solid, mp 144−145.5 °C; $R_f = 0.37$ (1:1 CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$) δ 1.84 (br s, 4 H), 2.75−2.81 (m, 4 H), 3.29 (s, 3 H), 5.89 (s, 1 H), 7.22−7.53 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 22.14, 22.33, 23.49, 24.04, 59.96, 83.40, 98.51, 106.34, 122.74, 123.90, 127.20, 127.65, 128.30, 130.30, 131.09, 133.19, 133.93, 136.67, 148.68, 150.68 (1 C not located); IR (neat) 3500 s, 2930 s, 1450 s, 1410 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 355 (25), 354 M$^+$ (100), 340 (25), 339 (85), 321 (12), 311 (15), 149 (25). Spectral data for **25**: bright yellow solid, mp 145−163 °C (soften); $R_f = 0.23$ (1:1 CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$) δ 1.77 (br s, 4 H), 2.53−2.56 (br s, 4 H), 7.25−7.33 (br s, 5 H), 7.41−7.50 (br s, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.03, 21.09, 21.40, 21.47, 83.97, 104.90, 122.17, 127.58, 127.76, 128.33, 129.33, 129.49, 130.42, 132.13, 132.71, 142.32, 143.16, 145.88, 183.79, 185.72; IR (neat) 2936 m, 2199 m, 1648 vs, 1343 m, 1298 s, 1275 m, 1219 m, 1142 m, 758 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 340 (60), 339 (35), 338 M$^+$ (100), 310 (45), 309 (25), 281 (17), 252 (17), 202 (15). Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 84.78; H, 5.35. Spectral data for **34**: orange solid; $R_f = 0.18$ (1:1 CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$) δ 1.65−1.82 (m, 3 H), 1.82−1.95 (m, 3 H), 2.55−2.92 (m, 4 H), 3.85 (s, 3 H), 4.62 (s, 1 H), 6.96−7.28 (m, 5 H), 7.28−7.56 (m, 5 H); IR (neat) 3505 w, 2939 w, 1951 s, 1876 s, 1491 w, 1449 m, 1396 m, 1323 m, 1210 m, 996 m, 757 m cm^{-1}.

Reaction of Phenyl(methoxy)carbene Complex 4a with Naphthylacetylene 5a. A mixture of 0.186 g (0.53 mmol) of alkyne **5a** and 0.275 g (1.59 mmol) of carbene complex **4a**[14] in 88.5 mL of THF was reacted at 80 °C for 24 h according to the procedure described above for **4a** with diyne **8**. The reaction mixture was opened and stirred in the presence of air for 24 h at room temperature. The separation of the products was accomplished on silica gel with a 1:9 mixture of EtOAc/hexane to give 0.051 g (0.10 mmol, 19%) of **26**, 0.086 g (0.17 mmol, 32%) of **27,** and 0.0562 g (0.12 mmol, 23%) of **28**. Spectral data for **26**: white solid, mp 99−123 °C (soften); $R_f = 0.35$ (1:5 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 3.31 (s, 3 H), 3.81 (s, 3 H), 5.34 (s, 1 H), 5.45 (s, 1 H), 6.97−7.10 (m, 10 H), 7.47−7.58 (m, 4 H), 8.03 (d, 1 H, $J = 7.3$ Hz), 8.13 (d, 1 H, $J = 8.3$ Hz), 8.19 (d, 1 H, $J = 8.2$ Hz), 8.26 (d, 1 H, $J = 8$ Hz); ^{13}C NMR ($CDCl_3$) δ 60.98, 61.80, 117.40, 121.83, 122.19, 122.39, 122.81, 123.02, 123.42, 124.16, 125.36, 125.45, 126.31, 126.49, 126.62, 126.92, 127.01, 128.02, 128.11, 128.57, 130.28, 130.32, 130.38, 130.78, 133.51, 136.01, 145.17, 145.40, 146.98, 148.16; IR (neat) 3528 s, 3059 m, 2933 m, 2842 m, 1719 w, 1662 m, 1587 m, 1495 m, 1450 m, 1365 s, 1289 s, 1211 m, 1143 m, 1074 s, 1028 w, 986 m, 909 m, 762s, 731 s, 701 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 498 M$^+$ (100), 482 (94), 467 (28), 421 (15), 289 (10), 276 (12), 249 (11), 233 (32), 163 (50), 121 (19); high-resolution EI MS calcd for $C_{34}H_{26}O_4$ *m/z* 498.1831, measd 498.1829. Spectral data for **27**: yellow solid, mp 112−114 °C; $R_f = 0.26$ (1:5 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 2.05−3.92 (4 br s, 6 H), 5.31 (s, 1 H), 6.72−6.74 (br s, 1 H), 7.08−7.67 (m, 16 H), 8.13−8.18 (m, 1 H), 8.33−8.37 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 52.61, 63.18, 100.81, 119.42, 120.17, 122.30, 123.08, 125.38, 126.10,126.24, 126.59, 127.04, 127.65, 128.10, 128.22, 128.75, 128.99, 129.41, 129.87, 130.19, 130.29, 131.23, 132.14, 134.35, 137.50, 145.48, 147.26, 192.10; IR (neat) 3530 m, 3059 m, 2931 m, 2849 w, 1754 s, 1616 m, 1447 m, 1390 m, 1369 m, 1296 m, 1197 w, 1140 m,1066 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 498 M$^+$ (100), 483 (3), 466 (4), 423 (8), 249 (12), 233 (18), 163 (12), 105 (87), 77 (43); high-resolution EI MS calcd for $C_{34}H_{26}O_4$ *m/z* 498.1831, measd 498.1819. Spectral data for **28**: white solid, mp = 256−258 °C; $R_f = 0.51$ (1:5 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 3.58 (s, 3 H), 4.21 (s, 3 H), 4.59 (s, 1 H), 5.74 (s, 1 H), 5.93 (d, 1 H, $J = 7.6$ Hz), 6.61 (d, 1 H, $J = 7.3$ Hz), 6.71 (t, 1 H, $J = 7.5$ Hz), 7.03−7.20 (m, 8 H), 7.44 (t, 1 H, $J = 7.4$ Hz), 7.52−7.57 (m, 4 H), 8.08 (d, 1 H, $J = 8.28$ Hz), 8.16 (d, 1 H, $J = 8.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 45.47, 59.00, 63.49, 118.87, 121.57, 122.26, 122.84, 123.77, 124.35, 125.40, 125.48, 126.11, 126.49, 126.56, 127.36, 127.61, 127.83, 127.94, 128.07, 128.46, 130.69, 131.43, 132.14, 134.48, 140.43, 145.31, 146.43, 148.64, 154.81; IR (neat) 3522 m, 3059 w, 2926 m, 2851 w, 1720 m, 1596 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 470 M$^+$ (75), 423 (17), 179 (21), 165 (28), 151 (34), 137 (41), 123 (62), 111 (100).

The regiochemistry of alkyne incorporation for the cyclobutenone **27** was shown to be the same as that for **26** by chemical conversion. A 25 mL flask equipped with a threaded stopcock that was flushed with nitrogen was charged with cyclobutenone **27** (0.0072 g, 0.014 mmol) and 5 mL of benzene. The flask was sealed by closing the stopcock at 25 °C and placed in an 80 °C oil bath for 48 h. The starting material was consumed at this point, and the only product obtained was 0.0051 g (0.010 mmol, 71% yield) of phenol **26**, which was isolated after flash chromatography with1:1:8 ether/CH_2Cl_2/hexane.

Reaction of 1-Naphthyl(butyloxy)carbene Complex 16b with Phenanthrylacetylene 19c. A mixture of 0.194 g (0.48 mmol) of carbene complex **16b** and 0.161 g (0.36 mmol) of alkyne **19c** in 12 mL of THF was reacted according to the procedure described above for the reaction of complex **4a** with diyne **8**. After the mixture was heated at 67 °C for 3 days and then at 85 °C for 1 day, the solvent was removed and residue was loaded onto a silica gel column and eluted with a 1:15 mixture of ethyl acetate/hexane to give 0.0478 g (0.11 mmol, 30%) of recovered alkyne **19c** and 0.1148 g (0.176 mmol, 48%) of the five-membered-ring annulated product **30** as an off-white semisolid. Spectral data for **30**: $R_f = 0.33$ (1:15 ethyl acetate/hexane); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H, $J = 7.3$ Hz), 0.95 (t, 3 H, $J = 7.4$ Hz), 1.20−1.75 (m, 6 H), 2.00-2.09 (m, 2 H), 3.69−3.72 (m, 2 H), 4.06 (q, 1 H, $J = 8.7$ Hz), 4.24−4.25 (m, 1 H), 4.64 (s, 1 H), 5.82 (d, 1 H, $J = 7.0$ Hz), 5.97 (s, 1 H), 6.11 (t, 1 H, $J = 7.1$ Hz), 6.72 (d, 1 H, $J = 7.1$ Hz), 6.86 (t, 1 H, $J = 7.3$ Hz), 7.04 (t, 1 H, $J = 7.4$ Hz), 7.16−7.24 (m, 3 H), 7.32 (d, 1 H, $J = 8.1$ Hz), 7.40−7.41 (m, 2 H), 7.58−7.61 (m, 2 H), 7.64−7.70 (m, 2 H), 7.75−7.82 (m, 3 H), 7.86 (d, 1 H, $J = 7.8$ Hz), 8.02 (d, 1H, $J = 9.0$ Hz), 8.40−8.42 (m, 1 H), 9.76 (d, 1 H, $J = 8.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 13.94, 14.06, 19.23, 19.50, 32.36, 32.57, 45.66, 71.91, 74.30, 120.83, 122.06, 122.43, 124.12, 124.21, 124.36, 124.96, 125.46, 125.93, 126.04, 126.45, 126.52, 126.84, 126.86, 127.26, 127.76, 127.99, 128.03, 128.10, 128.18, 128.37, 129.31, 129.60, 130.20, 131.18, 133.05, 133.09, 134.89, 135.79, 144.71, 145.36, 150.24, 156.72 (1 aryl C not located); IR (neat) 3533 s, 3052 m, 3033 w, 2957 s, 2933 s, 2872 m, 1594 s, 1516 w, 1493 m, 1409 m, 1363 w, 1332 m, 1309 m, 1255 m, 1214 s, 1133 m, 1064 m, 1002 w, 946 m, 909 s, 803 s, 758 m, 733 s, 700s cm^{-1}; mass spectrum, *m/z* (relative intensity) 654 M$^+$ (100), 597 (8), 580 (14), 541 (8), 524 (20), 423 (32), 257 (20), 155 (34), 105 (26); high-resolution EI MS calcd for $C_{47}H_{42}O_3$ *m/z* 654.3134, measd 654.3152. Anal. Calcd for $C_{47}H_{42}O_3$: C, 86.20; H, 6.47. Found: C, 86.21; H, 6.84.

Reaction of 1-Naphthyl(methoxy)carbene Complex 16a with Phenanthrylacetylene 19b. The reaction of 0.161 g (0.44 mmol) of **16a**[13,17] with 0.1475 g (0.44 mmol) of alkyne **19b** in 14.8 mL of THF was carried out at 75 °C for 40 h according to the procedure described for the reaction of complex **4a** with diyne **8**. The solvent was removed, and the residue was loaded onto a silica gel column and eluted with a 1:1 mixture of benzene/hexane to give 0.0744 g (0.14 mmol, 32%) of the bis-phenanthrol **31** and 0.0936 g of a mixture of several compounds that were not identified. Spectral data for **31**: $R_f = 0.21$ (1:9 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 1.40 (d, 6 H, $J = 7.0$ Hz), 1.49 (d, 6 H, $J = 7.0$ Hz), 2.89−2.94 (m, 2 H), 3.42 (br s, 3 H), 3.81 (s, 3 H), 4.81 (s, 1 H), 5.35 (s, 1 H), 7.57−7.92 (m, 8 H), 8.15 (d, 1 H, $J = 9.1$ Hz), 8.16 (d, 1 H, $J = 9.0$ Hz), 9.47 (d, 1 H, $J = 8.3$ Hz), 9.55 (d, 1 H, $J = 8.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 21.06, 21.58, 22.17, 29.54, 32.20, 59.69, 61.42, 119.18, 120.85, 120.97, 121.38, 123.54, 124.34, 125.06, 126.07, 126.36, 126.41, 126.72, 127.21, 127.69, 127.83, 127.90, 128.04, 128.25, 128.40, 129.03, 129.55, 129.68, 132.66, 132.98, 138.78, 144.52, 147.56, 151.40, 152.30; IR (neat) 3623 w, 3532 m, 3053 w, 2961 m, 2930 m, 2875 m, 2239 w, 1594 w, 1513 w, 1445 m, 1393 m, 1331 m, 1311 w, 1242 s, 1216 w, 1178 m, 1141 w, 1117 w, 1086 w, 1043 m, 1010 m, 987 m, 908 m, 826 m, 805 m, 757 m, 734 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 530 M$^+$ (100), 456 (8), 441 (12), 199 (11), 120 (53), 69 (56); high-resolution EI MS calcd for $C_{36}H_{34}O_4$ *m/z* 530.2457, measd 530.2452.

Reaction of cyclohexenyl(methoxy)carbene Complex 22 with Arylacetylene 23. (i) In Benzene with an Oxidative Workup. The reaction of carbene complex **22**[20] (0.25 g, 0.791 mmol) and alkyne **23** (0.1 g, 0.282 mmol) in 0.47 mL of benzene (1.7 M in **22**) was carried out at 70−74 °C for 10 h according to the procedure described above for the reaction of complex **4a** with diyne **8**. The reaction mixture was oxidized by stirring with a 0.5 M aqueous solution of CAN for 2 h. The organic layer was separated, diluted with CH_2Cl_2, washed with water and brine, and then dried over Na_2SO_4. Upon flash chromatography on silica gel with a 1:5 mixture of EtOAc/hexane, the quinone **32** was isolated as a yellow solid in 60% yield (0.0797 g, 0.168 mmol). Small amounts of other compounds were observed which were not identified. As indicated in Scheme 8, the same reaction at 0.016 M in **22** gave a 16% yield of **32**, and the reaction at 0.16 M gave a 42% yield of **32**. Spectral data for **32**: yellow solid, mp 145−164 °C (soften); $R_f = 0.30$ (1:5 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 1.68−1.73 (m, 8 H), 2.36−2.55 (m, 8 H), 6.50 (d, 4 H, $J = 7.4$ Hz), 7.13 (t, 4 H, $J = 7.6$ Hz), 7.22 (d, 2 H, $J = 6.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 20.90, 20.99, 22.59, 22.80, 127.57, 128.75, 129.07, 131.78, 138.83, 142.41, 142.67, 143.71, 185.60, 186.79; IR (neat) 2940 m, 1646 vs cm^{-1}; mass spectrum, *m/z* (relative intensity) 478 (55), 476 (60), 474 M$^+$ (97), 430 (100), 429 (70), 415 (67), 401 (40), 105 (60), 79 (72). Anal. Calcd for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52. Found: C, 79.68; H, 6.11.

(ii) In THF without an Oxidative Workup. The reaction of carbene complex **22**[20] (0.244 g, 0.772 mmol) and alkyne **23** (0.1 g, 0.282 mmol) in 0.47 mL of THF was carried out as described above for the reaction in benzene. The reaction mixture was diluted with CH_2Cl_2 and allowed to stir with silica gel at 25 °C for 2 h. After flash chromatography on silica gel with a 1:5 mixture of EtOAc/hexane, a 56% yield of phenol **33** (80.6 mg, 0.159 mmol) was isolated as a white solid. Small amounts of other compounds were observed which were not identified. Spectral data for **33**: white solid, mp 192.5−194 °C; $R_f = 0.35$ (1:5 EtOAc/hexane); ^{1}H NMR ($CDCl_3$) δ 1.74−1.85 (m, 8 H), 2.59−2.81 (m, 8 H), 3.08 (s, 3 H), 3.61 (s, 3 H), 4.72 (s, 1 H), 4.86 (s, 1 H), 6.87−6.88 (m, 2 H), 7.06−7.17 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 22.31, 22.37, 22.43, 22.50, 23.62, 23.69, 23.84, 24.18, 59.56, 60.23, 120.04, 123.48, 124.06, 125.30, 125.67, 126.03, 126.78, 127.61, 128.47, 130.05, 130.58, 130.88, 131.18, 134.05, 136.74, 146.89, 147.06, 148.68, 149.90 (1 C not located); IR (neat) 3527 s, 2933 s, 1449 s, 1403 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 508 (8), 507 (35), 506 M$^+$ (100).

(iii) With Excess Carbene Complex 22. The reaction of carbene complex **22**[20] (0.1933 g, 0.611 mmol) and 1,4-diphenyl-1,3-butadiyne (0.0412 g, 0.204 mmol) in 0.5 mL of THF was carried out at 66 °C for 9 h as described above for the reaction of complex **4a** with diyne **8**. The reaction mixture was opened to air and diluted with CH_2Cl_2. The major compound present as indicated by TLC was the arene complex **34** (see above, $R_f = 0.38$ in 1:5 EtOAc/hexane). Silica gel was added, and the mixture was allowed to stir in air at 25 °C for 1−2 days until **34** had dissappeared. After flash chromatography on silica gel with a 1:5 mixture of EtOAc/hexane, a 67% yield of monobenzannulated product **23** (48.3 mg, 0.136 mmol, $R_f = 0.40$) and a 4% yield of the double benzannulated product **33** (3.6 mg, 0.007 mmol, $R_f = 0.35$) were isolated, along with small amounts some unidentified compounds. The reaction was repeated at 70 °C for 60 h, with an additional 2 equiv of **22** being added after 20 and 40 h. The crude reaction mixture was stirred for 30 min at room temperature with 0.5 M aqueous CAN to give the quinones **32** and **25** in 5% and 0.6% yields, respectively.

(iv) With Excess Carbene Complex 22 in the Presence of Bu_3P. The reaction of carbene complex **22**[20] (0.205 g, 0.648 mmol), 1,4-diphenyl-1,3-butadiyne (0.0437 g, 0.216 mmol), and tri-*n*-butylphosphine (0.48 mL, 1.945 mmol) in 0.5 mL of THF was carried out at 70 °C for 10 h in the manner described above for the reaction of complex **4a** with diyne **8**. The reaction mixture was diluted with CH_2Cl_2 and allowed to stir with silica gel at 25 °C for 12 h. After flash chromatography on silica gel with 1:5 EtOAc/hexane, a 74% yield of the single benzannulated product **23** (57 mg, 0.161 mmol) and <1.3% yield of the regioisomer **24** (3.6 mg, 0.007 mmol) were isolated, along with small amounts of some unidentified compounds.

Preparation of the Ethylene-Bridged Bis-Carbene Complex 39. To a solution of 1.02 g (2.75 mmol) of tetramethylammonium metalate **38**[16] in 30 mL of dichloromethane at −20 °C was added 0.233 mL (3.0 mmol) of acetyl bromide. After the solution was stirred at −20 °C for 1 h, 0.077 mL (1.38 mmol) of ethylene glycol was added, and the resulting solution was stirred for an additional 16 h at −20 °C. The red reaction mixture was quenched by pouring into saturated aqueous $NaHCO_3$. The organic layer was washed with water and brine then dried with anhydrous $MgSO_4$. The solvent was removed, and the product was separated from the red residue by flash chromatography on silica gel with a 1:1:8 mixture of CH_2Cl_2/ether/hexane to give 0.67 g (1.08 mmol, 79%) of the bis-carbene complex **39**. Spectral data for **39**: red solid, mp 106−107 °C; $R_f = 0.48$ (1:1:8 CH_2Cl_2/ether/hexane); ^{1}H NMR ($CDCl_3$) δ 5.22 (br s, 4 H), 7.18 (br s, 4 H), 7.36 (br s, 6 H); ^{13}C NMR ($CDCl_3$) δ 76.77, 122.55, 128.36, 130.40, 153.23, 215.77, 224.02, 351.59; IR (neat) 3063 m, 2950 w, 2063 s, 1929 vs, 1721 w, 1593 w, 1441 w, 1254 w, 1222 w, 1199 w, 1145 w, 1102 w, 902 w, 759 w, 652 s, 619 w cm^{-1}; mass spectrum, *m/z* (relative intensity) 622 M$^+$ (1), 534 (1), 426 (1), 374 (6), 290 (35), 262 (8), 238 (17), 220 (43), 178 (100), 105 (70), 80 (61). Anal. Calcd for $C_{26}H_{14}O_{12}Cr_2$: C, 50.17; H, 2.27. Found: C, 50.42; H, 2.42.

Reaction of Bis-Carbene Complex 39 with 1,4-Diphenyl-1,3-butadiyne (8). The reaction of carbene complex **39** (100 mg, 0.16 mmol) with 0.9 equiv of 1,4-diphenyl-1,3-butadiyne (**8**) was carried out as described above for the reaction of complex **4a** with diyne **8**. The reaction times, temperatures, concentrations, and yields for the various runs are indicated in Scheme 11. After the mixture cooled to room temperature, 200 mg of silica gel was added, the volatiles were removed, and the residue was loaded on the top of a silica gel column. The products were eluted first with a 5:1 mixture of hexane/ethyl acetate and then with a 3:1 mixture. The only two predominate products observed for each run were the 2,2′-binaphthol **40** and the indenylnaphthol **41**. Purer samples of each product could be obtained if a 16:1:1 mixture of hexane/CH_2Cl_2/ether was used as eluant. Spectral data for **40**: whitish-yellow film; $R_f = 0.16$ (16:1:1 hexane/CH_2Cl_2/ether); ^{1}H NMR ($CDCl_3$, −20 °C) δ 4.20 (d, 2 H, $J = 8.5$ Hz), 4.57 (d, 2 H, $J = 8.5$ Hz), 5.63 (s, 2 H), 6.41 (d, 2 H, $J = 7.3$ Hz), 6.67 (d, 2 H, $J = 7.6$ H z), 6.96 (t, 2 H, $J = 7.6$ Hz), 7.14 (t, 2 H, $J = 7.4$ Hz), 7.20 (t, 2 H, $J = 7.4$ Hz), 7.53 (t, 2 H, $J = 7.7$ Hz), 7.62 (t, 2 H, $J = 7.1$ Hz), 8.14 (d, 2 H, $J = 8.4$ Hz), 8.19 (d, 2 H, $J = 8.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 73.26, 120.61, 122.03, 123.10, 125.08, 125.73, 125.85, 126.81, 127.19, 127.52, 128.18, 129.00, 130.17, 132.07, 134.33, 144.40, 148.51; IR (neat) 3526 m, 3332 w, 3061 w, 2923 m, 2851 w, 1720 m, 1391 m, 1359 m, 1296 m, 1064 s, 761 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 496 M$^+$ (100), 468 (7), 450 (2), 423 (2), 105 (12), 73 (22); high-resolution EI MS calcd for $C_{34}H_{24}O_4$ *m/z* 496.1675, measd 496.1643. Spectral data for **41**: whitish-yellow film; $R_f = 0.09$ (16:1:1 hexane/CH_2Cl_2/ether); ^{1}H NMR ($CDCl_3$) δ 3.44 (s, 1 H), 3.96 (t, 2 H, $J = 11.5$ Hz), 4.67 (td, 1 H, $J = 11.3$, 2.8 Hz), 4.92−5.00 (m, 1 H), 5.41 (s, 1 H), 6.72−6.75 (m, 3 H), 6.85−6.90 (m, 4 H), 7.14 (t, 1 H, $J = 7.5$ Hz), 7.21 −7.59 (m, 8 H), 8.00 (d, 1 H, $J = 8.3$ Hz), 8.08 (d, 1 H, $J = 8.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 54.67, 64.25, 68.77, 118.30, 119.94, 121.62, 122.82, 123.01, 124.39, 125.46, 126.00, 126.19, 126.32, 126.89, 127.87, 128.20, 128.46, 129.05, 129.80, 130.35, 130.38, 132.00, 136.13, 138.87, 139.42, 141.53, 144.53, 147.68, 155.57; IR (neat) 3531 s, 3059 m, 3026 w, 2938 w, 1723 w, 1599 s, 1584 s, 1499 s,, 1451 s, 1391 s, 1358 s, 1319 m, 1296 m, 1265 m, 1211 w, 1112 m, 1067 s, 1016 w, 892 w, 763 s, 737 s, 702 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 468 M$^+$ (100), 440 (4), 422 (4), 262 (6), 105 (5), 77 (3); high-resolution EI MS calcd for $C_{33}H_{24}O_3$ *m/z* 468.1725, measd 468.1676.

Preparation of *meso*-2,3-Butanediol-Bridged Bis-Carbene Complex 42. To a solution of tetramethylammonium metalate **38**[16] (0.426 g, 1.15 mmol) in 6 mL of a 1:1 mixture of dichloromethane/DMF at −20 °C was added acetyl bromide (0.093 mL, 1.26 mmol). After the

---

[20] 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.

mixture was stirred at −20 °C for 0.5 h, 2,3-butanediol (0.035 mL, 0.38 mmol, >90% meso) was added, and the resulting solution was stirred for 2 h at −20 °C and 2 h at 0 °C. The red mixture was poured into a sepratory funnel containing aqueous saturated $NaHCO_3$ and hexane. The organic layer was washed with water and brine and then dried with anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. The product was isolated from the red residue by flash chromatography on silica gel with a 1:1:16 mixture of ether/CH_2Cl_2/hexane to give 0.126 g (0.59 mmol, 51%) of complex **42**. Spectral data for **42**: red solid, mp = 114−115 °C; ^1H NMR ($CDCl_3$) δ 1.70 (br s, 6 H), 5.55 (br s, 2 H), 7.03 (br s, 4 H), 7.33 (br s, 6 H); ^{13}C NMR ($CDCl_3$) δ 16.24, 87.38, 122.29, 128.34, 130.15, 152.90, 215.84, 224.04, 349.65; IR (neat) 3065 w, 2990 w, 2943 w, 2062 s, 1933 vs, 1721 w, 1574 w, 1442 w, 1384 w, 1313 w, 1269 m, 1207 m, 1162 m, 1087 m, 1070 m, 979 w, 933 w, 900 m, 834 w, 759 w, 703 m, 690 m, 652 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 402 (5), 318 (33), 266 (16), 220 (32), 178 (46), 105 (100), 80 (97). Anal. Calcd for $C_{28}H_{18}O_{12}Cr_2$: C, 51.70; H, 2.79. Found: C, 51.87; H, 2.72.

Reaction of the *meso*-2,3-Butanediol-Bridged Bis-Carbene Complex 42 with 1,4-Diphenyl-1,3-butadiyne (8). The reaction of carbene complex **42** (0.1256 g, 0.19 mmol) with 0.9 equiv (0.0326 g, 0.16 mmol) of 1,4-diphenyl-1,3-butadiyne (**8**) in 6.4 mL of THF was carried out at 75 °C for 5 h according to the procedure described for the reaction of complex **4a** with diyne **8**. The product was isolated from the crude reaction on silica gel with a 1:1:8 mixture of ether/CH_2Cl_2/hexane to give 14.6 mg (0.029 mmol) of **43** as a white solid in 22% yield as a single diastereomer. Spectal data for **43**: R_f = 0.25 (1:9 EtOAc/hexane); ^1H NMR ($CDCl_3$) δ 1.29 (d, 3 H, J = 6.7 Hz), 1.31 (d, 3 H, J = 6.8 Hz), 4.12 (q, 1 H, J = 6.7 Hz), 4.65 (q, 1 H, J = 7.0 Hz), 5.13 (s, 1 H), 6.42 (d, 2 H, J = 7.5 Hz), 6.96 (t, 2 H, J = 7.3 Hz), 7.02 (t, 1 H, J = 7.2 Hz), 7.06 (d, 1 H, J = 7.4 Hz), 7.19−7.40 (m, 12 H), 7.48 (d, 1 H, J = 7.4 Hz); IR (neat) 3060 w, 3023 w, 2974 w, 2917 m, 2847 w, 1756 vs, 1613 w, 1587 s, 1542 s, 1489 m, 1447 m, 1409 m,1386 w, 1297 w, 1173 m, 1148 w, 1116 w, 1098 m, 1073 m, 1006 m, 909 m, 730 s, 697 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 496 M^+ (100), 440 (20), 424 (21), 363 (12), 336 (8), 307 (8), 289 (14), 276 (12), 247 (20) 236 (18), 194 (18), 105 (45), 77 (18); high-resolution EI MS calcd for $C_{35}H_{28}O_3$ *m/z* 496.2038, measd 496.2047. Anal. Calcd for $C_{35}H_{28}O_3$: C, 84.65; H, 5.68. Found: C, 84.85; H, 6.52.

Preparation of (2*R*,3*R*)-Butane-2,3-diol-Bridged Bis-Carbene Complex 44. To a solution of 1.216 g (3.28 mmol) of tetramethylammonium metalate **38**[16] in 10 mL of dichloromethane at −20 °C under argon was added 0.24 mL (3.28 mmol) of acetyl bromide. After the mixture was stirred at −20 °C for 1 h, 0.15 mL (1.64 mmol) of (2*R*,3*R*)-butane-2,3-diol was added, and the resulting solution was stirred at −15 °C for 7.5 h. The red mixture was poured into saturated aqueous $NaHCO_3$ solution. The organic layer was washed with water and brine and then dried with anhydrous $MgSO_4$. The solvent was removed, and the products were purified by flash chromatography on silica gel to give 0.193 g (0.30 mmol, 18%) of bis-carbene complex **44** (with a 1:1:30 mixture of ether/CH_2Cl_2/hexane) and 0.342 g (0.92 mmol, 28%) of a compound tentatively identified as the monocarbene complex **45** (with a 1:1:4 solvent mixture; R_f = 0.06 with a 1:1:16 solvent mixture) as red oils. Spectral data for **44**: R_f = 0.38 (1:1:16 ether/CH_2Cl_2/hexane), ^1H NMR ($CDCl_3$) δ 1.60 (br s, 6 H), 5.66 (br s, 2 H), 7.14 (br s, 4 H), 7.37 (br s, 6 H); ^{13}C NMR ($CDCl_3$) δ 17.96, 87.63, 122.22, 128.25, 130.01, 153.04, 215.79, 224.40, 350.37; IR (neat) 3060 w, 2986 w, 2939 w, 2062 s, 1929 vs, 1717 w, 1438 w, 1380 w 1268 w, 1201 m, 1159 w, 1073 m, 932 w, 900 w, 760 w, 676 m, 652 s, 619 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 650 M^+ (8), 594 (2), 566 (3), 539 (2), 510 (7), 403 (58), 318 (16), 281 (18), 267 (100), 253 (22), 197 (11), 177 (16).

Reaction of the (2*R*,3*R*)-Butane-2,3-diol-Bridged Bis-Carbene Complex 44 with 1,4-Diphenyl-1,3-Butadiyne (8). The reaction of 0.126 g (0.19 mmol) of complex **44** and 0.026 g (0.16 mmol) of 1,4-diphenyl-1,3-butadiyne (**8**) in 6.05 mL of THF was carried as described for the reaction of complex **4a** with **8** at 75 °C for 17 h. The solvent was removed slowly under vacuum, and the residue was loaded onto a silica gel column and eluted with a 1:9 mixture of ethyl acetate/hexane. The three products that were isolated were identified as the indenylnaphthalene **47** (0.0168 g, 21%, light yellow oil), the 2,2′-binaphthol **46** (0.0196 g, 23%, white solid), and the thermal dimerization product **48** (0.0099 g, 29%, white solid). Spectral data for **48**: R_f = 0.61 (1:9 EtOAc/hexane); ^1H NMR ($CDCl_3$) δ 1.37 (d, 6 H, J = 5.1 Hz), 3.88−3.90 (m, 2 H), 7.11−7.14 (m, 6 H), 7.19−7.22 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 16.89, 74.81, 127.25, 127.81, 128.91, 133.96, 135.30; IR (neat) 3038 w, 2971 m, 2927 m, 2890 w, 1644 m, 1495 w, 1446 m, 1271 s, 1155 m, 1094 s, 1020 w, 947 w, 764 s, 697 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 266 M^+ (28), 178 (3), 165 (4), 105 (100), 77 (40); high-resolution EI MS calcd for $C_{18}H_{18}O_2$ *m/z* 266.1307, measd 266.1351. Spectral data for **47**: R_f = 0.24 (1:9 EtOAc/hexane); ^1H NMR ($CDCl_3$) δ 1.53 (d, 3 H, J = 5.9 Hz), 1.71 (d, 3 H, J = 5.8 Hz), 3.45 (s, 1 H), 3.96−3.99 (m, 2 H), 5.27 (s,1 H), 6.80−6.99 (m, 8 H), 7.23−7.60 (m, 8 H), 8.11 (d, 1 H, J = 8.1 Hz), 8.20 (d, 1 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 18.90, 19.31, 53.15, 78.85, 83.06, 117.73, 119.82, 122.65, 122.93, 123.73, 124.14, 124.58, 125.39, 125.68, 126.32, 126.39, 126.48, 128.09, 128.28, 128.50, 128.60, 128.85, 129.91, 130.06, 130.16, 131,94, 135.66, 138.31, 138.81, 144.20, 147.38, 147.98, 156.39; IR (neat) 3595 m, 3054 w, 3017 w, 2975 m, 2933 w, 2869 m, 1601 w, 1586 m, 1495 m, 1442 m, 1381 s, 1354 m, 1313 m, 1296 m, 1266 m, 1210 w, 1177 w, 1138 w, 1122 s, 1092 w, 1063 s, 1029 s, 769 s, 761 s, 737 s, 700 s, 683 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 496 M^+ (45), 440 (21), 422 (14), 336 (23), 306 (16), 289 (14), 276 (16), 202 (17) 177 (56), 165 (12), 105 (100), 77 (34); high-resolution EI MS calcd for $C_{35}H_{28}O_3$ *m/z* 496.2038, measd 496.2102. Anal. Calcd for $C_{35}H_{28}O_3$: C, 84.65; H, 5.68. Found: C, 84.88; H, 6.34. Spectral data for **46**: R_f = 0.19 (1:9 EtOAc/hexane); white solid, mp = 184 °C dec; ^1H NMR ($CDCl_3$) δ 1.59 (d, 6 H, J = 5.7 Hz), 4.00 (m, 2 H), 5.59 (s, 2 H), 6.43 (s, 2 H), 6.74 (s, 2 H), 7.00 (br s, 2 H), 7.16 (m, 4 H), 7.54 (t, 2 H, J = 8.2 Hz), 7.64 (t, 2 H, J = 8.1 Hz), 8.13 (d, 2 H, J = 8.2 Hz), 8.26 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 19.13, 83.30, 120.48, 122.13, 123.26, 124.99, 125.44, 126.15, 126.63, 127.32, 127.39, 128.12, 129.12, 130.06, 132.10, 134.35, 144.12, 148.04; IR (neat) 3484 m, 3067 w, 2957 m, 2929 m, 2858 m, 1726w, 1588 w, 1448 w, 1387 m, 1380 m, 1360 w, 1298 s, 1276 s, 1125 m, 1064 s, 1031 m, 761 s cm^{-1}; mass spectrum, *m/z* (relative intensity) 524 M^+ (6), 496 (2), 468 (2), 408 (2), 380 (16), 336 (12), 308 (30), 291 (8), 276 (8), 231 (12), 202 (11), 177 (22), 105 (100), 91 (26), 77 (34); high-resolution EI MS calcd for $C_{36}H_{28}O_4$ *m/z* 524.1988, measd 524.2002.

In a control experiment, it was shown that **48** is a thermal decompostion product of the carbene complex **44**. A solution of 0.025 g (0.038 mmol) of **44** in 1.5 mL of THF was heated at 80 °C under argon for 16 h. After removal of the volatiles, the residue was loaded onto a silica gel column and eluted with a 1:30 mixture of EtOAc/hexane to give 0.052 g (0.02 mmol, 51%) of **48**, which was found to be identical with the major product from the thermolysis of complex **44** with 1,4-diphenyl-1,3-butadiyne.

Preparation of 2,2′-Binaphthyl Diacetate 49. A solution of binaphthol **46** (0.0813 g, 0.16 mmol), acetic anhydride (0.088 mL, 0.93 mmol), triethylamine (0.13 mL, 0.93 mmol) and DMAP (5 mg) in 10 mL of THF was introduced into a 25 mL single-necked flask that was modified by replacement of the 14/20 joint with a threaded high-vacuum stopcock. The flask was closed at 25 °C and placed in a 65 °C oil bath for 12 h. The solution was diluted with ether and washed with aqueous saturated sodium bicarbonate. The product was purified on silica gel with a 1:1:4 mixture of ether/CH_2Cl_2/hexane to give 0.0672 g (0.11 mmol) of the diacetate **49** in 71% yield. Spectral data for **49**: R_f = 0.36 (1:1:4 ether/CH_2Cl_2/hexane); ^1H NMR ($CDCl_3$) δ 1.63 (d, 6 H, J = 5.8 Hz), 1.94 (s, 6 H), 4.10−4.12 (m, 2 H), 6.48−6.55 (br s, 4 H), 6.83 (br s, 2 H), 7.06 (br s, 4 H), 7.51−7.76 (m, 6 H), 8.16 (d, 2 H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 19.01, 20.43, 83.53, 102.62, 122.26, 122.80, 126.46, 126.77, 126.86, 127.30, 128.12, 131.34, 131.41, 134.87, 140.01, 152.79, 168.57 (1 aryl C not located); IR (neat) 3072 w, 3026 w, 2982 w, 2935 w, 2914 w, 2256 w, 1765 s, 1591 w, 1566 w, 1494 w, 1444 w, 1380 w, 1355 s, 1200 s, 1177 m, 1152 m, 1110 w, 1059 m, 1032 m, 1006 w, 966 w, 912 m, 844 w, 762 m, 711 s, 698 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 608 M^+ (38), 566 (88), 524 (100), 468 (18), 451 (6), 421 (3), 289 (2), 233 (6), 105 (14); high-resolution EI MS calcd for $C_{40}H_{32}O_6$ *m/z* 608.2199, measd 608.2190.

Reaction of 2,2′-Binaphthyl Diacetate 49 with Ethanethiol and Aluminum Chloride. To a solution of the diacetate **49** (0.0404 g, 0.066 mmol) and aluminum chloride (0.151 g, 1.1 mmol) in 2 mL of

CH_2Cl_2 was added 2 mL of ethanethiol at 25 °C, and the solution was stirred 16 h at 25 °C. The solution was quenched with brine and extracted with ether. The organic layer was washed with aqueous saturated $NaHCO_3$ and water. Quinone **50** (0.0135 g, 0.029 mmol, 44%) was isolated by elution from a silica gel column with a 1:1:4 mixture of CH_2Cl_2/ether/hexane. The bis-quinone **50** from this reaction had an optical rotation of $[\alpha]^D = -76.4°$($c = 0.5$, THF). As described below, the optical rotation of optically pure bis-quinone **50** was shown to be $[\alpha]^D = 275.5°$ ($c = 0.54$, THF) for the *R* isomer, and therefore the compound **46** has *S*-configuration. Spectral data for **50**: yellow solid, mp = 253−255 °C; $R_f = 0.24$ (1:5 EtOAc/hexane); ^1H NMR ($CDCl_3$) δ 6.69 (d, 4 H, $J = 7.2$ Hz), 7.18 (t, 4 H, $J = 7.9$ Hz), 7.28−7.31 (m, 2 H), 7.75−7.83 (m, 4 H), 8.09−8.12 (m, 2 H), 8.18−8.21 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 126.68, 126.92, 127.65, 129.13, 129.25, 131.85, 131.96, 132.02, 133.91, 134.15, 142.02, 146.35, 183.40, 184.65; IR (neat) 3060 w, 2914 w, 1665 s, 1595 m, 1322 w, 1287 s, 759 w, 724 m, 708 m, 664 m cm^{-1}; mass spectrum, *m/z* (relative intensity) 466 M^+ (95), 422 (100), 361 (22), 276 (21), 105 (54), 76 (58); high-resolution EI MS calcd for $C_{32}H_{18}O_4$ *m/z* 466.1205, measd 466.1193.

A mixture of 0.112 g (0.26 mmol) of (*R*)-(+)-**48**[13] (optical purity ≥99% by HPLC measurement) and 0.025 g (0.077 mmol) of salcomine was dissolved in 30 mL of THF, and the solution was purged with oxygen for 4 h. After chromatography on silica gel with a 1:5 mixture of EtOAc/hexane, 0.1019 g (0.22 mmol, 85%) of quinone (*R*)-(+)-**50** was isolated. This material has a optical rotation of $[\alpha]^D= 275.5°$ ($c = 0.54$, THF). The same reaction was also carried out with racemic **51**, and racemic **50** was isolated in 71% yield.

Racemization of the Bis-2,2′-Naphthoquinone 50 with Ethanethiol and Aluminum Chloride. A flask was charged with 0.134 g (0.31 mmol) of (*R*)-(+)-**50**[13] [($[\alpha]^D = 275.5°$ at ($c = 0.54$)], 0.689 g (5.17 mmol) of $AlCl_3$, 3 mL of EtSH, and 3 mL of CH_2Cl_2 under nitrogen. The brown solution was stirred at 25 °C for 40 h, and then the volatiles were removed by vacuum. Brine and ether were added to the residue, and the aqueous layer was extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$, water, and brine and dried with anhydrous $MgSO_4$. The ^1H NMR spectrum and TLC both indicated that no bis-quinone **50** was present in the crude reaction mixture and that the major product was not the bis-naphthol **51**. The crude reaction mixture was dissolved in 5 mL of THF and 1.2 mL of 0.5 M aqueous CAN was added. After the mixture was stirred at 25 °C for 25 min, brine was added. The organic layer was washed with saturated aqueous $NaHCO_3$, water, and brine and then dried with anhydrous $MgsO_4$. After removal of solvent, the residue was loaded onto a silica gel column and eluted with a 1:5 mixture of EtOAc/hexane to give 0.0685 g (0.16 mmol, 51% yield) of bis-quinone **50**. This compound was found to have an optical rotation of $[\alpha] = 40.8°$ ($c = 0.48$, THF). This bis-quinone product (0.028 g, 0.065 mmol) was then dissolved in 2 mL of THF, and to this solution was added 0.3 mL of 0.5 M aqueous CAN (0.15 mmol). The mixture was stirred in air at 25 °C for 25 min, and then workup as described above afforded 0.0292 g (0.067 mmol, 100%) of bis-quinone **50**, which had an optical rotation of $[\alpha]^D = 43.3°$ ($c = 0.61$, THF).

Acknowledgment. This work was supported by the National Institutes of Health (PHS-GM 45326) and the National Science Foundation (CHE-8821326). We thank the NSF for summer fellowships for M.C.W. and M.J.F. The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program.

JA953146K