Phenol Formation from the Reactions of Amino-Stabilized Alkenyl Fischer Carbene Complexes

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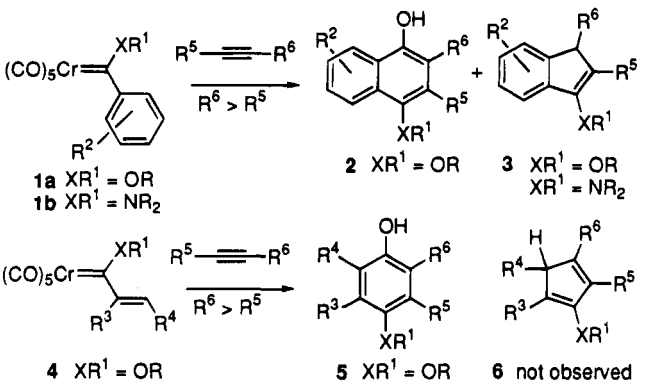
The first examples of phenol formation from the reactions of amino-stabilized α,β-unsaturated Fischer carbene complexes with alkynes are reported. A series of four dimethylamino complexes [$(CO)_5Cr{=}C(NMe_2)R$; **19**, R = cyclohexenyl; **26**, R = *trans*-propenyl; **27**, R = *trans*-styryl; **30**, R = isopropenyl] were examined with both internal and external alkynes. Their reactions with internal alkynes typically produced low yields of complex mixtures of products and were not synthetically useful. In contrast, their reactions with terminal alkynes were remarkably different giving good yields of 4-(dimethylamino)phenols, and in the presence of a trapping agent, good yields of the arene chromium tricarbonyl complexes of the protected 4-(dimethylamino)phenols. The selectivity for phenol formation was found to be greatest for reactions performed in noncoordinating solvents and at higher concentrations. In contrast, and as expected, the reaction of the aryl complex **45** [$(CO)_5Cr{=}C(NMe_2)Ph$] with 1-pentyne did not produce any six-membered ring product in DMF, THF, or benzene. An interesting solvent dependence was observed for this reaction where lactam **49** was the exclusive product in benzene and the indanone **46** was the exclusive product in DMF.

A paradigm for the reactions of carbene complexes with alkynes that has held with observations over the last eight years is that amino-stabilized complexes will react to give five-membered ring annulation products (indenes),[2,3] and alkoxy-stabilized complexes will react to give six-membered ring products (naphthols).[4,5] The first reaction of a carbene complex with an alkyne was reported 20 years ago[6] for an alkoxy–aryl carbene complex to give a naphthol product, and since that time this reaction has been extensively investigated because of the synthetic value of the phenol products and also because of its mechanistic complexity.[7] It has only been more recently that the reactions of amino complexes with alkynes have been investigated, and under the proper conditions this reaction provides a very efficient entry to indanones via the hydrolysis of the aminoindenes that are the primary products of the reaction.[2,3,8]

Scheme 1



The reactions of aryl-(alkoxy) carbene complexes can follow any of a number of reaction pathways, the partition between which can be influenced by the reaction conditions and functional group variations, with the end result often a formidable product distribution. Over 15 structurally different organic products have been reported from the reactions of aryl-(alkoxy) carbene complexes with alkynes.[4,5] The situation is not as complicated for alkenyl-(alkoxy) carbene complexes when phenol products are produced with high fidelity and with few side products.[4,5,13] Only in one case has a five-membered ring product been observed.[4] What has not yet been determined is whether the annulations of alkenyl-(amino) carbene complexes with alkynes will give five-membered ring products as do aryl-(amino) carbene complexes.[10] The

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(4) For citations to the literature on annulation of alkoxy complexes, see: Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P.; Mitchell, J.; Clardy, J. *Organometallics* **1994**, *13*, 102.

(5) 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) Dötz, K. H. In *Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field*; Dieck, H, de Meijere, A., Eds.; Springer: Berlin, 1988. (e) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5.

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

(7) For synthetic applications of benzannulations of alkoxy complexes, see footnotes 4 and 5 in ref 4.

(8) These observations were foreshadowed by an early related reaction: Dötz, K. H.; Pruskil, I. *Chem. Ber.* **1978**, *111*, 2059.

(9) Dötz, K. H.; Dietz, R. *Chem. Ber.* **1978**, *111*, 2517.

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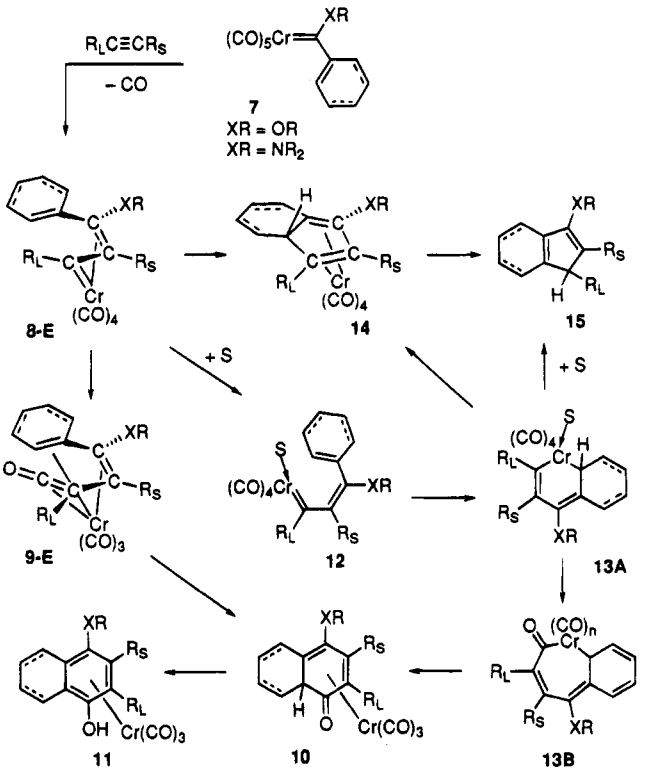
purpose of the present work is to provide the first study of the scope and product distribution from the reactions of a selected set of alkenyl-(amino) carbene complexes with alkynes.[3j-m]

The solvent is one of the many factors that affects the distribution of products from the reactions of carbene complexes with alkynes, especially between indene and phenol production.[3a,4,11,12] In some cases, each extreme in the distribution between five- and six-membered ring products from the reactions of aryl-(alkoxy) carbene complexes can be reached by varying the concentration, temperature and, most importantly, the polarity and/or coordinating ability of the solvent. With few exceptions, five-membered ring formation is fostered by the more polar solvents.[4,12] DMF and acetonitrile are known to strongly favor five-membered ring formation for the reactions of aryl-(alkoxy) carbene complexes.[3a,3b,11] In contrast, information about the effects of solvent on the annulations of aryl-(amino) carbene complexes is rare and most studies have been in DMF.[2,3] There are no studies of the effect of solvent on a given reaction, but indene products have been reported from the reactions of aryl-(amino) carbene complexes with internal alkynes in DMF, THF, and toluene.[2,3,17] The reactions with terminal alkynes have only been reported in DMF. Phenol products have never been reported from an intermolecular reaction of an amino carbene complex with an alkyne,[3j-m] but there is one report of phenol formation in an intramolecular reaction.[3i]

While the preference for indene over naphthol formation with amino-stabilized carbene complex is not clearly understood, it is likely played out in the set of intermediates that are pictured in Scheme 2.[14] The difference in product distribution between alkoxy and amino carbene complexes may lie in the solvent effect on the partitioning of the η^1,η^3-vinyl carbene complexed intermediate **8-E.** This is thought to be the first intermediate resulting from the loss of a carbon monoxide ligand from the carbene complex and the subsequent interaction with an alkyne.[15] The greater electron-donating ability of an amino versus an alkoxyl substituent XR in **8-E** would be expected to increase electron density at the metal center and increase the strength of the bonds to the carbon monoxide ligands. This would disfavor carbon monoxide insertion to give the vinyl ketene complex **9-E** relative to an electrocyclic ring closure of **8-E** to **14** and thus shift the distribution in favor of indene products. The source of the effect of the solvent on the partition between five- and six-membered ring annulation products is also far from understood; however, a possible explanation is that cyclization to the aryl (or alkenyl) substituent can be accelerated relative to carbon monoxide insertion by a two-electron donor.[14] It may be that this occurs by a

Scheme 2



solvent assisted displacement of the double-bond in intermediate **8-E** to give **12** which results in an increase in indene formation via intermediate **13**.[12] Alternatively, the solvent could play a role in facilitating reductiven elimination in **13** to give **15** relative to CO insertion to give **9-E**. It is also possible that the phenol product results from CO insertion into the metallacyclohexadiene intermediate **13A**. While some evidence has been presented to rule out this pathway in a specific system, there is no basis to rule out this pathway in the general sense.[12] While the mechanistic details of the reactions of carbene complexes with alkynes are far from sorted out, a consideration of the issues raised in Scheme 2 is useful for considering the effects of solvent and substituents on the reactions of carbene complexes with alkynes.

The annulations of arylamino carbene complexes have been most extensively studied with pyrrolidine and morpholine derived carbene complexes with the morpholino complexes giving the best yields of indene products.[2] Unfortuantely, we could not make the morpholino complex with the cyclohexenyl substituent on the carbene complex. Reaction of the cyclohexyl methoxy complex **17** with morpholine leads only to the formation of morpholine chromium pentacarbonyl in 50% yield. This type of cleavage has been seen with aryl[16] and alkyl[17] complexes but we have not yet attempted the alternate procedure that has been indicated to be useful for this problem.[17] The formation of the pyrrolidine carbene complex **21** was accompanied by some cleavage of the carbene ligand to give the pentacarbonyl amine complex **22**. As a result, we focused on the preparation and evaluation of the previously unknown dimethylamino carbene complexes **19**, **20**, **26**, **27**, and **30** since, in all

(10) (a) A β-aminovinyl carbene complex has been shown to give five-membered products: Duetsch, M.: Lackmann, R.; Stein, F.; de Meijere, A. *Synlett.* **1991**, 324. (b) A five-membered ring product has been observed with dimethylacetylene dicarboxylate: Barluenga, J.; Aznar, F.; Martin, A.; Garcia-Granda, S.; Perez-Carreno, E., *J. Am. Chem. Soc.* **1994**, *116*, 11191.

(11) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813.

(12) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293.

(13) (a) Chamblerin, S.; Wulff, W. D.; Bax, B. *Tetrahedron*, **1993**, *49*, 5531. (b) Chamberlin, S.; Wulff, W. D. *J. Org. Chem.* **1994**, *59*, 3047.

(14) For a discussion of the possible factors affecting five- versus six-membered ring formation, see refs 2 and 4 and citations therein.

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

(16) Fischer, E. O.; Heckl, B.; Werner, H. *J. Organomet. Chem.* **1971**, *28*, 359.

(17) Chelain, E.; Goumont, R.; Hamon, L.; Parlier, A.; Rudler, M.; Rudler, H.; Daran, J.-C.; Vaissermann, J. *J. Am. Chem. Soc.* **1992**, *114*, 8088.

Scheme 3

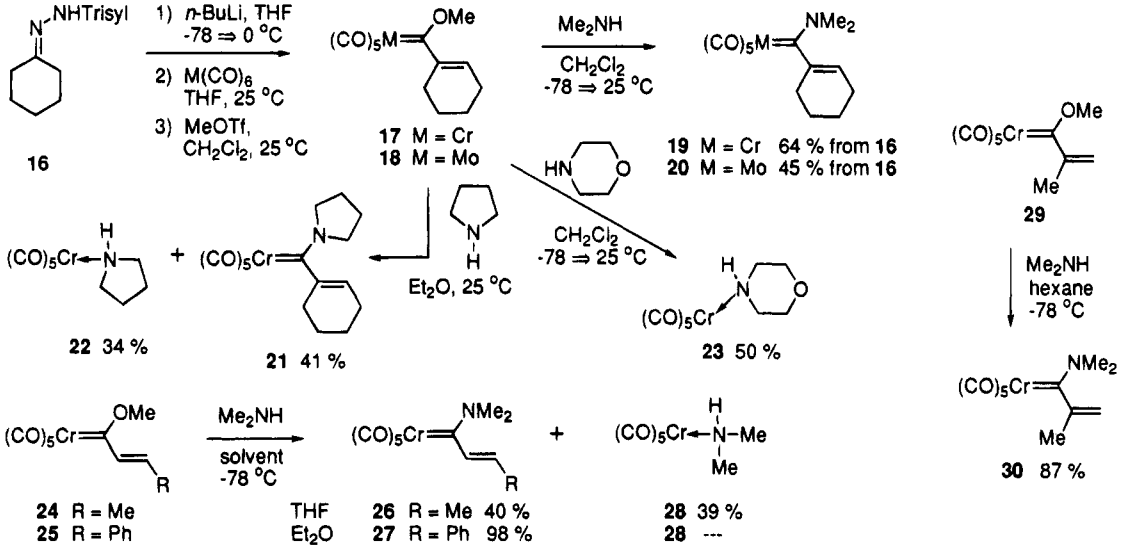
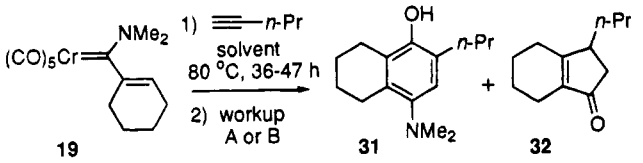


Table 1. Benzannulation of Complex 19 with 1-Pentyne[a]



entry	[19], M	solvent	workup[b] method	% yield 31[c]	% yield 32[c]
1	0.5	heptane	B	66	<2[d]
2	0.5	benzene	A	64	<1[d]
3	0.5	THF	A	57	12
4	0.005	THF	A	<22[d]	19[e]
5	0.5	CH_2Cl_2	B	18	<7[d]
6	0.5	CH_3CN[f]	A	<5[d]	13
7	0.5	DMF	A	25	13

[a] 2 equiv of alkyne added at $t = 0$ and 2 equiv alkyne added at $t = 18-24$ h. [b] Method A: 1 N HCl, THF/H_2O, 25 °C, 1 h. Method B: p-TsOH, THF/H_2O, 25 °C, 1 h. [c] Isolated yield unless otherwise specified. [d] Yield by ^1H NMR. [e] A 14 % yield of **32** and a 5 % yield of the nonconjugated cyclopentenone isomer of **32**. [f] An unidentified decomposition product of **19** was also observed.

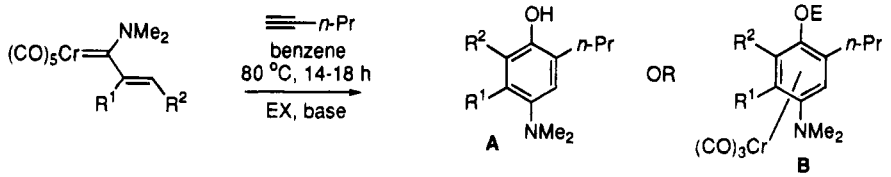
cases except the *trans*-propenyl complex **24**, the aminolysis with dimethylamine proceeds to give the desired amino carbene complex in high yield with no detectable formation of the pentacarbonyldimethylamine complex.

The original goal in pursuing the reaction of amino stabilized alkenyl carbene complexes with alkynes was to develop a new method for the synthesis of cyclopentenones (from **6** in Scheme 1), and thus the results from the reaction of complex **19** with 1-pentyne came as quite a surprise. As indicated in the last entry in Table 1, the reaction of the alkenyl amino complex **19** with 1-pentyne in DMF gives predominately phenol product whereas the reaction of the aryl amino carbene complex **1b** (R^2 = H, NR_2 = morpholino) with 1-hexyne in DMF gives exclusively an indanone product (Scheme 1).[2] Unlike the reaction of **1b**, however, the reaction of complex **19** is not synthetically useful since the mass balance is low (38%) and since a 2:1 mixture of the phenol **31** and the cyclopentenone **32** are produced. An acid workup is employed for these reactions to ensure complete hydrolysis of the aminocyclopentadienes which are the primary products of this reaction (**6** in Scheme 1). As indicated by the data in entries 3 and 4 in Table 1, the product distribution is dependent on the concentration; higher selectivity for phenol formation occurs at higher concentrations. This effect has been seen previously for the reactions of alkoxy carbene complexes with alkynes but not for amino carbene complexes.[3a,4,12] Likewise, the solvent has been observed to dramatically affect the product distribution from the reactions of alkoxy carbene complexes with alkynes, but such an effect of solvent has not been observed for the reactions of amino carbene complexes. As can be seen from the data in Table 1, there is a very strong influence of solvent on the distribution of the products from the reaction of the amino complex **19** with 1-pentyne. As has been observed with alkoxy complexes,[3a,4,12] phenol formation is more predominant with nonpolar or noncoordinating solvents. In heptane or benzene, the reaction of the amino complex **19** with 1-pentyne is completely selective for the formation of 4-(dimethylamino)phenol **31** and the yields are the same as for the 4-methoxylphenol obtained from the reaction of the methoxyl complex **17** with 1-pentyne.[4]

As indicated by the data in Table 2, other substituted amino phenols can also be selectively prepared by these reactions. The α-methyl and trans-β-methyl alkenyl complexes **30** and **26** react with 1-pentyne in benzene to give the 4-dimethylamino phenols **33** and **34**, respectively, both in 57% yield. The benzannulation of the *trans*-styryl complex **27** is less efficient giving the amino phenol **35** in only 39% yield. During purification of the 4-aminophenols from the reactions shown in Table 2 no other major product was observed as indicated by mobility on TLC or by analysis of the ^1H NMR spectrum of the crude reaction mixture. However, if the crude reaction mixture from the reaction of complex **27** was concentrated and allowed to stir in air for 2 h prior to chromatography, two products (**35** and **55**) were eluted from the column which were identified as the (dimethylamino)phenol **35** (27%) and as monomethylamino analog of **35** (4%). It is not known how the (dimethylamino)-phenol **35** is mono-demethylated under these conditions.

The potential utility[18] of these reactions was expanded with the finding that protected 4-(dimethylamino)phenol chromium tricarbonyl complexes could also be obtained from these reactions in good yields.[13] The *tert*-butyldimethylsilyl protected complex **36** can be obtained in higher yield than the free phenol **33** if the benzannulation

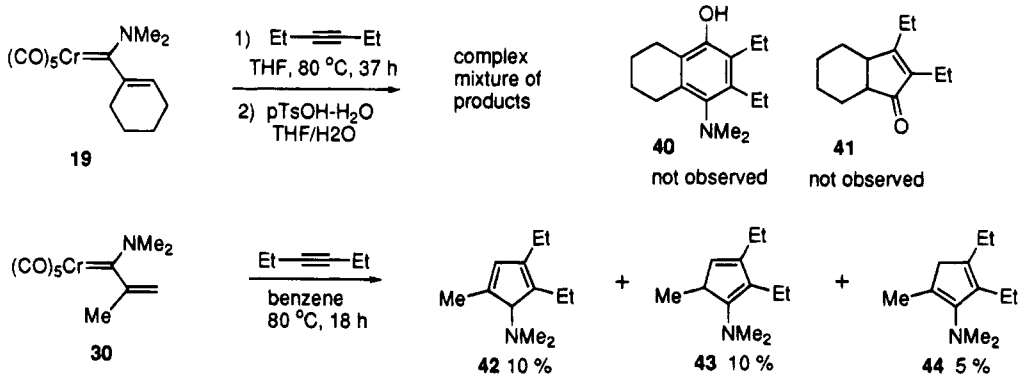
Table 2. Benzannulation of Amino Complexes with 1-Pentyne[a]



entry	complex	R^1	R^2	Ex (equiv)	base (equiv)	phenol **A** (% yield)[b]	complex **B** (% yield)[b]
1	**30**	Me	H	none	none	**33** (57)	
2	**30**	Me	H	TBSCl (2.0)	*i*-Pr_2EtN (3.0)		**36** (65)
3	**26**	H	Me	none	none	**34** (57)	
4	**26**	H	Me	TBSCl (2.0)	*i*-Pr_2EtN (3.0)		**37** (42)
5	**27**	H	Ph	none	none	**35** (39)	
6	**19**	$-(CH_2)_4-$		none	none	**31** (64)[c,d]	
7	**19**	$-(CH_2)_4-$		TBSOTf (1.5)	2,6-lutidine (2.5)		**38** (50)[c,e,f,g]
8	**19**	$-(CH_2)_4-$		Tf_2O (1.0)	*i*-Pr_2EtN (1.2)		**39** (25)[c,h]

[a] Unless otherwise specified all reactions were carried out with 1.9–2.0 equiv of alkyne at 0.25 M in carbene complex. [b] Isolated yields. [c] 0.5 M in **19**; 42–48 h reaction time. [d] 4 equiv of alkyne. [e] 2.0 equiv of alkyne added at $t = 0$ and 2.0 equiv of alkyne added at $t = 24$ h. [f] Heptane solvent. [g] 40 % yield in benzene (0.5 M, 48 h); 33 % yield in CH_2Cl_2 (0.05 M, 64 h). [h] Tf_2O and *i*-Pr_2EtN were added after the benzannulation was complete; triflation conditions 25 °C, 24 h.

Scheme 4



reaction of complex **30** with 1-pentyne is carried out in the presence of 2 equiv of *tert*-butyldimethylsilyl chloride and 3 equiv of Hünig's base as indicated in Table 2. The silylated arene complexes **37** and **38** can also be obtained in good yields although in the case of **38** the optimized yield of 50% was achieved with heptane as solvent. The in-situ protection could also be affected with triflic anhydride to give the aryl triflate complex **39**. The formation of **39** has not been optimized and has only been performed under the conditions indicated in Table 2 where the triflation step is carried out after the benzannulation was complete. Aryl triflate chromium tricarbonyl complexes are valuable in cross-coupling reactions which are facilitated by the activating effect of the chromium tricarbonyl group.[18a]

The utility of the benzannulation of amino alkenyl carbene complexes for the formation of 4-aminophenols appears to be limited to reactions with terminal alkynes. The reaction of the cyclohexenyl complex **19** with 3-hexyne in THF under the conditions described in entry 3 of Table 1 gives a complex mixture of minor products that were not separated nor characterized. The ^{1}H NMR spectrum of the crude reaction mixture did not contain absorptions that were anticipated for the phenol **40** nor absorptions that matched those reported for the hexahydroindenone **41**.[4] The latter compound has been observed as the major product from the reaction of an alkoxycyclohexenyl molybdenum complex with 3-hexyne following the same acid workup.[4] The same result was observed for the reaction of **19** with 3-hexyne in benzene. Similarly, the reaction of the *trans*-styryl carbene complex **27** with 3-hexyne in benzene (without an acid workup) gives several compounds that elute from a silica gel column but with a maximum of one-third of the total mass recovery. This mixture consisted of four compounds which rapidly decomposed when attempts were made to obtain them in pure form, and thus their structures were not further pursued. The reaction of the isopropenyl complex **30** with 3-hexyne, in the absence of an acid workup, produces a mixture of isomeric compounds that are tentatively identified as the cyclopentadienes **42**–**44**. The initial reaction mixture consists of isomers **42** and **43** but upon attempted purification on silica gel, the third isomer **44** is observed to grow in. These reactions may be producing cyclopentadiene products but isomerization and decomposition are obscuring the reaction analysis; it has been well established for the reactions of alkoxy complexes that internal alkynes tend to give higher proportions of five-membered ring products than do the same reactions of terminal alkynes.[4]

The dramatic difference between the product distribution from the reactions of alkenyl (amino) carbene complexes with terminal and internal alkynes prompts the question as to whether this difference will also be expressed in the reactions of aryl (amino) carbene complexes. This issue has not been properly addressed since most of the reported reactions of simple aryl (amino)

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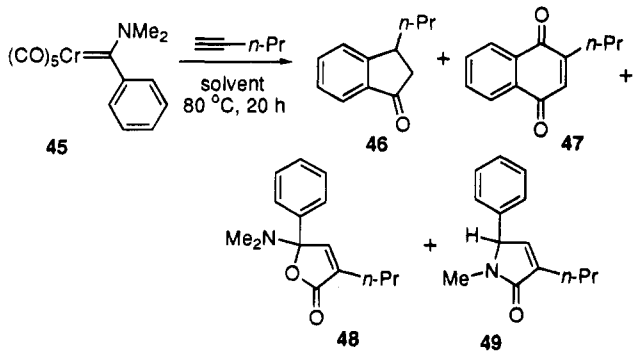
Table 3. Benzannulation of Complex 45 with 1-Pentyne[a]



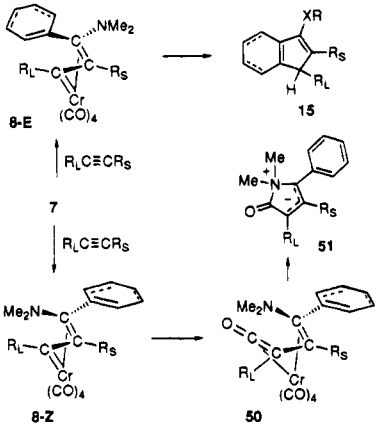
solvent	oxidative workup	% yield **46**	% yield **47**	% yield **48**	% yield **49**
DMF	no	32	<1[b]	<1	–
THF	no	19	<2[c]	12	15
benzene	yes	<4[c]	<4[c]	–	25

[a] Isolated yields, unless otherwise specified. [b] Minimum amount of naphthol as determined by ^{1}H NMR of nonoxidized reaction mixture. [c] Yield by ^{1}H NMR on oxidized (CAN) reaction mixture.

carbene complexes have been carried out in strongly coordinating solvents such as DMF. While the reactions of aryl (amino) carbene complexes with internal alkynes have been reported in both coordinating and noncoordinating solvents,[2,3,17] the reactions of these complexes with terminal alkynes have only been reported in coordinating solvents.[2,3] Therefore, we undertook an investigation of the effect of solvent on the reaction of the phenyl dimethylamino carbene complexes **45** with 1-pentyne. The results in Table 3 clearly reveal a distinct difference between the aryl and alkenyl (amino) carbene complexes. In stark contrast to the reaction of the cyclohexyl complex **19**, the reaction of the aryl complex **45** with 1-pentyne fails to give any of the six-membered ring annulated product in benzene. In addition, this reaction in DMF gives only the indene product **46** while in benzene this reaction gives exclusively the lactam **49**.[3a,17]

The effect of solvent on the distribution between the indene product **46** and the lactam **49** from the reaction of complex **45** is interesting in light of the differences in the behavior of aryl (amino) complexes that have been reported by Yamashita[2] and Rudler.[3a,17] Rudler demonstrated that lactam products as produced from nitrogen ylides of the type **51**.[17] Since these ylides can be derived only from the Z-isomer of the vinyl carbene intermediate **8** and since the indene **15** can be derived only from the *E*-isomer of **8**, it is clear that the solvent plays a decisive role in the reaction flux occurring through the *E*- and *Z*-isomers of intermediate **8** in the reactions of **45** with 1 pentyne. At this time it can not be determined whether the solvent plays this role by affecting the kinetic formation of **8-E** and **8-Z** or whether it does this by affecting the equilibrium between them. It has been observed in some cases that the presence of a species capable of coordinating to the metal has affected the distribution between products that are thought to be derived from different stereoisomers of the vinyl carbene intermediate.[4,21,22] However, since there has not been a significant study directed to the determination of the factors that control the stereochemistry of vinyl carbene intermediates in the benzannulation reaction, an interpretation of the observations summarized in Table 3 will have to wait.

Scheme 5



These studies have uncovered an unexpected utility for the reactions of amino carbene complexes with alkynes. With terminal alkynes, alkenyl (amino) complexes will undergo the benzannulation reaction to give 4-aminophenols in good yields, and in the presence of a silylation or triflation reagent, good yields of the chromium tricarbonyl complexes of the protected 4-aminophenols. It has previously been thought that phenol products could be obtained from the reactions of alkenyl (amino) carbene complexes only if the amino substituent was electronically deactivated with a carbonyl group.[3j-m] The reactions of aryl (amino) complexes with terminal alkynes do not give benzannulated products even in noncoordinating solvents. This disparity between the reactions of alkenyl- and aryl-(amino) carbene complexes with alkynes was not anticipated from a consideration of the differences between the reactions of alkenyl- and aryl-(alkoxy) carbene complexes with alkynes.

Experimental Section

General Information. Unless otherwise indicated, all common reagents and solvents were used as obtained from commercial suppliers without further purification. Prior to use, tetrahydrofuran, diethyl ether, and benzene were distilled from a Na/benzophenone ketyl; heptane, methylene chloride, and acetonitrile were distilled from CaH_2; and *N,N'*-dimethylformamide was stirred over BaO, decanted, and distilled under reduced pressure. 1-Pentyne and 3-hexyne were filtered through a short column of basic alumina immediately prior to use. Melting points were taken on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Routine ^{1}H NMR spectra were recorded on a DS 1000 (Chicago built) 500 MHz spectrometer, a 400 MHz Varian XL spectrometer, or a General Electric QE 300 MHz spectrometer with tetramethylsilane (δ 0.0) as an internal reference. Routine ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer at 75 MHz with the central peak of the $CDCl_3$ triplet (δ 77.0), the central peak of the CD_2Cl_2 triplet (δ 53.8), or the central peak of the C_6D_6 triplet (δ 128.0) as an internal reference. Infrared spectra were recorded on a Nicolet 20SXB FTIR spectrometer. Low-resolution mass spectra were recorded on a Finnigan 1015 instrument, and high-resolution mass spectra were recorded on a VG 70-250 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories Knoxville, TN.

Cyclohexenyl Dimethylamino Chromium Carbene Complex 19. To a −78 °C solution of 6.1 g (16.11 mmol) of

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the trisyl hydrazone of cyclohexanone **16**[23] in 50 mL of THF was added 13.3 mL (32.23 mmol) of a 2.42 M solution of *n*-BuLi in hexanes dropwise over 10 min. The resulting orange solution was warmed to 0 °C over 20 min and was then added via cannula to a room temperature slurry of 3.55 g (16.11 mmol) of $Cr(CO)_6$ and 50 mL of THF. The resulting brown solution was stirred at room temperature for 45 min, all volatiles were recovered on a rotary evaporator, and the resulting yellow/brown residue was exposed to high vacuum (0.01 mm) for 90 min. To this residue was added 50 mL of CH_2Cl_2 followed by 2.74 mL (3.97 g, 24.17 mmol) of methyl triflate, and the resulting red solution was stirred at room temperature for 45 min. The reaction mixture was poured into 150 mL of saturated $NaHCO_3$ solution and extracted with 3 × 50 mL of CH_2Cl_2. The combined organics were dried over $MgSO_4$, filtered, and evaporated to a solution volume of 50 mL. The solution was cooled to −78 °C, and Me_2NH was bubbled through the solution for 3 min causing the red solution to turn yellow. After warming to room temperature and evaporation of solvent, the remaining yellow residue was flash chromatographed on silica gel, eluting with a 10/1/1 mixture of hexanes/CH_2Cl_2/Et_2O, to give 3.41 g (10.36 mmol, a 64% yield) of carbene complex **19** (R_f = 0.28, 10/1/1 hexanes/CH_2Cl_2/Et_2O) as a yellow crystalline solid. Spectral data for **19**: mp 65−67 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60−1.70 (m, 4 H), 1.77−1.83 (m, 1 H), 2.00−2.08 (m, 1 H), 2.19−2.25 (m, 1 H), 2.28−2.36 (m, 1 H), 3.28 (s, 3 H), 3.77 (s, 3 H), 5.01 (br s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7 (2 CH_3), 23.9, 25.1, 28.1, 44.1, 114.8, 150.0, 217.8, 223.6, 276.3; IR (NaCl, thin film, cm^{-1}) 2934w, 2051m, 1968w, 1907br s, 1534w, 672m, 655m; mass spectrum (EI) *m*/*z* (% relative intensity) 329 (M^+, 2), 301 (M^+ − CO, 20), 273 (M^+ − 3 CO, 5), 217 (M^+ − 4 CO, 25), 189 (M^+ − 5 CO, 100), 134 (45), 95 (55); *m*/*z* calcd for $C_{14}H_{15}O_5Cr$ 329.0355, measd 329.0311. Anal. Calcd for $C_{14}H_{15}O_5NCr$: C, 51.07; H, 4.60; N, 4.25; Cr, 15.79. Found: C, 50.23; H, 4.82; N, 4.25; Cr, 15.75.

Cyclohexenyl Dimethylamino Molybdenum Carbene Complex 20. Using 5.0 g (13.21 mmol) of hydrazone **16**,[23] 10.61 mL (26.42 mmol) of a 2.49 M solution of *n*-BuLi in hexanes, 3.49 g (13.21 mmol) of $Mo(CO)_6$, and 2.24 mL (3.25 g, 19.82 mmol) of MeOTf and following the procedure given above for the synthesis of carbene complex **19**, 2.18 g (5.84 mmol, 45% yield) of carbene complex **20** (R_f = 0.31, 10/1/1 hexanes/CH_2Cl_2/Et_2O) was produced as a yellow crystalline solid. Spectral data for **20**: mp 65−70 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.56−1.64 (m, 1 H), 1.60−1.70 (m, 3 H), 1.76−1.82 (m, 1 H), 2.01−2.09 (m, 1 H), 2.19−2.25 (m, 1 H), 2.30−2.38 (m, 1 H), 3.25 (s, 3 H), 3.74 (s, 3 H), 5.01 (br s, 1 H); ^{13}C NMR (75 MHz, C_6D_6) δ 22.0, 22.1, 24.0, 24.8, 41.5, 51.6, 114.9, 150.2, 207.3, 214.1, 268.7; IR (NaCl, thin film, cm^{-1}) 2932w, 2929w, 2061m, 1910s, 1538w; mass spectrum (EI) *m*/*z* (% relative intensity) 375 (^{98}Mo, M^+, 2), 347 (^{98}Mo, M^+ − CO, 40), 319 (^{98}Mo, M^+ − 2 CO, 15), 291 (^{98}Mo, M^+ − 3 CO, 15), 263 (^{98}Mo, M^+ − 4 CO, 65), 259 (100), 231 (95), 190 (60); *m*/*z* calcd for $C_{14}H_{15}O_5N^{98}Mo$ 372.9997, measd 373.0005; *m*/*z* calcd for $C_{14}H_{15}O_5N^{98}Mo$ 375.0004, measd 375.0007.

Cyclohexenyl Pyrrolidino Chromium Carbene Complex 21. A solution of 100 mg (0.316 mmol) of cyclohexenyl methoxy chromium pentacarbonyl complex **17**[3a] in 0.5 mL of diethyl ether was stirred at room temperature while 0.029 mL (24.7 mg, 0.348 mmol) of pyrrolidine was added dropwise. After 30 min, the reaction mixture was concentrated. Purification of the crude product by column chromatography on silica gel with a 1:1:10 mixture of diethyl ether:methylene chloride:hexane gave 46 mg (0.130 mmol) of **21** as a yellow oil in 41% yield and 26.8 mg (0.102 mmol) of **22**[24] as a yellow solid in 34% yield. Spectral data for **21**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.57−1.87 (m, 5H), 2.01−2.41 (m, 7H, includes q at 2.03, *J* = 6.5 Hz and q at 2.15, *J* = 6.4 Hz), 3.37 (dt, 1H, *J* = 13.4 Hz, 6.8 Hz), 3.88 (dt, 1H, *J* = 13.4 Hz, 6.8 Hz), 4.01 (dt, 1H, *J* = 13.5 Hz, 6.9 Hz), 4.13 (dt, 1H, *J* = 13.5 Hz, 6.7 Hz), 4.97 (s, 1H); ^{13}C NMR (75 MHz, CDCl3) δ: 21.7, 21.9, 23.9, 24.6, 25.1, 25.4, 53.3, 59.1, 113.3, 151.1, 218.1, 270.7, 228.8; IR (NaCl, thin film, cm^{-1}) 2985−2837w, 2048m, 1962m, 1930s, 1903s, 1884s, 1508m, 1450w, 1328w cm^{-1}; mass spectrum (EI) *m*/*z* (% relative intensity) 355 (M^+, 1), 327 (M^+ − CO, 13), 299 (M^+ − 2CO, 4), 271 (M^+ − 3CO, 4), 243 (M^+ − 4CO, 15), 215 (M^+ − 5CO, 100), 163 (34), 148 (7), 134 (6), 121 (26), 108 (4), 91 (13), 79 (12), 70 (36), 52 (65). Anal. Calcd for $C_{18}H_{17}NO_5Cr$: C 54.09, H 4.82, N 3.94, Cr 14.63. Found: C 53.96, H 4.91, N 3.66, Cr 14.63. Spectral data for **22**: mp 58−59 °C (lit. 58−60 °C[24]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.61−1.70 (m, 2H), 1.83−1.89 (m, 2H), 2.13 (br s, 1H), 2.41−2.53 (m, 2H), 3.17 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 58.4, 214.1, 219.7; IR (NaCl, thin film, cm^{-1}) 3290w, 2977−2832w, 2066m, 1976 shoulder, 1907s; mass spectrum (EI) *m*/*z* (% relative intensity) 263 (M^+, 14), 235 (M^+ − CO, 8), 207 (M^+ − 2CO, 3), 179 (M^+ − 3CO, 2), 164 (3), 151 (M^+ − 4CO, 16), 136 (4), 123 (M^+ − 5CO, 100), 108 (4), 93 (2), 80 (7), 70 (64), 52 (43).

Attempted Preparation of the Cyclohexenyl Morpholinomethylene Chromium Pentacarbonyl. The preparation of the cyclohexenyl morpholino chromium carbene complex was attempted according to the procedure described above for **19**; however, the only product obtained that was mobile on silica gel was morpholine pentacarbonyl chromium **23** which was isolated in 50% yield. This compound was identified on the basis of its known melting point (found 107−109 °C dec; lit.[24] 110 °C dec). Spectral data for **23**: R_f = 0.11, 10/1/1 hexanes/CH_2Cl_2/Et_2O; ^{1}H NMR (500 MHz, C_6D_6) δ 0.89 (br t, 1 H), 1.73 (d, *J* = 13.3 Hz, 2 H), 2.08 (qd, *J* = 12.2, 1.3 Hz, 2 H), 2.23 (td, *J* = 11.8, 0.9 Hz, 2 H), 2.90 (dd, *J* = 12.1, 1.9 Hz, 2 H); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.11 (br t, 1 H), 2.96 (m, 4 H), 3.43 (t, *J* = 12.0 Hz, 2 H), 3.79 (d, *J* = 11.9 Hz, 2 H); IR (NaCl, thin film, cm^{-1}) 2067w, 1979sh, 1909s; IR (NaCl, Nujol, cm^{-1}) 2068w, 1933s; [lit.[25] IR (Nujol, cm^{-1}) 2049w, 1985s, 1942s].

***trans*-Propenyl Dimethylamino Chromium Carbene Complex 42.** *trans*-Propenyl dimethylamino chromium carbene complex **26** was prepared from 250.0 mg (0.91 mmol) of the corresponding methoxy complex **24**[26] by purging a THF solution (10 mL) with excess dimethylamine at −78 °C. Dimethylamine was usually added until the color of the solution turned from deep red to golden yellow (a few minutes). The reaction mixture was further stirred for 5 min before it was stripped of volatiles and loaded onto a silica gel column (20% CH_2Cl_2 in hexane). The first band, containing 103.9 mg (40%) of an orange-yellow oil with R_f = 0.62 (50% CH_2Cl_2/hexane), was characterized as the amino carbene complex **26**. Spectral data for **26**: ^{1}H NMR (CD_2Cl_2) δ 1.83 (dd, 3H, *J* = 1.4, 6.8 Hz), 3.35 (s, 3H), 3.82 (s, 3H), 5.05 (dq, 1H, *J* = 16.1, 6.8 Hz), 6.49 (d, 1H, *J* = 16.1 Hz); ^{13}C NMR (CD_2Cl_2) δ 17.8, 45.6, 51.6, 119.4, 142.2, 218.3 (cis CO), 224.4, 269.6; IR (neat) cm^{-1} 2947w, 2933w, 2053s, 1904s, 1537m, 1448w, 1403w; mass spectrum (EI) *m*/*z* (% relative intensity) 289 (3) M^+, 261 (75), 233 (11), 205 (10), 177 (58), 149 (100), 134 (45), 123 (23), 109 (30); *m*/*z* calcd for $C_{11}H_{11}CrNO_5$ 289.0042, measd 289.0027. The second band, containing 82.7 mg (39%) of a thick orange glass, was identified as the known $(CO)_5Cr$-$NH(CH_3)_2$ **28**.[27] Spectral data for **28**: R_f = 0.54 (50% CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$) δ 2.28 (m, 1H), 2.53 (s, 3H), 2.54 (s, 3H)[27]; ^{13}C NMR ($CDCl_3$) δ 49.6, 213.8, 219.7; IR (neat) cm^{-1} 3316w, 2913w, 2068s, 1918s, 1473s, 1015w, 901m; mass spectrum (EI): *m*/*e* (% relative intensity) 237 (19) M^+, 125 (82), 97 (100), 80 (10). The preparation of **26** with modifications of the above procedure all lead to less desirable results. For example, attempted catalysis of the reaction with the 1.5 equiv of NaOMe[33] or the use of hexane as solvent both provided yields in the range of 4−21% for the amino complex **26** and yields in the range of 45−55% for dimethylamino chromium pentacarbonyl **28**.

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***trans*-Styryl Dimethylamino Chromium Pentacarbonyl Carbene Complex 27.**[28] A solution of 1.08 g (3.193 mmol) of *trans*-styryl methoxy chromium pentacarbonyl carbene complex **25**[29] in 25 mL of diethyl ether was cooled to −78 °C. Dimethylamine was bubbled through the reaction mixture for approximately 30 s. The dark red-brown reaction mixture turned bright yellow within approximately 2 min and was stirred at −78 °C for 10 min. The reaction mixture was poured into a sepratory funnel containing water and diethyl ether. The organic layer was washed with water and brine and then dried with $MgSO_4$. After filtration and concentration, the crude product was purified on a silica gel column with a 1:1:4 mixture of diethyl ether:methylene chloride:hexane as eluent which afforded 1.105 g (3.146 mmol) of **27** as an orange oil in 98% yield. Spectral data for **27**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.44 (s, 3H), 3.89 (s, 3h), 5.83 (d, 1H, J = 16.8 Hz), 7.12 (d, 1H, J = 16.7 Hz), 7.25−7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.7, 51.0, 120.6, 126.5, 127.9, 128.8, 136.0, 137.6, 217.4, 223.5, 269.8; IR (thin film) 3071−2831w, 2052s, 1971shoulder, 1904s, 1540m, 1496w, 1448w, 1404w, 1157w, 1022w, 959w, 750w, 706w; mass spectrum (EI) m/z (% relative intensity): 323 (M^+ − CO, 16), 295 (M^+ − 2CO, 4), 267 (M^+ −3CO, 7), 239 (M^+ − 4CO, 22), 211 (M^+ − 5CO, 62), 158 (22), 144 (16), 115 (32), 95 (37), 52 (100). Anal. Calcd for $C_{16}H_{13}NO_5Cr$: C 54.71, H 3.73, N 3.99, Cr 14.80. Found: C 54.55, H 3.82, N 3.97, Cr 15.13.

Isopropenyl Dimethylamino Chromium Carbene Complex 30. Isopropenyl dimethylamino chromium carbene complex **30** was prepared in a similar manner to that described above for **26** except that hexane was used as solvent. A solution of 710.0 mg (2.57 mmol) of the isopropenyl methoxy carbene complex **29**[26] in 40 mL of hexane was treated with dimethylamine to give 635.5 mg (85%) of the pure amino complex **30** as isolated from a silica gel column (eluent: 20% CH_2Cl_2 in hexane) as a light yellow solid. Spectral data for **30**: mp 47−48 °C, orange yellow needles from CH_2Cl_2/hexane; R_f = 0.60 (50% CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$) δ 1.83 (s, 3H), 3.31 (s, 3H), 3.79 (s, 3H), 4.32 (s, 1H), 4.66 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 19.7, 44.2, 50.8, 103.9, 154.3, 217.6 (cis CO), 223.3, 276.5; IR (neat) cm^{-1} 2923w, 2053s, 1903s, 1539m, 1404w; mass spectrum (EI) m/z (% relative intensity) 289 (3) M^+, 261 (17), 233 (4), 205 (6), 177 (20), 149 (100), 132 (6), 109 (29); m/z calcd for $C_{11}H_{11}CrNO_5$ 289.0042, measd 289.0047. Anal. Calcd for $C_{11}H_{11}CrNO_5$: C, 45.68; H, 3.83; N, 4.84. Found C, 45.67; H, 3.86, N, 4.73. The yields for **30** were consistently higher than those for the *trans*-propenyl dimethylamino chromium carbene complex **26**. This may be because **30** was virtually insoluable in hexane at −78 °C and precipitated out as it was formed. $(CO)_5Cr$-$NH(CH_3)_2$ was not detected in the formation of **30**.

General Procedure for the Benzannulation Reaction of Amino Carbene Complexes with Alkynes. Illustrated for the Reaction of Cyclohexenyl Carbene Complex 19 with 1-Pentyne in THF. Carbene complex **19** (200 mg, 0.61 mmol), 0.12 mL (83 mg, 1.22 mmol) of 1-pentyne, and 1.2 mL of THF were combined in a single-necked flask equipped with a threaded high-vacuum stopcock. The reaction mixture was deoxygenated by the freeze-pump-thaw method (−196 °C/25 °C) and, after the flask was back-filled with argon and the stopcock sealed at 25 °C, the flask was immersed in an oil bath at 80 °C. TLC after 22 h showed that carbene complex **19** was still present. Therefore, a second portion of 0.12 mL (83 mg, 1.22 mmol) of 1-pentyne was added and the mixture deoxygenated as before and heated at 80 °C. After a total of 47 h, TLC showed that the carbene complex **19** had been completely consumed. The solvent was evaporated and the residue was dissolved in a mixture of 15 mL of THF and 5 mL of H_2O and the resulting solution stirred with 50 mg (0.26 mmol) of p-TsOH·H_2O under air at room temperature for 1 h. The reaction mixture was poured into 25 mL of saturated aqueous $NaHCO_3$ and extracted with 3 × 25 mL of Et_2O. The combined organics were washed with 1 × 75 mL H_2O and 1 × 75 mL of brine, dried over $MgSO_4$, filtered, and evaporated to a yellow oil. Flash chromatography on silica gel, eluting with hexanes/CH_2Cl_2/Et_2O (10/1/1 to 4/1/1) gave 80 mg (0.34 mmol, a 57% yield) of phenol **31** (R_f = 0.33, 4/1/1 hexanes/CH_2Cl_2/Et_2O) as a yellow oil, in addition to 13 mg (0.07 mmol, a 12% yield) of cyclopentenone **32** (R_f = 0.25, 4/1/1 hexanes/CH_2Cl_2/Et_2O) as a yellow oil. Spectral data for phenol **31**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (t, J = 7.5 Hz, 3 H), 1.27 (sextet, J = 6.9 Hz, 2 H), 1.62 (q, J = 7.5 Hz, 2 H), 1.69−1.73 (m, 2 H), 1.80−1.84 (m, 2 H), 2.52 (t, J = 7.5 Hz, 2 H), 2.60 (br s, 6 H), 2.71 (t, J = 5.8 Hz, 2 H), 4.37 (br s, 1 H, OH exchanges with D_2O), 6.70 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 22.6, 23.2, 23.5, 25.4, 32.5, 45.0, 117.5, 122.7, 123.3, 124.5, 131.3, 145.3, 147.3; IR (NaCl, thin film, cm^{-1}) 3550−3350br w, 2956s, 2931s, 2858m, 2820w, 2775w, 1475m, 1441m, 1208w, 1187w, 1094w, 912w; mass spectrum (EI) m/z (% relative intensity) 233 (M^+, 100), 218 (M^+ − CH_3, 65), 203 (M^+ −2CH_3, 10), 175 (10); m/z calcd for $C_{15}H_{23}ON$ 233.1780, measd 233.1786. Spectral data for cyclopentenone **32**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (t, J = 7.0 Hz, 3 H), 1.18−1.40 (m, 3 H), 1.57−1.80 (m, 5 H), 2.03 (d, J = 18.6 Hz, 1 H), 2.05−2.20 (m, 3 H), 2.37−2.43 (m, 1 H), 2.49 (dd, J = 6.4, 18.6 Hz, 1 H), 2.66 (br s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 19.9, 20.4, 21.7, 22.2, 26.4, 35.0, 41.0, 41.7, 138.4, 176.6, 208.4; IR (NaCl, thin film, cm^{-1}) 2956m, 2929s, 2861m, 1701s, 1647m, 1457w, 1392w, 1277w; mass spectrum (EI) m/z (% relative intensity) 178 (M^+, 100), 149 (M^+ − C_2H_5, 50), 136 (M^+ − C_3H_6, 100), 107 (90), 91 (50), 79 (85); m/z calcd for $C_{12}H_{18}O$ 178.1358, measd 178.1371. All of the reactions indicated in Table 1 were carried out using the above procedure. When not able to be isolated, the amount of cyclopentenone **32** was determined by ^{1}H NMR of the crude reaction mixture.

Benzannulation of the *trans*-Propenyl Carbene Complex 26 with 1-Pentyne in Benzene. The dimethylamino *trans*-propenyl carbene complex **26** (45.0 mg, 0.16 mmol) was reacted with 29.2 μL (0.30 mmol) of 1-pentyne in 0.65 mL of benzene [0.25 M] at 80 °C for 16 h according to the general procedure described above for **19**. This reaction produced 17.1 mg (57%) of the amino phenol product **34** which was isolated from column chromatography on silica gel (25% CH_3CN in CH_2Cl_2) followed by preparative TLC (plate size: 20 × 20 cm with 0.25 mm in thickness; eluent: 15% CH_3CN in CH_2Cl_2; two elutions) as a light pink oil. Spectral data for **34**: R_f = 0.64 (25% CH_3CN/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 0.98 (t, 3H, J = 7.3 Hz), 1.63 (sext, 2H, J = 7.5 Hz), 2.22 (s, 3H), 2.53 (t, 2H, J = 7.7 Hz), 2.82 (s, 6H), 4.09 (brs, 1H), 6.42 (brs, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 16.5, 23.2, 32.8, 42.0, 113.9, 114.5, 123.9, 128.6, 144.2, 145.2; IR (neat) cm^{-1} 3394 (brd)m, 2956s, 2925s, 2871m, 1608w, 1488s, 1453m, 1204m, 1198m; mass spectrum (EI): m/z (% relative intensity) 193 (100) M^+, 177 (7), 164 (27), 149 (6), 136 (4), 121 (3), 93 (3); m/z calcd for $C_{12}H_{19}NO$ 193.1467, measd 193.1466. The ^{1}H NMR spectrum of **34** indicated the presence of a trace amount of impurity that could not be separated using preparative methods. Oxidation of **34** with ceric ammonim nitrate cleanly provided 2-*n*-propyl-6-methylbenzoquinone (**54**)[30,31] in quantitative yield as a yellow oil. Spectral data for quinone **54**: R_f = 0.37 (CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 0.97 (t, 3H, J = 7.3 Hz), 1.53 (m, 2H), 2.04 (s, 3H), 2.39 (t, 2H, J = 7.6 Hz), 6.46 (s, 1H), 6.51 (s,1H); ^{13}C NMR ($CDCl_3$) δ 13.8, 16.1, 21.1, 31.1, 132.4, 133.1, 145.9, 149.3, 186.3, 187.9; IR (neat) cm^{-1} 2963w, 1653s, 1614m, 1297m, 779w; mass spectrum (EI) m/z (% relative intensity) 164 (68) M^+, 149 (6), 135 (17), 110 (100), 96 (20), 90 (32); m/z calcd for $C_{10}H_{12}O_2$ 164.0837, measd 164.0837.

Benzannulation of the *trans*-Styryl Carbene Complex 27 with 1-Pentyne in Benzene. The reaction of 559.1 mg (1.583 mmol) of *trans*-styryl dimethylamino chromium pentacarbonyl carbene complex **27** and 0.312 mL (215.6 mg, 3.166 mmol) of 1-pentyne in 6.3 mL of benzene was performed as indicated in the general procedure described above for **19**. The reaction was complete in 17 h at 84 °C, and after removal of the volatiles the crude mixture was immediately loaded onto

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a silica gel column. Two bands eluted from the column with a 1:1:4 mixture of diethyl ether:methylene chloride:hexane. As soon as the faster moving yellow band was collected, it decomposed to **35** which eluted as the slower colorless band. The fractions from the yellow band were rechromatographed to give a combined yield of phenol **35** of 39% (58.5 mg, 0.621 mmol) as a brownish oil. Spectral data for **35**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, 3H, J = 7.3 Hz); 1.67 (sextet, 2H, J = 7.6 Hz); 2.61 (t, 2H, J = 7.7 Hz); 3.86 (s, 6H); 4.71 (s, 1H); 6.51 (d, 1H, J = 2.9 Hz); 6.63 (d, 1H, J = 2.9 Hz); 7.37 – 7.47 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 23.2, 33.0, 41.9, 113.3, 116.0, 127.6, 128.2, 129.1, 129.2, 129.8, 138.2, 142.6, 145.0; IR (thin film, cm^{-1}) 3580–3483w, 2979–2779w, 1598m, 1481s, 1436s, 1365w, 1223m; mass spectrum (EI) *m/z* (% relative intensity) 255 (M^+, 100), 240 (3), 226 (5), 211 (11), 196 (2), 182 (4), 162 (2), 153 (3), 141 (2), 115 (2). Anal. Calcd. for $C_{17}H_{21}NO$: C 79.96, H 8.29, N 5.49. Found: C 79.90, H 8.50, N 5.36.

Slow Air Oxidation. When the same procedure as above was used, starting from 199 mg (0.567 mmol) of **27** and 0.112 mL (77.4 mg, 1.133 mmol) of 1-pentyne in 2.25 mL benzene, and the crude reaction mixture was stirred in air for 2 h before column chromatography, a side-product was observed that was identified as 4-(*N*-methylamino)-2-phenyl-6-*n*-propylphenol (**55**). Purification of these two products by column chromatography with a 1:1:4 mixture of diethyl ether:methylene chloride:hexane afforded 33.9 mg (0.133 mmol, 23 % yield) of the (dimethylamino)phenol **35** and 11.2 mg (0.046 mmol, 8% yield) of 4-(*N*-methylamino)-2-phenyl-6-*n*-propylphenol (**55**) as a brownish oil. Spectral data for 4-(*N*-methylamino)-2-phenyl-6-*n*-propylphenol (**55**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (t, 3H, J = 7.3 Hz); 1.69 (sextet, 2H, J = 7.5 Hz); 2.62 (t, 2H, J = 7.7 Hz); 2.82 (s, 3H); 3.42 (broad s, 1H, exchanges with D_2O); 4.52 (s, 1H, exchanges with D_2O); 6.38 (d, 1H, J = 2.7 Hz); 6.47 (d, 1H, J = 2.6 Hz); 7.35–7.45 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 23.1, 31.7, 32.8, 111.8, 114.9, 127.6, 128.5, 129.1, 129.2, 130.2, 138.3, 142.7, 143.0; mass spectrum (EI), *m/z* (% relative intensity) 241 (M^+, 100), 228(5), 212(12), 197(30), 182-(9), 165(5), 152(7), 141(6), 128(6), 115(8), 102(6), 91(4), 77(8), 65(3), 51(4).

CAN Oxidation. The reaction of 420.3 mg (1.197 mmol) **27** and 0.236 mL (163.1 mg, 2.393 mmol) 1-pentyne in 4.76 mL benzene was repeated with the procedure as above. The crude reaction mixture was concentrated and redissolved in 12 mL of methylene chloride and stirred with 12 mL of 0.5 M aqueous ceric ammonium nitrate for 30 min. After separation of the layers and concentration of the organic fraction, the product was purified by column chromatography on silica gel with a 1:1:10 mixture of diethyl ether:methylene chloride:hexane and obtained as a yellow oil in 15% yield (41.2 mg, 0.182 mmol). This yellow material had a ^{1}H NMR spectrum that was consistent with the expected 2-phenyl-6-*n*-propylquinone (**56**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (t, 3H, J = 7.3 Hz), 1.61 (q, 2H, J = 7.4 Hz), 2.49 (t, 2H, J = 7.4 Hz), 6.61 (s, 1H), 6.78 (d, 1H, J = 1.6 Hz), 7.45–7.43 (m, 5H). This reaction was performed to see if the low yield of **35** (39%) was due to loss of metal complexed species during the separation on silica gel which was performed in the presence of air. However, given the low mass balance for this reaction with the CAN workup, this could not be determined. The low mass balance was not accounted for but a few percent of a quinone was isolated in which the *n*-propyl group was oxidized in the benzylic position.

Benzannulation of the Isopropenyl Carbene Complex 30 with 1-Pentyne in Benzene. The dimethylamino carbene complex **30** (100.0 mg, 0.35 mmol) was reacted with 64.8 μL (0.66 mmol) of 1-pentyne in 1.40 mL of benzene [0.25 M] at 80 °C for 24 h according to the general procedure described above for **19**. This gave 38.8 mg (57%) of the aminophenol **33** which was isolated using column chromatography (eluent: 25% CH_3CN in CH_2Cl_2) followed by preparative TLC (plate size: 20 × 20 cm and 0.25 mm in thickness; eluent: 5% CH_3-CN in CH_2Cl_2; two elutions) as a colorless oil. Spectral data for **33**: R_f = 0.70 (25% CH_3CN/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 0.97 (t, 3H, J = 7.3 Hz), 1.61 (sext, 2H, J = 7.3 Hz), 2.23 (s, 3H), 2.51 (t, 2H, J = 7.6 Hz), 2.61 (s, 6H), 4.33 (brs, 1H), 6.55 (s, 1H), 6.76 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 17.5, 23.2, 32.1, 44.9, 117.7, 120.5, 125.8, 131.3, 145.8, 149.0; IR (neat) cm^{-1} 3423 (brd)m, 2953s, 2932s, 2872m, 1681m, 1676w, 1609w, 1453m, 1414m, 1410w; mass spectrum (EI) *m/z* (% relative intensity) 193 (100) M^+, 178 (44), 164 (34), 149 (9), 139 (24), 121 (9), 105 (3), 91 (11), *m/z* calcd for $C_{12}H_{19}NO$ 193.1467, measd 193.1464.

The reaction was repeated with 67.7 mg (0.23 mmol) of **30** and 43.8 μL (0.45 mmol) of 1-pentyne in 1.0 mL of benzene at 80 °C for 18 h. The crude reaction mixture was oxidized by stirring with 0.5 M aqueous cerric ammonium nitrate at 25 °C for 30 min to give after purification on silica gel 23.1 mg (60%) of the 2-*n*-propyl-5-methylbenzoquinone **57**[30,31] as a yellow oil (R_f = 0.49 (CH_2Cl_2). Spectral data for quinone **57**: ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 3H, J = 7.3 Hz), 1.53 (sext, 2H, J = 7.5 Hz), 2.02 (s, 3H), 2.37 (t, 2H, J = 7.7 Hz), 6.50 (s, 1H), 6.54 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.7, 15.4, 21.0, 31.6, 132.5, 133.5, 145.5, 149.3, 187.8, 188.3; IR (neat) cm^{-1} 2962m, 2933m, 2874w, 1658s, 1349m, 1249m, 1134w, 915w; mass spectrum (EI) *m/z* (% relative intensity) 164 (15) M^+, 149 (100), 112 (36); *m/z* calcd for $C_{10}H_{12}O_2$ 164.0837, measd 164.0830.

General Procedure for the Synthesis of Amino Arene Chromium Tricarbonyl Complexes from Amino Carbene Complexes and Alkynes. Illustrated for the Preparation of Silyloxy Arene Chromium Tricarbonyl Complex 36. The isopropenyl dimethylamino carbene complex **30** (75.0 mg, 0.26 mmol) and a small magnetic stir bar were placed in a flame-dried, single-necked flask that has been modified by replacement of the 14/20 joint with a 10-mm threaded high vacuum stopcock (Kontes No. 826610). The stopcock was replaced with a rubber septum, and the flask was evacuated and backfilled with argon. One half of the total amount of anhydrous benzene (1.0 mL) required for a 0.25 M solution of the carbene complex, 48.5 μL (0.49 mmol, 1.9 equiv) of 1-pentyne, 135.3 μL (0.78 mmol, 3.0 equiv) of Hünig's base (freshly distilled and/or passed through a pipette size basic Al_2O_3 gel column), 78.1 mg (0.52 mmol, 2.0 equiv) of TBSCl, and the remaining solvent were added via syringe. The septum was replaced with the threaded stopcock, and the reaction mixture was deoxygenated using the freeze-thaw method (three to four cycles, −196 °C/25 °C). The reaction flask was backfilled with argon at the end of the last cycle, sealed with the stopcock, and heated at 80 °C for 17 h. After cooling to room temperature, the reaction mixture was analyzed by TLC (50% CH_2Cl_2/hexane, UV/PMA), concentrated under reduced pressure, and subjected to column chromatography on silica gel (eluent: 10–50% CH_2Cl_2 in hexane) to give 74.8 mg (65%) of the arene complex **36** as a yellow solid. Spectral data for **36**: mp 74–75 °C, yellow needles from ether: pentane; R_f = 0.43 (50% CH_2Cl_2/hexane); ^{1}H NMR (CD_2Cl_2) δ 0.31 (s, 3H), 0.41 (s, 3H), 1.02 (s, 9H), 1.03 (t, 3H, J = 7.5 Hz), 1.59 (m, 2H), 2.19 (m, 1H), 2.24 (s, 3H), 2.61 (s, 6H), 2.63 (m, 1H), 5.05 (s, 1H), 5.50 (s, 1H); ^{13}C NMR (CD_2Cl_2) δ −4.2, −3.8, 14.3, 18.4, 18.6, 24.8, 25.8, 32.7, 45.1, 86.1, 89.5, 102.0, 106.1, 126.5, 135.8, 236.0; IR (neat) cm^{-1} 2959m, 2932m, 2861w, 1951s, 1868s, 1473m, 1364m, 1266m, 1172w, 945m, 862w, 842m, 784w; mass spectrum (EI) *m/z* (% relative intensity) 443 (46) M^+, 387 (25), 359 (100), 307 (64), 250 (9), 120 (14); *m/z* calcd for $C_{21}H_{33}CrNO_4Si$ 443.1584, measd 443.1566. Anal. Calcd for $C_{21}H_{33}CrNO_4Si$: C, 56.86; H, 7.50; N, 3.16; Cr, 11.73. Found C, 56.64; H, 7.84, N, 3.05; Cr, 11.56.

Preparation of Silyloxy Arene Chromium Tricarbonyl Complex 37. The reaction of *trans*-propenyl dimethylamino carbene complex **26** (39.2 mg, 0.14 mmol) with 25.3 μL (0.26 mmol) of 1-pentyne in 0.50 mL of benzene [0.25 M] in the presence of 71.1 μL (0.41 mmol, 3.0 equiv) of Hünig's base and 41.0 mg (0.27 mmol, 2.0 equiv) of TBSCl was carried out at 80 °C for 14 h as described above for the preparation of **36**. This gave 25.1 mg (42%) of the arene complex **37** after purification by column chromatography (eluent: 10–50% CH_2-Cl_2 in hexane) as a yellow solid. Spectral data for **37**: m.p. 130–131 °C, yellow transparent cubes from ether:pentane; R_f = 0.43 (50% CH_2Cl_2/ hexane); ^{1}H NMR (CD_2Cl_2) δ 0.38 (s, 3H), 0.39 (s, 3H), 1.03 (s, 9H), 1.05 (t, 3H, J = 7.3 Hz), 1.60 (m, 1H), 1.71 (m, 1H), 2.22 (m, 1H), 2.24 (s, 3H), 2.82 (m, 1H), 2.84 (s, 6H), 4.37 (d, 1H, J = 2.9 Hz), 4.38 (d, 1H, J = 2.9 Hz);

^{13}C NMR (CD_2Cl_2) δ −2.5, −2.3, 14.2, 18.8, 19.2, 24.1, 26.3, 33.9, 40.2, 75.7, 77.0, 104.3, 109.1, 126.0, 131.8, 236.7; IR (neat) cm^{-1} 2956m, 2930w, 1932s, 1857s, 1560m, 1491w, 1442w, 1375w, 1259w, 927w, 841m, 860m, 780w; mass spectrum (EI) *m/z* (% relative intensity) 443 (16) M^+, 387 (10), 359 (100), 307 (98), 274 (8), 250 (14), 207 (9), 192 (6), 165 (9), 126 (32); *m/z* calcd for $C_{21}H_{33}CrNO_4Si$ 443.1584, measd 443.1582. Anal. Calcd for $C_{21}H_{33}CrNO_4Si$: C, 56.86; H, 7.50; N, 3.16; Cr, 11.73. Found: C, 56.59; H, 7.51, N, 2.96; Cr, 12.29.

Preparation of Silyloxy Arene Chromium Tricarbonyl Complex 38. The cyclohexenyl dimethylamino carbene complex **19** (200 mg, 0.61 mmol), 0.12 mL (83 mg, 1.21 mmol) of 1-pentyne, 1.2 mL of heptane, 0.18 mL (163 mg, 1.52 mmol), of 2,6-lutidine, and 0.21 mL (241 mg, 0.91 mmol) of TBSOTf were combined in a single-necked flask equipped with a threaded high-vacuum stopcock. The reaction was carried out as described in the general procedure for the synthesis of complex **36**. After 24 h, TLC showed that carbene complex **19** was still present, and therefore, a second portion of 0.12 mL (83 mg, 1.22 mmol) of 1-pentyne was added and the mixture deoxygenated as before and heated at 80 °C. After a total of 48 h, TLC revealed that carbene complex **19** was consumed. The reaction mixture was diluted with 50 mL of Et_2O, washed with 1 × 50 mL of brine, 1 × 50 mL of 1 N HCl, 1 × 50 mL H_2O, and 1 × 50 mL of brine, dried over $MgSO_4$, filtered, and evaporated to give a yellow oil. Flash chromatography on silica gel and elution with a mixture of hexanes/CH_2Cl_2/Et_2O (20/1/1 to 10/1/1) gave 138 mg (0.30 mmol, 50% yield) of arene complex **38** (R_f = 0.48, 4/1/1 hexanes/CH_2Cl_2/Et_2O) as a yellow solid. Spectral data for **38**: mp 101−103 °C; ^1H NMR (500 MHz, C_6D_6) δ 0.417 (s, 3H), 0.423 (s, 3H), 0.90 (t, J = 5.3 Hz, 3 H), 0.99 (s, 9 H), 1.19−1.23 (m, 2H), 1.40−1.56 (m, 2H), 1.60−1.72 (m, 2H), 2.10−2.25 (complex m, 2 H), 2.29 (s, 6 H), 2.51−2.59 (m, 1 H), 2.60−2.66 (m, 1 H), 2.80−2.86 (m, 1 H), 2.91−2.97 (m, 1 H), 4.87 (s, 1 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ −2.9, −1.7, 14.2, 19.2, 22.3, 22.4, 25.8, 26.1, 26.2, 26.3, 32.4, 44.5, 84.1, 103.3, 104.9, 108.5, 129.1, 130.2, 236.0; IR (NaCl, thin film, cm^{-1}) 2957w, 2933m, 2861w, 1945s, 1857s, 1464w, 1423w, 1258w, 929w, 841w, 782w; mass spectrum (EI) *m/z* (relative intensity) 483 (M^+ 25), 427 (M^+ − 2CO, 15), 399 (M^+ − 3CO, 100), 347 (M^+ − $Cr(CO)_3$, 30); *m/z* calcd for $C_{24}H_{37}O_4NCrSi$ 483.1897, measd 483.1901.

Preparation of Triflate Arene Chromium Tricarbonyl Complex 39. The cyclohexenyl dimethylamino carbene complex **19** (200 mg, 0.61 mmol), 0.24 mL (166 mg, 2.44 mmol) of 1-pentyne and 1.2 mL of benzene were combined in a single-necked flask equipped with a threaded high-vacuum stopcock. The reaction was carried out according to the general procedure described above for **30**. It is crucial that the thawed mixture be allowed to completely warm to room temperature and stirred for 10 min during each freeze cycle in order to obtain optimal results. The reaction mixture was heated at 80 °C until TLC indicated the disappearance of the carbene complex (84 h). After cooling to room temperature, 0.13 mL (94 mg, 0.73 mmol) of *i*-Pr_2NEt and 0.10 mL (188 mg, 0.67 mmol) of Tf_2O were added, and the reaction mixture was again deoxygenated by the freeze-pump-thaw method as before and stirred at room temperature. When TLC indicated no further conversion to the triflate complex (24 h), the reaction mixture was poured into 25 mL of brine and extracted with 2 × 25 mL of Et_2O. The combined organics were washed with 1 × 25 mL of 1 N HCl, 1 × 25 mL of H_2O, and 1 × 25 mL of brine and then dried over $MgSO_4$, filtered, and evaporated to give a yellow-brown oil. Flash chromatography on silica gel, eluting with mixtures of hexanes/CH_2Cl_2/Et_2O (50/1/1 to 20/1/1) gave 76 mg (0.115 mmol, a 25% yield) of triflate complex **39** (R_f = 0.56, 4/1/1 hexanes/CH_2Cl_2/Et_2O) as a yellow oil. Spectral data for **39**: ^1H NMR (500 MHz, C_6D_6) δ 0.90 (t, J = 7.3 Hz, 3 H), 1.20−1.65 (complex m, 5 H), 2.12 (s, 6 H), 2.37−2.43 (m, 2 H), 2.51−2.59 (m, 2 H), 2.75−2.80 (m, 2 H), 2.95−3.01 (m, 1 H), 4.74 (s, 1 H); ^{13}C NMR (75 MHz, C_6D_6) δ 14.0, 21.3, 21.8, 24.6, 24.9, 25.8, 32.7, 43.7, 81.5, 103.7, 104.6, 105.5, 118.9 (q, J = 315 Hz), 124.2, 131.6, 232.9; IR (NaCl, thin film, cm^{-1}) 2958m, 2943m, 2875m, 1961s, 1887s, 1407m, 1217m, 1136m, 1032w, 973w, 907w, 837w; mass spectrum (EI) *m/z* (relative intensity) 501 (M^+, 10), 445 (M^+ − 2 CO, 5), 417 (M^+ − 3 CO, 10), 365 (M^+ − $Cr(CO)_3$, 1), 303 (100); *m/z* calcd for $C_{19}H_{22}O_6NCrF_3S$ 501.0525, measd 501.0521.

Reaction of *trans*-Styryl Dimethylamino Carbene Complex 35 with 3-Hexyne.

According to the general procedure described above for **19**, the reaction of 456.6 mg (1.3 mmol) of **27** and 0.154 mL (2.6 mmol) of 3-hexyne in 5.2 mL of benzene was carried out at 86 °C for 19 h. After concentration, the reaction mixture was filtered through silica gel with a 1:1:1 mixture of diethyl ether: methylene chloride:hexane to give 134 mg of a crude product mixture that consisted of five spots on the TLC plate. The crude product mixture was loaded onto a silica gel column. Elution first with a 1:1:10 mixture of diethyl ether:methylene chloride:hexane gave two fractions (first, 5.4 mg; second, 30.3 mg). The second fraction contained starting material **27** as well as another compound. Further elution with a 1:1:4 mixture of diethyl ether:methylene chloride:hexane gave a third fraction (10.4 mg) consisting of a rapidly decomposing mixture of compounds. Finally, elution with a 1:1:1 mixture of diethyl ether:methylene chloride:hexane gave a fourth fraction (4.4 mg) which was also a complex mixture. Given the insignificant amounts and/or relative instability of the products obtained from this reaction further analysis of the outcome of this reaction was not pursued.

Reaction of Isopropenyl Dimethylamino Carbene Complex 30 with 3-Hexyne. The dimethylamino carbene complex **30** (72.3 mg, 0.25 mmol) was reacted with 54.5 μL (0.48 mmol) of 3-hexyne in 1.0 mL of benzene [0.25 M] at 80 °C for 18 h according to the general procedure described above for **19**. This gave 11.6 mg (25% yield) of a 2:2:1 mixture of cyclopentadienes **42**, **43**, and **44** which was isolated from column chromatography on silica gel (eluent: 25% CH_3CN in CH_2Cl_2) followed by preparative TLC (plate size: 20 × 20 cm and 0.25 mm in thickness: eluent: 10% CH_3CN in CH_2Cl_2) as a yellow oil (R_f = 0.59 (10% CH_3CN/CH_2Cl_2)). The following spectral data were taken from spectra collected on the mixture of **42**−**44**. ^1H NMR ($CDCl_3$) δ **42**: 1.18 (t, 6H, J = 7.0 Hz), 2.40 (s, 3H), 2.71 (q, 4H, J = 6.9 Hz), 2.94 (s, 6H), 4.48 (brd, 1H, J = 1.3 Hz), 4.90 (d, 1H, J = 1.3 Hz); **43**: 1.14 (t, 6H, J = 7.8 Hz), 1.42 (d, 3H, J = 6.6 Hz), 1.78 (m, 1H), 2.22 (q, 4H, J = 7.7 Hz), 2.94 (s, 6H), 5.10 (brs, 1H); **44**: 1.08 (t, 3H, J = 7.3 Hz), 1.13 (t, 3H, J = 7.3 Hz), 1.61 (m, 2H), 2.35 (m, 2H), 2.38 (s, 3H), 2.51 (q, 2H, J = 7.1 Hz), 2.90 (s, 6H); IR (neat) cm^{-1} 2969s, 2932m, 2874w, 1652s, 1581s, 1453m, 1432s, 1412s, 1353w, 1056m; mass spectrum (EI) *m/z* (% relative intensity) 179 (5) M^+, 164 (12), 151 (5), 149 (12), 135 (19), 121 (10), 109 (16), 95 (11), 72 (64), 43 (100); *m/z* calcd for $C_{12}H_{21}N$ 179.1674, measd 179.1649. The three isomers were not separable using several different solvent systems. The crude mixture actually contained only isomers **42** and **43**, and the isomer **44** was found only after subjection to column chromatography and preparative TLC. Presumably **44** resulted from the isomerization of either or both **42** or **43**.

Reaction of the Phenyl Dimethylamino Chromium Carbene Complex 45 with 1-Pentyne. The carbene complex **45**[32] (162.6 mg, 0.50 mmol) was reacted with 93.7 μL (0.95 mmol) of 1-pentyne in 1.0 mL of benzene [0.25 M] at 80 °C for 20 h according to the general procedure described above for **19**. The reaction mixture was oxidized by stirring with an excess of a 0.5 M aqueous solution of ceric ammonium nitrate at 25 °C for 30 min. The only major product that was observed for this reaction was the lactam **49** (22.4 mg, 21% yield) which was obtained after purification from column chromatography on silica gel (eluent: 25% CH_3CN in CH_2Cl_2) followed by three consecutive preparative TLC elutions (plate size: 20 × 20 cm and 0.25 mm in thickness; eluent: 5% CH_3CN in CH_2Cl_2 for the first two plates, and 25% CH_3CN in CH_2Cl_2 for the third plate) as a colorless oil. Spectral data for lactam **49**: R_f = 0.51 (25% CH_3CN/CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 0.96 (t, 3H, J = 7.4 Hz), 1.59 (sext, 2H, J = 7.5 Hz), 2.31 (brt, 2H, J = 6.7 Hz), 2.80 (s, 3H), 4.79 (brs, 1H), 6.55 (brs, 1H), 7.06 (d, 2H, J = 7.1 Hz), 7.31 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 13.8, 20.8, 27.2, 27.7, 66.7, 127.1, 128.5, 129.1, 135.8, 138.8, 139.7, 167.8; IR

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(neat) cm^{-5} 2959m, 2929m, 2873w, 1689s, 1639m, 1455m, 1424w, 1392m, 1263w, 1062w; mass spectrum (EI) *m/z* (% relative intensity) 215 (95) M^+, 200 (17), 186 (94), 172 (100), 158 (6), 144 (10), 128 (19), 118 (6), 105 (34), 91 (14), 77 (28); *m/z* calcd for $C_{14}H_{17}NO$ 215.1320, measd 215.1317. With the aid of authentic samples of the quinone **47**[4] and the indanone **46**,[4] analysis of the ^1H NMR spectrum of the crude reaction mixture revealed that **47** and **46** were both formed in less than 3% yield. The reaction was repeated at 0.25 mmol scale and the crude reaction mixture divided into two equal parts one of which was oxidized with CAN. The lactam **49** was isolated in 16% yield (8.4 mg) from the oxidized half of the total crude material and in 12% yield (6.7 mg) from the unoxidized half. While the quinone **47** and indanone **46** could not be detected, the maximum yields of the quinone **47** and indanone **46** for the total reaction were determined to be 5% by analysis of the ^1H NMR of the crude products in the oxidized fraction.

When the reaction of **45** (0.50 mmol) with 1-pentyne (1.9 equiv) was carried out in THF for 18–22 h at 80 °C, the indanone **46** and lactam **49** were isolated in 19% and 15% yields, respectively, which are the averages over several runs. The quinone **47** was found to be present in ≤2% yield by the ^1H NMR spectrum of a portion of the crude reaction mixture that was oxidized with CAN. Also isolated from the reaction in THF (nonoxidative workup) was a colorless oil that was identified as the lactone **48** in 12% average yield. Spectral data for **48**: $R_f = 0.16$ (10% EtOAc/hexane); ^1H NMR ($CDCl_3$) δ 0.90 (t, 3H, $J = 7.3$ Hz), 1.55 (sext, 2H, $J = 7.4$ Hz), 2.22 (m, 1H), 2.26 (m, 1H), 2.31 (s, 6H), 6.81 (s, 1H), 7.31 (m, 3H), 7.44 (d, 2H, $J = 7.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 13.6, 20.7, 27.1, 38.6, 104.2, 126.0, 128.4, 128.7, 133.1, 139.3, 149.7, 173.6; IR (neat) cm^{-1} 2963m, 2958w, 2934w, 2874w, 1753s, 1636w, 1458m, 1448m, 1271m; mass spectrum (EI) *m/z* (% relative intensity) 245 (2) M^+, 229 (53), 201 (100), 172 (9), 158 (12), 140 (5), 115 (9), 105 (98), 91 (10), 77 (37); m/z calcd for $C_{15}H_{19}NO_2$ 245.1416, measd 245.1419. When the reaction was carried out in DMF at 0.25 mmol scale, the indanone **46** was isolated in 32% yield and **47** and **48** were found to be present in <1% yield each by the ^1H NMR spectrum of the crude reaction mixture, and lactam **49** could not be detected.

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Supporting Information Available: Proton NMR spectra for compounds **20**, **26**, **28**, **30–34**, **36–39**, **42–44**, **48**, **49**, **54**, and **57** (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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