Synthons for the Parent Vinyl Carbene Complex in the Benzannulation Reaction

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The benzannulation reaction of Fischer carbene complexes with alkynes to produce phenols was found not be synthetically useful for the parent vinyl carbene complex **6a**. The β-silylated vinyl carbene complex **6c** is more stable than the parent vinyl complex **6a** and can be effectively used as a synthon for **6a** since during the benzannulation the silicon migrates to the phenol function preferentially over hydrogen to give the arene chromium tricarbonyl complexes of the type **19**. This reaction is general for a number of alkynes that have incorporated important functionality and is more useful for terminal alkynes than for internal alkynes. The migration of the silicon is responsible for the fact that stable arene chromium tricarbonyl complexes can be isolated from these reactions and makes possible transformations that take advantage of the activating ability of the chromium tricarbonyl group. This is demonstrated in intramolecular aromatic nucleophilic additions reactions. It is also shown in a single example that the α-silylated vinyl carbene complex **10b** can in principle also serve as a synthon for the parent vinyl carbene complex **6a**, since the benzannulated product can be disilylated with trifluoroacetic acid.

The diversity of synthetically attractive transformations that are known and continually being discovered for Fischer carbene complexes has served not only to stimulate investigations of their chemistry but also to establish the value of these complexes in applications in synthetic organic chemistry.[2] The synthesis of phenols from the reactions of Fischer carbene complexes with alkynes is presently the most synthetically important of these transformations. This reaction provides the controlled construction of a new benzene ring in an annulation process that occurs under neutral conditions and at near ambient temperatures. Three new carbon–carbon bonds are formed in this overall process from the carbene ligand, the alkyne, and a carbon monoxide ligand as indicated in Scheme 1. The reaction can be highly regioselective for alkyne incorporation where the largest substituent is incorporated adjacent to the phenol function. The applications of this benzannulation reaction in organic synthesis first were developed for aryl complexes where naphthols are the primary products[3] and then for alkenyl complexes where phenols of the type 4 can be efficiently generated.[4]

The reactions of alkenyl complexes with alkynes are generally more selective for the benzannulated product than are the reactions of aryl complexes which often give rise to many structurally interesting alternative organic products.[2] One of the shortcomings of the benzannulation
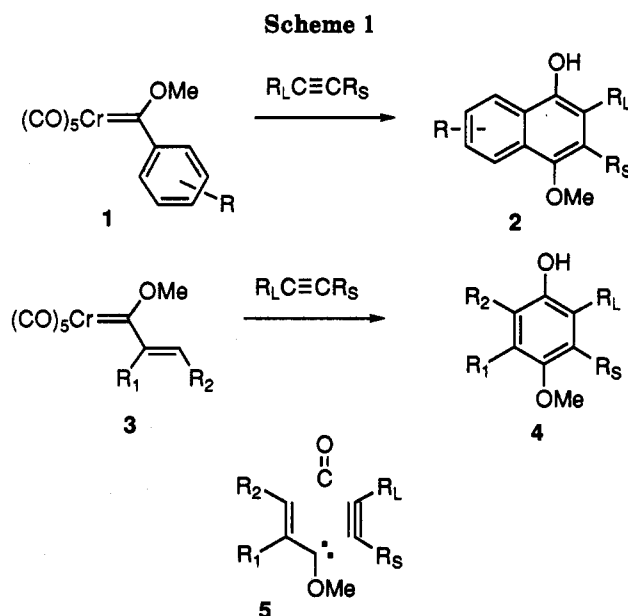
Scheme 1

of alkenyl complexes is that the scope of the reaction does not include the parent vinyl complex **6a** (complex **3** in Scheme 1, $R_1, R_2 = H$).[5] This outcome was not surprising considering that Fischer had reported that the parent vinyl complex is quite unstable.[6] The vinyl complex **6a** can be purified on silica gel and if the solvent is removed at a temperature below its melting point it can be isolated and stored as a solid.[6,7] However, if the solvent is removed at room temperature, **6a** is obtained as a red oil which quickly turns to a red glass presumably as the result of an acrylate-type polymerization.[6,8]

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(1) American Chemical Society Organic Division American Cyanamid Fellow, 1991–1992.

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

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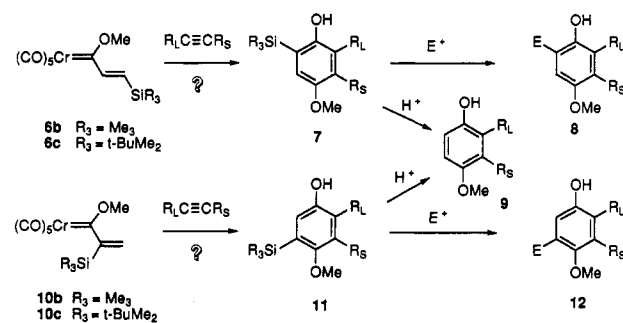**Table 1. Benzannulations of Complex 6 with Oxidative Workup**
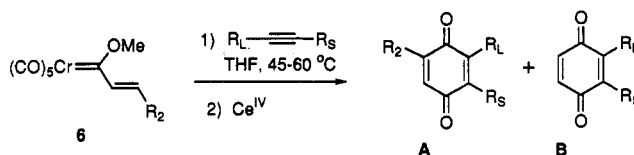
entry	R_2	carbene complex	R_L	R_S	product A	% yield of A	product B	% yield of B
1	H	6a	Et	Et			26	<5
2[a]	SiMe₃	6b	Ph	Ph	21	27	27	25
3	Si-t-BuMe₂	6	Ph	Ph	22	35	27	17
4	Si-t-BuMe₂	6c	Ph	H	23	<5	28	54
5	Si-t-BuMe₂	6c	Et	Et	24	<6	26	<6
6	Si-t-BuMe₂	6c	n-Pr	H	25	<5	29	<5

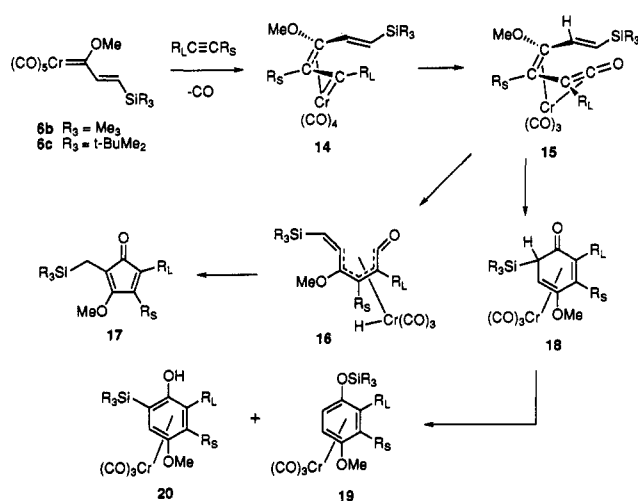[a] An 11 % yield of 17 was isolated with an oxidative workup was not employed (ref 9).

It has been observed in many cases that α,β-unsaturated carbene complexes of the type 3 are more stable when the β-carbon has at least one non-hydrogen substituent. Therefore, in the design of a synthon for the parent vinyl carbene complex 6a in the benzannulation reaction, the silyl complexes 6 and 10 were given the highest consideration. Silyl substituents should function to stabilize the carbene complex and to serve as a synthon for hydrogen since it can be anticipated that the silyl-substituted phenols 7 or 11 should readily undergo protodesilylation to 9. The analysis presented in Scheme 2 does not suggest that either of the silylated complexes 7 or 11 should necessarily be better than the other as a synthon for 6a; however, since we anticipated that a β-silyl substituent would lend greater stability to the carbene complex we chose to investigate the benzannulations of 6. While not yet pursued, it should be pointed out that the synthetic implications of the benzannulations of silylated carbene complexes greatly extends beyond synthons for the parent vinyl carbene complex since the silyl groups in the initial products 7 and 11 could be replaced by a number of electrophiles other than protons.

We have previously reported the preparation and a single benzannulation reaction of the (trimethylsilyl)vinyl carbene complex 6b (with diphenylacetylene, Table 1, entry 2).[9] While the complex 6b was more stable than the parent vinyl complex 6a as expected, it still was not as stable as most alkyl-substituted vinyl carbene complexes. In addition, this reaction was not selective for a single product as expected but rather produced a mixture of the three products indicated in Table 1 (entry 2). The unprecedented cyclopentadienone product 17 (R_L, R_S = Ph, Scheme 3) was obtained in 11% yield as a purple crystalline

Scheme 2

Scheme 3

(4) (a) Chamberlin, S.; Wulff, W. D.; Bax, B. M. *Tetrahedron* **1993**, *49*, 5531. (b) Chamberlin, S.; Wulff, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 10667. (c) King, J.; Quayle, P.; Malone, J. F. *Tetrahedron Lett.* **1990**, *31*, 5221. (d) Dötz, K. H.; Popall, M.; Mueller, G.; Ackermann, K. *J. Organometal. Chem.* **1990**, *383*, 93. (e) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organometal. Chem.* **1987**, *334*, 9. (f) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (g) Wulff, W. D.; Chan, K. S.; Tang, P. C. *J. Org. Chem.* **1984**, *49*, 2293. (h) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565. (i) Wulff, W. D.; Tang, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 434. (j) Dötz, K. H.; Kuhn, W. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 732.

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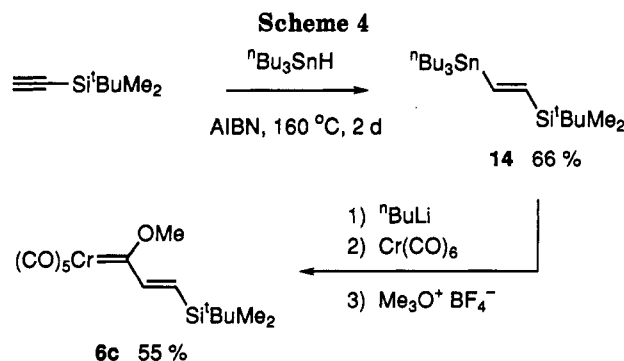
solid in a separate run that did not employ an oxidative workup. This product would not stand up to oxidation with cerric ammonium nitrate. When an oxidative workup was employed, only the silylated quinone 21 and the non-silylated analog 27 eluted from a silica gel column. The nonoxidized forms of the benzannulated products could not be easily obtained from this reaction due to the fact that separation of the products was difficult prior to oxidation since many of the products were isomeric and/or were complexed by metal fragments. Given the fact that the trimethylsilyl complex 6b was not as stable as deemed necessary and the fact that the benzannulation reaction with diphenylacetylene was not selective, we have not investigated the reaction of complex 6b with any other acetylene. Instead, we have decided to undertake the study of the benzannulations of the β-*tert*-butyldimethylsilyl)-vinyl carbene complex 6c which is the subject of the present work.[10]

The mechanism shown in Scheme 3 depicts the processes

that are likely to be encountered in a general study of the benzannulation of the complex **6c**. The cyclopentadienone products are thought to arise as indicated in Scheme 3 from a β-hydride elimination in the vinyl ketene complex **15** to give the η[5]-pentadienoyl chromium hydride complex **16** which could undergo an electrocyclic ring closure, readdition of the metal hydride, and finally an olefin isomerization to give the observed cyclopentadienone product **17**.[9,11] Whereas, hydrogen activation is known for the reactions of carbene complexes in which the hydrogen is on an sp[3]-carbon,[9] this is only known to occur from a vinyl carbon for the β-silyl complex **6b**.[9] Products of the type **17** have never been observed for any other vinyl carbene complex. This suggests that the β-hydride elimination in the vinyl ketene intermediate **15** is facilitated by the silyl substituent and thus there was some concern for the general success of the benzannulation of silyl carbene complex **6c** in a screen with a variety of alkynes. The isolation of the quinones **21** and **27** from the reaction of **6b** with diphenylacetylene suggests that silicon-migrated and non-silicon-migrated phenol complexes **19** and **20** are both formed in this reaction (Scheme 3). While obtaining mixtures of silyl-migrated and non-migrated products does not affect the feasibility of employing β-silyl vinyl carbene complexes as synthons for the parent vinyl complexes, this method would be far more attractive if the silyl-migrated product were produced exclusively, because then the need for the protodesilylation step would be obviated. The isolation of both the silylated and the non-silylated quinones **21** and **27** from this reaction was not a surprise since we had previously demonstrated that silicon groups will migrate to the oxygen in cyclohexadienone intermediates of the type **18**; however, this has previously only been observed in situations where the migration of silicon was not in direct competition with a migration of hydrogen.[4e,g,10] The factors that determine the relative rates with which silicon and hydrogen undergo 1,3-migration to oxygen in intermediates such as **18** have never been examined and would be difficult to predict *a priori*. However, if steric interactions are involved it then may not necessarily be the case that the β-*tert*-butyldimethylsilyl complex **6c** will be as unselective as the trimethylsilyl complex **6a** in producing a mixture of silyl- and non-silyl-substituted quinones.

Benzannulations of the β-(*tert*-Butyldimethylsilyl)vinyl Carbene Complex 6c. The β-(*tert*-butyldimethylsilyl)vinyl carbene complex **6c** was prepared by the standard Fischer method from chromium hexacarbonyl and an organolithium that in this case was generated by tin–lithium exchange from the vinylstannane **14**.[12] The vinylstannane was in turn prepared by a hydrostannylation of (*tert*-butyldimethylsilyl)acetylene by a procedure that was similar to that reported for the corresponding (triisopropylsilyl)acetylene (Scheme 4).[13] The yield of the carbene complex prepared by this procedure was consistently between 50–55%. The deep-red complex **6c** was obtained as an oil at room temperature and was stable enough to be handled and purified at the bench without

(10) We have recently communicated the reaction of complex **6c** with 6-cyano-1-hexyne.[4b]

(11) Yongskulrote, W.; Bramlett, J. M.; Mike, C. A.; Durham, B.; Allison, N. T. *Organometallics* **1989**, *8*, 556.

(12) This procedure does not work well for (tributylcyclohexenyl)stannane: Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K. S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Murray, C. K.; Yang, D. C. *J. Org. Chem.* **1986**, *51*, 277.

(13) Jomes, T. K.; Denmar, S. E. *Helv. Chim. Acta.* **1983**, *66*, 2397.

Scheme 4

any special precautions and can be stored for months in a vial fitted with a rubber septum, flushed with argon, and kept cold in a freezer.

The effect of the size of the silyl substituent in the carbene complex **6** on the distribution between silyl-migrated and non-migrated quinone products from reactions with diphenylacetylene was small and changed by only a factor of two in favor of the non-silyl-migrated product for the *tert*-butyldimethylsilyl complex **6c** relative to the trimethylsilyl complex **6b** (Table 1, entries 2 and 3). In the reactions indicated in Table 1 an oxidative workup was employed and thus no information regarding the amount of cyclopentadienone product **17** from this reaction could be obtained since it is known that the product is destroyed with this workup. It will be shown later that with a nonoxidizing workup there is one minor product from this reaction whose spectral data is consistent with a cyclopentadienone, and an upper limit of 8% yield could be placed on its formation (Table 2, entry 4). The reaction of the *tert*-butyldimethylsilyl complex **6c** with phenylacetylene produced the interesting finding that only the silyl-migrated quinone **28** was produced in this reaction. This result suggested that with terminal acetylenes the reaction might be selective for the silyl-migrated product and thus an investigation of the scope benzannulation reaction of carbene complex **6c** was undertaken.

The reactions of the *tert*-butyldimethylsilyl complex **6c** with 1-pentyne and 3-hexyne followed by an oxidative workup with cerric ammonium nitrate (CAN) failed to give anything more than small amounts of fractions from a silica gel column that could be spectroscopically consistent with either of the possible quinone products and even then these fractions were not pure (Table 1, entries 5 and 6). This observation was unexpected, and more interestingly, the same as that made for the reaction of the parent vinyl complex **6a** with 3-hexyne.[5] Since complex **6c** is not unstable to polymerization under these conditions, this raised the question of whether the failure of benzannulation of the parent complex **6a** with 3-hexyne was due to the instability of the carbene complex as had been originally thought.[5] It was shown that the low yield of **26** (from **6c**) was not due to loss of the quinone in the aqueous phase during workup and thus it was concluded that the most likely explanation is that quinone **26** (and **29**) is destroyed by cerric ammonium nitrate during the workup. In previous studies of related reactions where the quinone products are substituted at either the 5- or 6-positions we have not encountered this problem,[4f] and thus it appears that only the 5,6-unsubstituted quinones might be susceptible to degradation by cerric ammonium nitrate.

The data shown in Table 2 reveals that, in fact, the quinones **26** and **29** are sensitive to oxidative degradation

by cerric ammonium nitrate. While the reaction of complex 6c with 1-pentyne with an oxidative workup gives less than 5% yield of the quinone 29 (Table 1, entry 6), the same reaction without an oxidative workup gives a 72% yield of the silylated phenol complex 19 (Table 2, entry 6). Methylene chloride is used as solvent rather than THF since it has been shown in other cases that while the yields of the benzannulation reaction are essentially the same in these two solvents, the chromium tricarbonyl unit is more readily retained in methylene chloride.[4a] That the solvent does not play a role is revealed in the fact that the yields of benzannulated product from the reaction of the parent vinyl carbene complex 6a with 3-hexyne are quite low with and without an oxidative workup (Tables 1 and 2). This result thus reaffirms the original assumption that the failure of the benzannulation reaction of the parent vinyl carbene complex is due to the instability of the carbene complex under the reaction conditions.[5] The products 9a and 9b were presumably initially generated as chromium tricarbonyl complexes, but such complexes of unprotected phenols are very air-sensitive and normally the chromium tricarbonyl fragment is quickly lost upon exposure to air to give the free arene in high efficiencies.[4a]

In contrast to the parent vinyl complex 6a, the benzannulation of the β-(tert-butyldimethylsilyl)vinyl carbene complex 6c works well with a number of acetylenes as indicated in Table 2. An oxidative workup was not employed for these reactions and the benzannulated product was isolated as the silyl-migrated chromium tricarbonyl complexes 19. The yields are good for terminal acetylenes, but drop off for the two internal acetylenes that were examined. While the only functional groups on the alkyne that we tested for compatibility with complex 6c are those shown in Table 2, the fact that nitrile, iodoaryl, and propargyl acetals are compatible suggests that there will be a reasonable latitude in functional group choice in the synthetic applications of benzannulations of complex 6c. The selectivity of these reactions for the silyl-migrated benzannulated product is quite general and to a greater degree than might have been expected from the initial reaction of the trimethylsilyl complex 6b with diphenylacetylene.[9] Since no oxidative workup was employed for the reactions in Table 1, the cyclopentadienone products 17 should have been noted during isolation particularly since they are normally highly colored compounds. In a few cases colored bands were noticed, but in terms of mass balance they were usually insignificant. In the case of the reaction with diphenylacetylene (entry 4), two colored bands were collected and one of them had spectral properties such that it was possible it was a mixture of isomers of 17 (exocyclic double bonds). These compounds were not further separated or characterized, but if they were isomers of 17 the yield would have been 8%.

It is clear that at least for the reactions of the terminal alkynes shown in Table 2 that silicon migration occurs preferentially over hydrogen from the intermediate 18 (Scheme 3). All of the reactions in Table 2 were only screened for the silyl-migrated chromium tricarbonyl complexes. The reaction mixtures from terminal alkynes were generally quite clean by TLC, whereas, those from internal alkynes revealed several side-products which were not isolated or characterized. It was not determined, however, whether the ratio of the quinones A and B indicated in Table 1 reflect the ratio of hydrogen versus

Table 2. Benzannulations of Complex 6 without an Oxidative Workup

| entry	carbene complex	R_L	R_S	product 9	yield 9	product 19	Yield 19
1	6a	Et	Et	9a	~10		
2	6a	n-Pr	H	9b	~13		
3	6c	Et	Et			19a	43
4	6c	Ph	Ph			19b	26[a]
5	6c	Ph	H			19c	44
6	6c	n-Pr	H			19d	72
7	6c	(cyclohexenyl)	H			19e	40
8	6c	i-Pr	H			19f	68
9	6c	NC~~~	H			19g	68
10	6c	(iodobenzyl)	H			19h	57
11	6c	(EtO)2CH	H			19i	53

[a] An 8% yield of a material that was tentatively identified as a mixture of isomers of 17 was also obtained.

silicon migration. Specifically it was not determined whether quinone B results from the loss of silicon from oxygen or carbon. The formation of 19b (Table 2) presumably occurs with the formation of 9b, but this was not determined. At this point the question is raised as to why silicon preferentially migrates to oxygen over hydrogen in the reactions of the terminal alkynes indicated in Table 2. It is our suspicion that this is related to the stereochemical relationship of the silicon and metal in the intermediate 18 in Scheme 3, but the answer to this question must await future investigations.

The advantages of the benzannulations of the (tert-butyldimethylsilyl)vinyl carbene complex 6c transcends its ability to function as a synthon for the parent vinyl carbene complex 6a. The fact that silicon preferentially migrates over hydrogen means that the primary product of the reaction is the protected phenol chromium tricarbonyl complex 19 rather than the unprotected phenol complex 20. This result allows the consideration of employing the protected chromium tricarbonyl phenol complexes 19 in aromatic nucleophilic addition reactions since the unprotected phenol complexes 20 in the presence of nucleophiles would probably just undergo deprotonation.[4b] The reaction of complex 6c with 6-cyano-1-hexyne was originally carried out to test this idea and as indicated in Table 2 this reaction was found to produce the protected phenol complex 19g in 68% yield.[10] The intramolecular nucleophilic addition of a nitrile-stabilized carbanion generated by treating 19g with LDA is successful, and as indicated in Scheme 5, the regiochemistry of the addition can be controlled with temperature to give either the spirocyclohexadienone 31 in 46% overall yield or the fused addition product 32 in 38% overall yield. The reactions indicated in Scheme 5 are carried out in one pot without isolation of the chromium tricarbonyl complex 19g. Since the isolated yield of 19g was determined to be 68%, the yields for the aromatic nucleophilic substitutions are 68% for 31 and 56% for 32.

As indicated in Scheme 2, the α-silyl-substituted

Scheme 5
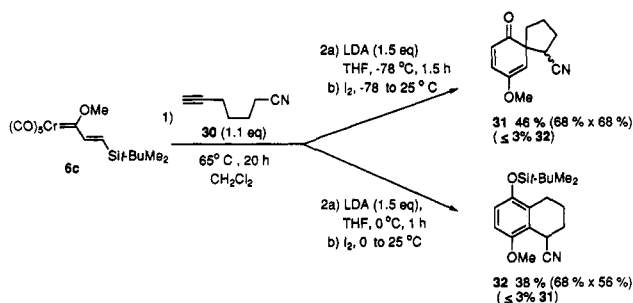
Scheme 6
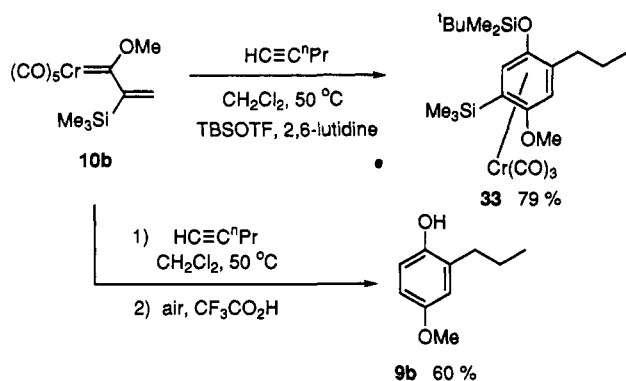
complex 10 could also function as a synthon for the parent vinyl carbene complex 6a. We had originally chosen the β-silyl complexes 6 since it was anticipated that they would be more stable than the α-silyl complexes. This did not turn out to be the case as it was found that the α-trimethylsilyl-substituted complex 10b is more stable than either the β-trimethylsilyl complex 6b or the β-tert-butyldimethylsilyl complex 6c. This may be due to a greater preference for a perpendicular conformation of the vinyl group in 10b relative to 6b due to the steric consequences of the α-silyl group. Furthermore, complex 10b is directly accessible in a single step from the commercially available (α-bromovinyl)trimethylsilane in 78% yield.[4a] The benzannulation of complex 10b with 1-pentyne proceeds smoothly and in the presence of a silylating agent will give rise to the chromium tricarbonyl complex 33 in 79% yield which is slightly higher than the yield of 19c (Table 2) from the reaction of the β-silyl complex 6c with 1-pentyne. Furthermore, in one unoptimized attempt it was shown that the silyl group could be removed from the benzannulation product with a workup with trifluoroacetic acid to give the phenol 9b in 60% yield.

It has been shown that both the α- and β-silylated vinyl carbene complexes can serve as synthons for the parent vinyl complex in the benzannulation reaction and that each has unique advantages. The β-silyl complex 6c reacts with a preferential migration of silicon over hydrogen to give silyl-protected arene chromium tricarbonyl complexes that will allow for further transformations that take advantage of the presence of the chromium tricarbonyl group. The α-silyl complex 10b has the potential of serving as a synthon for a variety of vinyl carbene complexes that might be difficult to prepare or handle since, as indicated in Scheme 2, the silicon could be replaced by a number of nucleophiles other than proton. These aspects of the silylated carbene complexes 6 and 11 are currently being explored.

Experimental Section

NMR spectra were recorded at 500 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. THF was distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. All reactions were performed in flame-dried glassware which had been evacuated and backfilled with argon. Unless otherwise specified R_f values were determined with ternary solvent mixtures of diethyl ether, dichloromethane, and hexanes (v/v/v). Column chromatography was performed with EM Science 330–400 mesh silica gel. 3-Methyl-1-butyne was purchased from Wiley Organics; phenylacetylene, diphenylacetylene, and 1-ethynylcylohexene were purchased from Aldrich; 1-pentyne and 3-hexnyne were purchased from Farchan. Alkynes which are oils at room temperature were purified immediately prior to use by distillation or gravity filtration through a short plut of neutral alumina. Diphenylacetylene was used as received. 6-Heptyne-nitrile was prepared from 5-hexyn-1-ol (Farchan) according to a literature procedure.[14] 1-(2-Iodophenyl)-2-propyne was prepared according to the manner of Ochiai.[15] (Vinylmethoxycarbene)pentacarbonylchromium(0) (6a) was prepared according to the literature procedure.[16]

(*E*)-[(*tert*-Butyldimethylsilyl)vinyl]-tri-*n*-butylstannane (14). A Paar high-pressure reaction vessel was charged with a spatula tip of AIBN, evacuated, and backfilled with argon (two cycles). (tert-Butyldimethylsilyl)acetylene (3.70 g, 26.42 mmol) and freshly distilled tributyltin hydride (8.44 g, 27.74 mmol) were combined in a 50-mL pear-shaped flask fitted with a three-way stopcock and degassed by the freeze-pump-thaw method (three cycles, −196 to 25 °C). The solution was transferred to the pressure reactor via cannula under an argon stream. The sealed vessel was heated in an oil bath at 160–70 °C for 48 h. The reaction mixture was cooled to room temperature and distilled at reduced pressure to yield 14 (7.57 g, 17.54 mmol, 66%) as a colorless oil. Spectral and physical data for 14: colorless oil, bp = 108–112 °C/0.1 mm, R_f = 0.72, hexanes; ^{1}H NMR (CDCl₃) δ 0.04 (s, 6 H), 0.86–0.91 (m, 24 H), 1.32 (sextet, 6 H, J = 7.2 Hz), 1.48–1.61 (m, 6 H), 6.57 (d, 1 H, J = 23.0 Hz), 6.96 (d, 1 H, J = 22.7 Hz); ^{13}C NMR (CDCl₃) δ 102.6, 83.1, 29.1, 27.2, 26.4, 13.67, 13.72, 9.5, −6.5; IR (neat film) 2955 s, 2926 s, 2855 m, 1463 m, 1252 m, 1011 m, 836 sh, 827 s cm⁻¹; a satisfactory mass spectrum for this compound could not be obtained.

(*E*)-[[(1-*tert*-butyldimethylsilyl)vinyl]methoxycarbene]-pentacarbonylchromium(0) (6c). To a solution of 14 (1.441 g, 3.341 mmol) in 20 mL of THF at −78 °C was added 2.3 mL of 1.6 M butyllithium in hexanes (3.67 mmol) dropwise. The resulting reddish-brown solution was stirred 10 min at −78 °C and then allowed to come to rt over 20 min. This solution was then added via cannula to a suspension of Cr(CO)₆ in 20 mL THF at rt. After 1 h, solvent was removed first by rotary evaporation and then by high vacuum for 1 h. The resulting reddish-brown gum was dissolved in a minimal amount of water and filtered through Celite. Tetrabutylstannane was removed by washing the aqueous solution with three ∼50-mL portions of hexanes. Pentane was layered onto the aqueous solution, and trimethyloxonium tetrafluoroborate was added to the stirred solution until the pH of the aqueous layer was <7. After 15 min the reaction mixture was poured into 300 mL of brine and extracted repeatedly with petroleum ether (35–60 °C) until the organic layers were nearly colorless. The combined organic layers were washed once with brine, dried over Na₂SO₄, filtered, concentrated, and flash chromatographed on silica gel by elution with hexanes. Collection of the deep red band, concentration, and final removal of the solvent by high vacuum at 0 °C yielded 6c (0.692 g, 1.84 mmol, 55%) as a dark red oil. Spectral data for 6c (R_f = 0.70, hexanes): ^{1}H NMR (CDCl₃) δ 0.14 (s, 6 H), 0.93 (s, 9 H), 4.78 (s, 3 H), 6.24 (d, 1 H, J = 18.4 Hz), 7.54 (d, 1 H, J = 18.4 Hz); ^{13}C NMR (CDCl₃) δ −6.4, 16.8, 26.4, 66.6, 132.2, 155.3, 216.6, 224.1, 338.0; IR (neat film) 2060 s, 1985 sh, 1928 vs,

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1249 m cm^{-1}; mass spectrum m/z (relative intensity) 376 M$^+$ (10), 348 (10), 320 (5), 292 (10), 264 (30), 236 (50), 180 (100).

Reactions of Carbene Complex 6c with Alkynes Followed by an Oxidative Workup. Diphenylacetylene. A solution of carbene complex **6c** (0.2030 g, 0.540 mmol) and diphenylacetylene (0.144 g, 0.809 mmol) in 11 mL of THF was deoxygenated by the freeze-thaw method (−196 to 25 °C, three cycles) in a pear-shaped single-necked flask fitted with a threaded high-vacuum Teflon stopcock. The stopcock was closed at 25 °C and 1 atm of argon and then the flask was heated at 65 °C for 44 h. After being cooled to rt, the volatiles were removed *in vacuo*. The residue was dissolved in 15 mL of ether and stirred vigorously for 30 min with a solution of ceric ammonium nitrate (2.30 g, 4.20 mmol) in 10 mL of water. The aqueous layer was extracted once with ether. The combined ether layers were dried with brine and anhyd MgSO$_4$. Concentration and chromatography on silica gel (5–10% EtOAc/hexanes) gave quinone **22** (0.0699 g, 0.187 mmol, 35%) and the known quinone **27**[9] (0.0241 g, 0.093 mmol, 17%). Spectral data for 2,3-diphenyl-5-(*tert*-butyldimethylsilyl)-1,4-benzoquinone (**27**): yellow-orange solid [MeOH], mp = 122–3 °C, R_f = 0.65, 1:1:10; ^{1}H NMR (CDCl$_3$) δ 0.33 (s, 6 H), 1.02 (s, 9 H), 7.33–7.40 (m, 10 H), 7.48 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ −5.8, 17.1, 26.4, 128.40, 128.43, 129.12, 129.14, 130.0 (2 C), 130.1 (2 carbons), 142.6, 147.6 (vinyl CH), 149.8, 152.2, 190.2, 192.2; IR (neat film) 1690 s, 1351 m, 1123 m, 830 m, 691 m cm^{-1}; mass spectrum m/z (relative intensity) 359 M$^+$ − CH$_3$ (20), 317 (M − t-Bu, 100), 285 (10), 245 (10), 215 (30), 178 (5), 159 (10); calcd for C$_{23}$H$_{23}$O$_2$Si (M − CH$_3$) m/z 359.1467, found 359.1464.

Phenylacetylene. The reaction of carbene complex **6c** (0.1965 g, 0.522 mmol) and phenylacetylene (0.090 mL, 0.78 mmol) in 10 mL of THF was carried out at 65 °C for 17 h and gave the known quinone **28**[17] (0.0521 g, 0.283 mmol, 54%). A less-polar yellow band (8.5 mg) containing several coeluting compounds was taken from the chromatography column and was found to have a weak IR stretch at 1690 cm^{-1} and thus could have contained 2-phenyl-6-(*tert*-butyldimethylsilyl)-1,4-benzoquinone (**23**) (~5% yield if fraction was pure).

1-Pentyne. The reaction of carbene complex **6c** (0.2085 g, 0.554 mmol) and 1-pentyne (0.083 mL, 0.83 mmol) in 10 mL of THF was carried out at 65 °C for 22 h. After the workup described above, the crude residue was loaded onto a silica gel column and elution with 10% EtOAc/hexanes did not yield any fractions containing significant (>5%) amounts of any quinone product.

3-Hexyne. The reaction of carbene complex **6c** (0.2005 g, 0.554 mmol) and 3-hexyne (0.091 mL, 0.80 mmol) in 10 mL of THF was carried out at 65 °C for 20 h. After the workup described above, the crude residue was loaded onto a silica gel column and elution with 5% EtOAc/hexanes gave a yellow band containing several compounds of which one could have been 2,3-diethyl-6-(*tert*-butyldimethylsilyl)-1,4-benzoquinone (**24**) (0.0077 g, 0.031 mol, <6%, IR 1691 cm^{-1}, ^{1}H NMR reveals the presence of TBS and ethyl groups and a vinyl singlet). No other quinone products could be identified.

Reactions of Carbene Complex 6a with Alkynes Followed by an Oxidative Workup. 1-Pentyne. Freshly prepared carbene complex **6a**[16] (0.244 g, 0.932 mmol) was introduced as a concentrated hexane solution into a tared single-necked flask modified with a threaded high-vacuum Teflon stopcock. The hexane was then removed under vacuum at −20 °C (0.4 mm) leaving a deep red solid. The flask was backfilled with argon and weighed. Anhydrous dichloromethane (10 mL) and 1-pentyne (0.18 mL, 1.86 mmol) were added to the reaction vessel. The reaction mixture was deoxygenated by the freeze-thaw method (−196 to 25 °C, three cycles), the stopcock was closed at 25 °C and 1 atm of argon, and then the flask was heated at 50 °C for 13 h. After cooling, the volatiles were removed *in vacuo* and the dark red residue was taken into 20 mL of chloroform and stirred in air for 30 min. Concentration and chromatography on silica gel (10% EtOAc/hexanes) gave a red-orange band (R_f = 0.4–0.5, 10% EtOAc/hexanes) which consisted of several red-orange compounds by TLC and was presumed to be a mixture of alkyne oligomers. Slightly impure phenol **9b** (20.3 mg, 0.122 mmol, <13%) was obtained after further elution. Spectral data for

3-*n*-propyl-4-hydroxyanisole (**9b**): amber oil, R_f = 0.17, 10% EtOAc/hexanes; ^{1}H NMR (CDCl$_3$) δ 1.00 (t, 3 H, J = 7.3 Hz), 1.66 (sextet, 2 H, J = 7.4 Hz), 2.57 (t, 2 H, J = 7.5 Hz), 3.76 (s, 3 H), 4.50 (br s, 1 H), 6.61 (dd, 1 H, J = 8.3, 2.3 Hz), 6.67–6.70 (m, 2 H); IR (neat film) 3418 br m, 1691 m, 1507 m, 1430 m, 1201 m cm^{-1}; mass spectrum m/z (relative intensity) 166 M$^+$ (100), 151 (25), 137 (100), 123 (35), 109 (65), 94 (35); calcd for C$_{10}$H$_{14}$O$_2$, m/z 166.0994, found 166.0996.

3-Hexyne. Analogously to the reaction of complex **6a** with 1-pentyne, a solution of carbene complex **6a** (0.207 g, 0.790 mmol) and 3-hexyne (0.18 mL, 1.58 mmol) in 16 mL of dichloromethane was heated at 50 °C for 13 h. Isolated from the crude reaction mixture on silica gel was a red-orange band (R_f = 0.4) which was not characterized and impure phenol **9a** (0.0144 g, 0.080 mmol, <10%). Spectral data for 2,3-diethyl-4-hydroxyanisole (**9a**): amber oil, R_f = 0.18, 10% EtOAc/hexanes; ^{1}H NMR (CDCl$_3$) δ 1.13 (t, 3 H, J = 7.4 Hz), 1.18 (t, 3 H, J = 7.5 Hz), 2.668 (q, 2 H, J = 7.4 Hz), 2.673 (q, 2 H, J = 7.5 Hz), 3.77 (s, 3 H), 4.33 (br s, 1 H), 6.58 (s, 2 H); IR (neat film) 3420 br m, 1695 m, 1457 m, 1248 m, 1117 m cm^{-1}; mass spectrum m/z (relative intensity) 180 M$^+$ (100), 165 (75), 150 (10), 137 (10), 121 (5), 107 (10), 91 (15); calcd for C$_{11}$H$_{16}$O$_2$, m/z 180.1150, found 180.1159.

General Procedure for Benzannulation of 6c with Alkynes without an Oxidative Workup. Complex **6c** (1.0 equiv), alkyne (1.2–1.5 equiv) and a small stir bar are placed in a single-necked, pear-shaped flask that has been modified by replacement of the 14/20 joint with a 10-mm threaded high vacuum stopcock (Kontes no. 826610). Anhydrous dichloromethane is added to make the reaction mixture 0.05 M in carbene complex. The reaction mixture is deoxygenated by the freeze-pump-thaw method (three cycles, −196 to 25 °C). After backfilling with argon, the flask is sealed at room temperature and under 1 atm of argon and heated at 65–70 °C until **6c** is consumed, generally 15–18 h. Workup consists of simply cooling the reaction mixture to rt, removal of volatiles by rotary evaporation, and flash column chromatography on silica gel. The stable arene–Cr(CO)$_3$ complexes are all bright yellow and easily identified on a TLC plate, since they are oxidized nearly on contact at rt by ethanolic phosphomolybdic acid.

With 3-Hexyne To Give 19a. A solution of carbene complex **6c** (0.085 g, 0.226 mmol) and 3-hexyne (0.038 mL, 0.34 mmol) in 4.5 mL of CH$_2$Cl$_2$ was heated at 65 °C for 15 h to give after purification on silica gel (1:1:16) **19a** (0.0416 g, 0.097 mmol, 43%) as a yellow-orange solid. Spectral data for η^6-[2,3-diethyl-4-[(*tert*-butyldimethylsilyl)oxy[anisole] chromium tricarbonyl (**19a**): yellow-orange needles [pentane], mp = 119.0–120.0 °C, R_f = 0.39, 1:1:10; ^{1}H NMR (CDCl$_3$) δ 0.31 (s, 3 H), 0.37 (s, 3 H), 0.99 (s, 9 H), 1.22 (t, 3 H, J = 7.8 Hz), 1.24 (t, 3 H, J = 7.8 Hz), 2.45–2.51 (m, 2 H), 2.77–2.81 (m, 2 H), 3.63 (s, 3 H), 5.02 (s, 2 H); ^{13}C NMR (CDCl$_3$) δ −4.6, −4.4, 15.5, 15.6, 18.0, 20.8, 21.0, 25.4, 56.3, 73.9, 80.1, 106.5, 107.6, 131.1, 135.3, 234.8; IR (neat film) 1954 s, 1869 s, 1431 w, 1255 m, 832 m cm^{-1}; mass spectrum m/z (relative intensity) 430 M$^+$ (20), 374 (15), 346 (100), 290 (10), 237 (13), 126 (25); calcd for C$_{20}$H$_{30}$CrO$_5$Si m/z 430.1268, found 430.1297.

With Diphenylacetylene To Give 19b. A solution of carbene complex **6c** (0.1230 g, 0.3268 mmol) and diphenylacetylene (0.087 g, 0.49 mmol) in 6.5 mL of CH$_2$Cl$_2$ was heated at 65 °C for 24 h to give after purification on silica gel (1:1:16) **19b** (0.045 g, 0.0855 mmol, 26%) as a yellow solid. A faster moving red band was also collected. Rechromatographing this fraction (gradient elution: hexanes to 1:1:32) gave two fractions. The first (12.3 mg, red-purple oil) had no carbonyl stretches; the second (orange-brown oil, 9.0 mg) had a very strong stretch at 1691 cm^{-1}. The ^{1}H NMR spectrum revealed that this second fraction was not a single compound, so the upper limit of cyclopentadienone product (FW 378.5) would be <8%. The fractions from the column were not screened for the phenol **7**. Spectral data for η^6-[2,3-diphenyl-4-[(*tert*-butyldimethylsilyl)oxy]anisole]chromium tricarbonyl (**19b**): yellow needles [ether/pentane], mp = 146.0–148.5 °C, R_f = 0.56, 1:1:4; ^{H} NMR (CDCl$_3$) δ 0.09 (s, 3 H), 0.69 (s, 9 H), 3.60 (s, 3 H), 5.25 (d, 1 H, J = 7.2 Hz), 5.29 (d, 1 H, J = 7.1 Hz), 7.08–7.15 (m, 7 H), 7.22–7.31 (m, 3 H); ^{13}C NMR (CDCl$_3$) δ −5.14–5.18, 17.3, 24.6, 56.6, 76.2, 79.7, 107.6, 109.5, 126.9, 127.0, 127.2, 129.9, 131.80, 131.87, 131.91, 132.2, 132.5, 133.8, 233.8; IR (neat film) 1956 s, 1870 s, 1521 m. 1453 m, 1421 m, 1300 m, 1238 m, 1016 m. 946 m, 862 m cm^{-1}; mass spectrum m/z (relative

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intensity) 526 M$^+$ (10), 442 (100), 427 (8), 390 (20), 333 (65), 318 (20), 303 (15), 287 (5), 126 (7), 73 (10); calcd for C$_{28}$H$_{30}$CrO$_5$Si m/z 526.1268, found 526.1293.

With Phenylacetylene To Give 19c. A solution of carbene complex **6c** (0.1808 g, 0.4805 mmol) and freshly distilled phenylacetylene (0.079 mL, 0.72 mmol) in 9.5 mL of CH$_2$Cl$_2$ was heated at 65 °C for 18.5 h to give after purification on silica gel (1:1:16) 19c (0.0955 g, 0.212 mmol, 44%) as a yellow solid. Spectral data for η^6-[3-phenyl-4-[(*tert*-butyldimethylsilyl)oxy]anisole]chromium tricarbonyl (19c): yellow needles [ether/pentane], mp = 117.0–118.0 °C, R_f = 0.41, 1:1:4; ^{1}H NMR (CDCl$_3$) δ –0.03 (s, 3 H), 0.19 (s, 3 H), 0.79 (s, 9 H), 3.66 (s, 3 H), 5.20 (d, 1 H, J = 7.0 Hz), 5.30 (dd, 1 H, J = 7.0, 2.3 Hz), 5.50 (d, 1 H, J = 2.1 Hz), 7.33–7.38 (m, 3 H), 7.54 (d, 2 H, J = 7.0 Hz); ^{13}C NMR (CDCl$_3$) δ –4.8, –4.6, 17.9, 25.2, 56.4, 80.0, 82.8, 83.0, 104.3, 127.9, 128.5, 130.7, 131.5, 134.4, 135.8, 233.9; IR (neat film) 1959 s, 1878 s, 1471 m, 1442 w, 1250 m, 1216 m, 909 m, 842 m cm^{-1}; mass spectrum m/z (relative intensity) 450 M$^+$ (20), 366 (100), 350 (15), 310 (20), 294 (5), 279 (5), 257 (20), 241 (10). Anal. Calcd for C$_{22}$H$_{26}$CrO$_5$-Si: C, 58.65; H, 5.82. Found: C, 59.25; H, 5.79.

With 1-Pentyne To Give 19d. A solution of carbene complex **6c** (0.1095 g, 0.291 mmol) and 1-pentyne (0.045 mL, 0.436 mmol) in 6 mL of THF was heated at 70 °C for 11 h to give after purification on silica gel (1:1:10) 19d (0.0867 g, 0.208 mmol, 72%) as a yellow semisolid. Spectral data for η^6-[3-*n*-propyl-4-[(*tert*-butyldimethylsilyl)oxy]anisole]chromium tricarbonyl (19d): yellow prisms [pentane], mp = 60.5–62.5 °C, R_f = 0.43, 1:1:10; ^{1}H NMR (CDCl$_3$) δ 0.31 (s, 3 H), 0.36 (s, 3 H), 0.98 (s, 9 H), 1.03 (t, 3 H, J = 7.0 Hz), 1.55–1.62 (m, 1 H), 1.66–1.71 (m, 1 H), 2.14–2.20 (m, 1 H), 2.75–2.82 (m, 1 H), 3.62 (s, 3 H), 4.98 (dd, 1 H, J = 7.0, 2.4 Hz), 5.16 (d, 1 H, J = 6.9 Hz), 5.22 (d, 1 H, J = 2.5 Hz); ^{13}C NMR (CDCl$_3$) δ –4.7, –4.4, 14.0, 18.0, 23.7, 25.4, 32.6, 55.9, 75.7, 82.4, 83.4, 105.8, 130.1, 137.7, 234.4; IR (neat film) 1957 s, 1871 s, 1472 m, 671 m cm^{-1}; mass spectrum m/z (relative intensity) 416 M$^+$ (30), 360 (15), 332 (100), 280 (25), 247 (10), 223 (25), 193 (20). Anal. Calcd for C$_{19}$H$_{28}$CrO$_5$Si: C, 54.79; H, 6.78. Found: C, 54.47; H, 6.82.

With 1-Ethynyl-1-cyclohexene To Give 19e. A solution of carbene complex **6c** (0.0818 g, 0.2174 mmol) and ethynyl-1-cyclohexene (0.040 mL, 0.33 mmol) in 4.5 mL of CH$_2$Cl$_2$ was heated at 65 °C for 19 h to give after purification on silica gel (1:1:16) 19e (0.0394 g, 0.0867 mmol, 40%) as a yellow solid. Spectral data for η^6-[3-cyclohexenyl-4-[(*tert*-butyldimethylsilyl)oxy]anisole]chromium tricarbonyl (19e): yellow needles [ether/pentane], mp = 92.5–93.5 °C, R_f = 0.40, 1:1:10; NMR (CDCl$_3$) δ 0.24 (s, 3 H), 0.30 (s, 3 H), 0.96 (s, 9 H), 1.65 (pentet, 2 H, J = 5.7 Hz), 1.71–1.76 (m 2 H), 2.15–2.20 (m, 2 H), 2.24–2.29 (m, 1 H), 2.40–2.45 (m, 1 H), 3.61 (s, 3 H), 4.99 (d, 1 H, J = 7.1 Hz), 5.27 (d, 1 H, J = 7.0, 2.3 Hz), 5.38 (d, 1 H, J = 2.2 Hz), 5.98 (brs, 1 H); ^{13}C NMR (CDCl$_3$) δ –4.36, –4.30, 18.1, 21.9, 23.0, 25.4, 25.7, 30.3, 56.6, 80.8, 81.5, 84.3, 107.1, 130.9, 132.6, 132.7, 134.4, 234.4; IR (neat film) 1957 s, 1867 s, 1467 m, 1276 sh, 1259 m, 904 m, 843 m, 670 m cm^{-1}; mass spectrum m/z (relative intensity) 454 M$^+$ (20), 370 (100), 350 (10), 310 (20), 293 (5), 261 (15), 251 (8), 193 (10), 126 (25). Anal. Calcd for C$_{22}$H$_{30}$CrO$_5$Si: C, 58.13; H, 6.65. Found: C, 58.58; H, 6.13.

With 3-Methyl-1-butyne To Give 19f. A solution of complex **6c** (0.1907 g, 0.5066 mmol) and 3-methyl-1-butyne (0.104 mL, 1.01 mmol) in 5 mL of CH$_2$Cl$_2$ was heated at 65 °C for 20 h to give after purification on silica gel (1:1:16) 19f (0.143 g, 0.342 mmol, 68%) as a yellow solid. Spectral data for η^6-[3-isopropyl-4-[(*tert*-butyldimethylsilyl)oxy]anisole]chromium tricarbonyl (19f): yellow prisms [ether/pentane], mp = 119.0–120.0 °C, R_f = 0.58, 1:1:4; ^{1}H NMR (CDCl$_3$) δ 0.32 (s, 3 H), 0.37 (s, 3 H), 0.99 (s, 9 H), 1.22 (d, 3 H, J = 6.8 Hz), 1.28 (d, 3 H, J = 6.9 Hz), 3.16 (septet, 1 H, J = 6.9 Hz), 3.62 (s, 3 H), 5.02 (dd, 1 H, J = 7.0, 2.4 Hz), 5.05 (d, 1 H, J = 7.0 Hz), 5.32 (s, 1 H, J = 2.4 Hz); ^{13}C NMR (CDCl$_3$) δ –4.6, –4.3, 18.1, 20.2, 24.3, 25.4, 27.1, 56.1, 75.5, 80.6, 81.5, 112.2, 130.8, 136.8, 234.3; IR (neat film) 1950 s, 1871 vs, 1470 m, 1216 m, 1026 m, 891 m, 841 m, 672 m cm^{-1}; mass spectrum m/z (relative intensity) 416 M$^+$ (20), 360 (15), 332 (100), 276 (5), 260 (5). Anal. Calcd for C$_{19}$H$_{28}$CrO$_5$Si: C, 54.79; H, 6.78. Found: C, 55.01; H. 6.34.

With 6-Heptynenitrile To Give 19g. A solution of carbene complex **6c** (0.3283 g, 0.872 mmol) and 6-heptynenitrile (0.190 g, 1.77 mmol) in 18 mL of CH$_2$Cl$_2$ was heated at 65 °C for 11 h.

The temperature of the oil bath was then raised to 73 °C and the reaction mixture was heated until it was clear and yellow (4 h). Concentration and chromatography on silica gel (1:1:6) afforded 19g (0.269 g, 0.590 mmol, 68%) as a yellow solid. Spectral data for η^6-[3-(4'-cyano-*n*-butyl)-4-[(*tert*-butyldimethylsilyl)oxy]anisole]chromium tricarbonyl (19g): yellow prisms [ether/pentane], mp = 83.5–85.0 °C, R_f = 0.24, 1:1:4; ^{1}H NMR (CDCl$_3$) δ 0.32 (s, 3 H), 0.36 (s, 3 H), 0.98 (s, 9 H), 1.70–1.83 (m, 4 H), 2.32–2.38 (m, 1 H), 2.41 (t, 2 H, J = 6.4 Hz), 2.80–2.88 (m, 1 H), 3.63 (s, 3 H), 5.00 (dd, 1 H, J = 2.6, 7.0 Hz), 5.16 (d, 1 H, J = 7.0 Hz), 5.20 (d, 1 H, J = 2.6 Hz); ^{13}C NMR (CDCl$_3$) δ –4.8, –4.5, 16.9, 17.9, 25.1, 25.3, 29.2, 29.8, 55.9, 75.8, 82.1, 83.2, 104.3, 119.2, 130.0, 137.6, 234.1; IR (neat film) 2250 vw, 1955 vs, 1866 vs, 1472 m, 1258 m cm^{-1}; mass spectrum m/z (relative intensity) 455 M$^+$ (5), 371 (95), 356 (5), 314 (15), 262 (100). Anal. Calcd for C$_{21}$-H$_{29}$CrNO$_5$Si: C, 55.37; H, 6.42; N, 3.07. Found: C, 55.50; H, 6.35; N, 2.89.

With 2-Iodo-1-propargylbenzene to Give 19h. A solution of carbene complex **6c** (0.2570 g, 0.6829 mmol) and 2-iodo-1-propargylbenzene[15] (0.260 g, 1.07 mmol) in 13.5 mL of CH$_2$Cl$_2$ was heated at 65 °C for 20 h to give after purification on silica gel (1:1:16) 19h (0.2296 g, 0.389 mmol, 57%) as a yellow solid. Spectral data for η^6-[3-(2'-iodobenzyl)-4-[(*tert*-butyldimethylsilyl)oxy]anisole]chromium tricarbonyl (19h): yellow solid, mp = 104.0–106.0 °C, R_f = 0.36, 1:1:4; ^{1}H NMR (CDCl$_3$) δ 0.28 (s, 3 H), 0.38 (s, 3 H), 0.92 (s, 9 H), 3.55 (s, 3 H), 3.82 (d, 1 H, J = 16.7 Hz), 4.15 (d, 1 H, J = 16.5 Hz), 4.96 (d, 1 H, J = 1.0 Hz), 5.06 (dd, 1 H, J = 6.4, 1.0 Hz), 5.20 (d, 1 H, J = 7.0 Hz), 6.96 (t, 1 H, J = 7.5 Hz), 7.27 (d, 1 H, J = 7.4 Hz), 7.32 (t, 1 H, J = 7.4 Hz), 7.86 (d, 1 H, J = 7.8 Hz); ^{13}C NMR (CDCl$_3$) δ –4.5, –4.3, 18.0, 25.4, 40.9, 56.1, 76.7, 82.4, 83.3, 101.3, 102.7, 128.6, 128.8, 130.1, 136.9, 139.6, 140.7, 234.1; IR (neat film) 1958 s, 1871 s, 1465 m, 1273 m, 1257 m cm^{-1}; mass spectrum m/z (relative intensity) 590 M$^+$ (25), 506 (100), 491 (5), 450 (30), 378 (35), 327 (20), 307 (5), 270 (20), 255 (10), 239 (10). Anal. Calcd for C$_{23}$H$_{27}$CrO$_5$ISi: C, 46.79; H, 4.61. Found: C, 47.07; H, 4.12.

With Propiolaldehyde Diethyl Acetal To Give 19i. A solution of carbene complex **6c** (0.2170 g, 0.5758 mmol) and propiolaldehyde diethyl acetal (0.148 g, 1.15 mmol) in 10 mL of CH$_2$Cl$_2$ was heated at 65 °C for 20 h to give after purification on silica gel (1:1:16) 19i (0.146 g, 0.306 mmol, 53%) as a viscous yellow oil. Spectral data for η^6-[3-(diethoxymethyl)-4-[(*tert*-butyldimethylsilyl)oxy]anisole]chromium tricarbonyl (19i): fine yellow needles [methanol], mp = 64.0–65.0 °C, R_f = 0.40, 1:1:4; ^{1}H NMR (CDCl$_3$) δ 0.30 (s, 3 H), 0.36 (s, 3 H), 1.00 (s, 9 H), 1.21 (t, 3 H, J = 5.9 Hz), 1.36 (t, 3 H, J = 5.4 Hz), 3.55–3.71 (m, 5 H), 3.85–3.90 (br s, 2 H), 5.01 (d, 1 H, J = 6.8 Hz), 5.21 (br s, 1 H), 5.47 (s, 1 H), 5.81 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ –4.5, –4.4, 15.10, 15.13, 18.1, 25.3, 56.4, 61.1, 65.9, 80.1, 80.2, 81.2, 97.6, 99.1, 132.1, 134.9, 233.9; IR (neat film) 1961 s, 1878 s, 1472 m, 1144 m, 1135 m, 1118 m cm^{-1}; mass spectrum m/z (relative intensity) 476 M$^+$ (15), 431 (15), 392 (60), 363 (10), 348 (25), 317 (30), 304 (100), 291 (10), 263 (10), 248 (25). Anal. Calcd for C$_{21}$H$_{32}$CrO$_7$Si: C, 52.93; H, 6.77. Found: C, 52.81; H, 7.10.

One-Pot Conversion of Carbene Complex 6c to Spirocyclodecadienone 31 via Sequential Benzannulation/Nucleophilic Addition. Carbene complex **6c** (212.5 mg, 0.565 mmol), 1-cyano-5-hexyne (66.6 mg, 0.621 mmol), and a small stir bar are placed in a 100-mL single-necked flask modified by replacement of the 14/20 joint with a 10-mm threaded high vacuum Teflon stopcock (Kontes no. 826610) under argon. The contents are dissolved in 11.3 mL of anhydrous dichloromethane, deoxygenated by the freeze-thaw method (–196 to 25 °C, three cycles, and sealed under 1 atm of argon at 25 °C. After heating with stirring at 65 °C for 20 h, the reaction flask was cooled to 0 °C and opened to high vacuum to strip off the volatiles, followed by 2 h at rt at high vacuum. The residue was taken into 30 mL of THF, deoxygenated, and backfilled with argon. Under an argon stream, the threaded stopcock was replaced with a rubber septum. The flask was then cooled to –78 °C. A deoxygenated THF solution of LDA (0.847 mmol) was cooled to –78 °C and added via cannula. The reaction mixture was stirred at this temperature for 1.5 h. A –78 °C, a deoxygenated THF solution of iodine (1.15 g, 4.52 mmol) was added to the reaction mixture. After stirring the resulting solution for 1 h at –78 °C, the cold bath was removed. After 2.5 h of stirring at rt, the mixture was

poured into diethyl ether/10% $Na_2S_2O_3$ (aq). The layers were separated, and the aqueous layer was extracted once with ether. The combined organic layers were dried with brine, followed by anhyd $MgSO_4$, filtered, and concentrated. Chromatography on silica gel with a 1:1:6 mixture of ether:methylene chloride:hexanes yielded **31** as separable mixture of diastereomers (29.8 mg, 0.147 mmol, 26.0%; 23.4 mg, 0.115 mmol, 20.4%). Spectral data for **31** (major diastereomer): colorless solid, mp = 88.0–89.5 °C; R_f = 0.19, 1:1:4; ¹H NMR ($CDCl_3$) δ 1.83 (quintet, 1 H, J = 6.3 Hz), 1.94–2.00 (m, 2 H), 2.04–2.16 (m, 2 H), 2.39–2.46 (m, 1 H), 3.31 (t, 1 H, J = 9.1 Hz), 3.66 (s, 3 H), 5.27 (d, 1 H, J = 2.5 Hz), 6.09 (d, 1 H, J = 10.1 Hz), 6.90 (dd, 1 H, J = 10.1, 2.7 Hz); ¹³C NMR ($CDCl_3$) δ 23.9, 30.8, 39.6, 40.8, 55.1, 57.9, 105.9, 119.7, 126.6, 142.3, 150.9, 201.7, IR (neat film) 2240 ww, 1670 m, 1641 s, 1582 m, 1453 m, 1408 m, 1250 m, 824 m cm⁻¹; mass spectrum m/z (relative intensity) 203 M⁺ (70), 188 (15), 175 (25), 171 (10), 161 (30), 147 (90), 137 (100), 133 (50), 122 (40), 117 (40), 105 (50), 91 (65), 77 (90); calcd for $C_{12}H_{13}NO_2$ 203.0946, found 203.0915. Spectral data for **31** (minor diastereomer): amber oil, R_f = 0.14, 1:1:4; ¹H NMR ($CDCl_3$) δ 1.74–1.78 (m, 1 H), 1.83–1.91 (m, 1 H), 2.12–2.19 (m, 2 H), 2.21–2.29 (m, 1 H), 2.38–2.46 (m, 1 H), 2.76 (t, 1 H, J = 9.5 Hz), 3.63 (s, 3 H), 4.93 (d, 1 H, J = 2.6 Hz), 6.04 (d, 1 H, J = 10.1 Hz), 6.83 (dd, 1 H, J = 10.2, 2.8 Hz); ¹³C NMR ($CDCl_3$) δ 23.4, 30.1, 38.5, 40.5, 55.0, 58.5, 107.6, 119.5, 126.7, 141.5, 151.3, 202.0; IR (neat film) 2240 w, 1669 w, 1642 s, 1408 m, 1242 m cm⁻¹; mass spectrum m/z (relative intensity) 203 M⁺ (45), 188 (10), 175 (15), 171 (5), 161 (25), 147 (25), 137 (90), 121 (25), 107 (40), 91 (45), 77 (100); calcd for $C_{12}H_{13}NO_2$ 203.0946, found 203.0948.

One-Pot Conversion of Carbene Complex 6c to Tetrahydronaphthalene 32 via Sequential Benzannulation/Nucleophilic Addition. Carbene complex **6c** (155.5 mg, 0.414 mmol) and 1-cyano-5-hexyne (71 mg, 0.663 mmol) were reacted according to the procedure described above for the formation of **31** at 65 °C for 21 h. The procedure for nucleophilic addition was also the same as above except that the annulation residue was taken into only 8.5 mL of THF (~0.05 M) and that 10 min after

the addition of LDA to the reaction mixture, the dry ice/acetone bath was replaced with an ice–water bath. After 1 h at 0 °C, the iodine solution (0.79 g, 3.11 mmol in 5 mL of THF) was added at 0 °C and stirred at rt for 3 h prior to workup as above. Chromatography with 1:1:10 yielded **32** (49.7 mg, 0.157 mmol, 37.8%). Spectral data for 1-methoxy-4-[(*tert*-butyldimethylsilyl)oxy]-8-cyanotetralin (**32**): colorless solid, mp = 72.0–74.5 °C; R_f = 0.52, 1:1:4; ¹H NMR ($CDCl_3$) δ 0.22 (s, 3 H), 0.23 (s, 3 H), 1.02 (s, 9 H), 1.80–1.84 (m, 1 H), 1.88–1.94 (m, 1 H), 1.95–2.04 (m, 1 H), 2.25 (br d, 1 H, J = 13.0 Hz), 2.47 (ddd, 1 H, J = 17.7, 11.4, 5.7 Hz), 2.86 (br d, 1 H, J = 17.4 Hz), 3.84 (s, 3 H), 4.06 (br s, 1 H), 6.59 (d, 1 H, J = 8.7 Hz), 6.68 (d, 1 H, J = 8.7 Hz); ¹³C NMR ($CDCl_3$) δ –4.2, 18.2, 19.1, 23.6, 25.0, 25.7, 26.1, 55.7, 107.6, 117.1, 119.9, 121.7, 129.3, 147.2, 151.3; IR (neat film) 2237 w, 1594 w, 1476 s, 1252 s, 1090 m, 905 m, 861 m cm⁻¹; mass spectrum m/z (relative intensity) 317 M⁺ (65), 261 (20), 233 (100), 218 (10), 159 (15), 144 (5), 129 (5), 115 (10), calcd for $C_{18}H_{27}NO_2Si$ 317.1811, found 317.1828.

Supplementary Material Available: ¹H NMR spectral data for compounds **19a, 19b, 14, 27, 31** (major and minor), and **32** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.