Stereoselective Benzannulations and Cyclohexadienone Annulations of Fischer Carbene Complexes in the Synthesis of Decala-2,4-dien-1-ones and in the Synthesis of Tetralin Chromium Tricarbonyl Complexes

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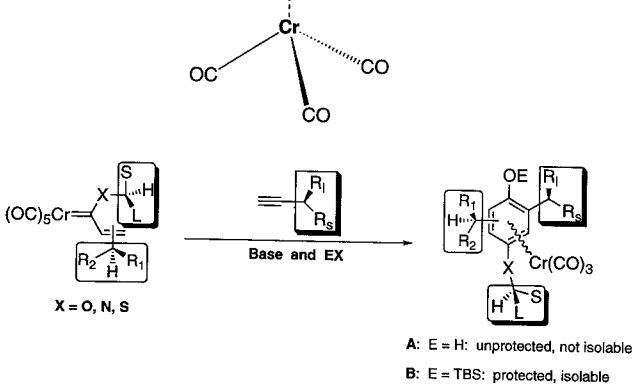
The first general study is reported on the stereoselectivity of the benzannulation reaction involving diastereoselection at the planar center of chirality of the newly formed arene ring complexed to chromium that is induced from a chiral carbon center on the carbene complex. The stereochemistry of a number of 5- and 8-substituted tetralin chromium tricarbonyl complexes, which are produced from the benzannulations of cyclohexenyl carbene complexes with chiral centers at the 3- and 6-positions, is determined. These results are compared with the stereochemistry of the formation of 5,9- and 8,9-disubstituted decala-2,4-dien-1-ones produced from the reactions of the same carbene complexes bearing an additional substituent in the 2-position of the cyclohexenyl ring. The benzannulation reaction is most selective with 3-substituted cyclohexenyl carbene complexes giving predominately the *anti*-isomer of the 8-substituted tetralin chromium tricarbonyl complexes. In contrast, the cyclohexadienone annulation is most selective with 6-substituted cyclohexenyl carbene complexes giving predominately the *trans*-isomer of the 5,9-disubstituted decala-2,4-dien-1-ones. A mechanistic accounting of the stereochemical results is proposed which is predicated on three assumptions: 1) that the η^1,η^3-vinyl carbene complexed intermediate is in equilibrium, 2) vinyl ketene complex formation is irreversible and occurs with a carbon monoxide migration that is in concert with coordination of the double bond of the cyclohexene ring, and 3) the electrocyclic ring closure of the vinyl ketene complex is stereospecific.

The utilization of chiral arene chromium tricarbonyl complexes in organic synthesis has seen a renewal in interest in the last few years.[2] All the arene chromium tricarbonyl complexes that have been used in these studies up to this point have been prepared by the addition of a chromium tricarbonyl fragment to an existing arene ring. The benzannulation reaction of Fischer carbene complexes with alkynes represents an alternative method in which the arene ring is synthesized at the same time that the chromium tricarbonyl group is coordinated to the ring.[3] This reaction is a proven valuable method for the synthesis of new benzene rings where the six carbons of the new arene rings are derived from the two carbons of the alkyne, the carbene carbon of the carbene complex, two carbons of an unsaturated substituent of the carbene carbon and the carbon of a carbon monoxide ligand. Overall, the newly formed ring is generated from three organic fragments in the coordination sphere of the metal generating an arene chromium tricarbonyl complex as the primary product of the reaction. As indicated in Scheme 1, a chiral center is formed when the arene ring is made as a result of the fact that the chromium tricarbonyl group can be located on either of the diastereotopic faces of the newly formed arene ring. The evidence suggests that the arene chromium tricarbonyl complexes that are observed are kinetic products of the reaction and that under the reaction conditions the chromium tricarbonyl group does not migrate to other arene rings.[4,7c] Thus it is possible that benzannulation reactions with chiral alkynes or with chiral carbene complexes possessing a chiral center either in the heteroatom-stabilizing substituent or on the unsaturated carbene carbon substituent could occur with induction of a particular stereochemistry at the newly formed arene-chromium chiral center. In the past it has not been possible to test for asymmetric induction of this type since the free phenol complexes typically are quite air-sensitive and the metal is usually rapidly lost upon exposure to air. However, recently, methods[5] have been developed for the protection of the free phenol function in the newly formed arene chromium tricarbonyl complex and this directly led to the first examination of stereochemical induction in a benzannulation reaction. In the initial study, it was found that high stereochemical selectivities could be obtained with chiral propargyl ethers.[6] Subsequent reports have shown that induction can also be observed from a chiral center on the chiral auxiliary of the carbene complexes and from a chiral center on the carbene carbon substituent although in each case no more than two examples were investigated.[7]

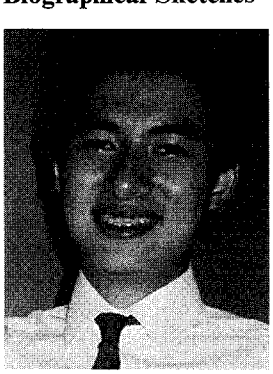


Scheme 1

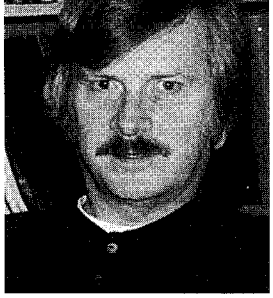
Tetralin arene chromium tricarbonyl complexes have proven to be valuable intermediates in synthesis.[2d,8,9] The arene-chromium chiral center in these complexes has

been used to control the introduction of additional centers of chirality. In the past these complexes have been exclusively prepared by a reaction that introduced the chromium tricarbonyl group onto an existing arene ring of the tetralin system. We decided to undertake the development of an entirely new approach to this class of arene complexes that involves the reactions of cyclohexenyl carbene complexes with alkynes. Previously, we have demonstrated that the unsubstituted cyclohexenyl carbene complexes would undergo reactions with alkynes to generate high yields of tetralin chromium tricarbonyl complexes with various alkynes.[5,10] We then initiated studies to determine the stereoselectivity of the formation of tetralin complexes **5** from the reactions of chiral cyclohexenyl carbene complexes and the findings are reported here for a number of tetralin complexes with substituents in the 5- or 8-positions. The results are discussed in terms of data from a parallel system that were culled from prior[11a] and present studies on the stereoselectivity of the cyclohexadiene annulation reaction. If substituent R^1 on the cyclohexenyl carbene complex **1** is non-hydrogen, then the product of the reaction is the decaladienone **4**. Although the metal is lost from the decaladienone product, the stereoselectivity of the two processes might be expected to be related given the mechanistic commonality of the transient cyclohexadienone metal complex **2** that undergoes tautomerization in the case of $R^1 = H$ and loss of metal in the case when $R^1 \pm H$.[11b]

Biographical Sketches

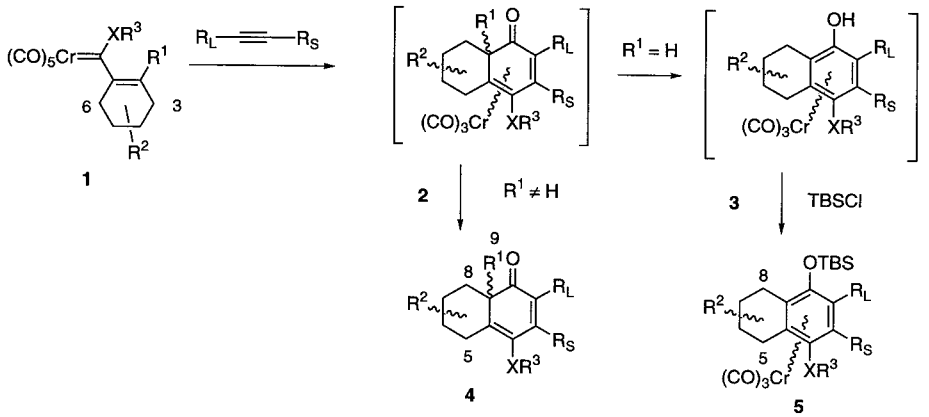


Richard Hsung (1966) received his Ph. D. degree with Professor William D. Wulff at the University of Chicago in 1994. After a post-doctoral stay (1995–1996) with Professor Lawrence R. Sita at the University of Chicago, he joined Professor Gilbert Stork's laboratory at Columbia University as a NIH post-doctoral fellow.



Professor Wulff received his Ph. D. degree from Iowa State University in 1979 with Professor Thomas Barton. After post-doctoral work with Martin Semmelhack at Princeton University, he accepted a position at the University of Chicago in 1980. Professor Wulff's research interests are the applications of organometallics in organic synthesis as both reagents and catalysts.

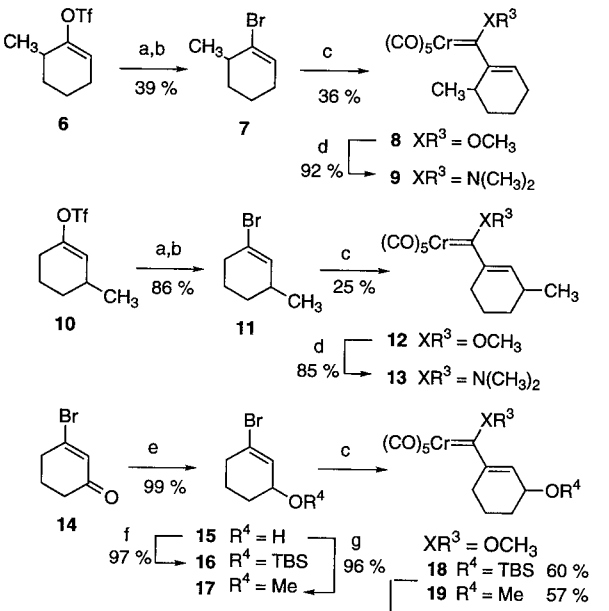
Cynthia Challener received her Ph. D. at the University of Chicago in 1990 studying the mechanisms and reactivity of Fischer carbene complexes with various acetylenes. From 1990 to 1993 she worked at ARCO Chemical Company, first in basic research, and then providing technical support for speciality chemicals. From 1994 to the present she has served as Technical Service Director for Bedoukian Research, Inc., a small manufacturer of flavor and fragrance chemicals and insect pheromones.



Scheme 2

Preparation of Chiral Cyclohexenyl Chromium Carbene Complexes

The set of chiral cyclohexenyl carbene complexes to be examined are presented in Scheme 3 along with their synthesis. This set includes complexes with methyl groups in positions destined to be located at the 5- and 8-positions in the tetralin complexes **5** and also complexes with methoxyl and *tert*-buytyldimethylsilyl groups that will become substituents in the 8-position. In addition, for each of these substitution patterns on the cyclohexenyl ring, complexes containing both methoxyl and dimethylamino groups as the heteroatom-stabilizing group on the carbene complex will be examined. All of the carbene complexes are prepared by the standard Fischer method involving the reaction of chromium hexacarbonyl with a cyclohexenyllithium which was generated from the corresponding cyclohexenyl bromide. The cyclohexenyl bromide **7** was prepared in a regioselective fashion from 2-methylcyclohexanone via the triflate **6**[12] by coupling with tributylstannyl cuprate and then subsequent bromination.[13] The vinyl bromide **11** was made in a similar fashion from the vinyl triflate **10** which was available from 3-methylcyclohexenone by the method of Scott and Crisp.[14] The oxygenated cyclohexenyl carbene complexes were prepared from the alcohol **15**[15] which in turn was prepared by the reduction of the bromoenone **14**.[16] An attractive feature of this synthesis of the carbene complexes **18–21** is that they could easily be obtained in optically pure form since the allylic alcohol **15** can be prepared enantiomerically pure either by using $LiAlH_4$ reduction of the enone **14** in the presence of DARVON alcohol which gives *R*-**15** or NOVRAD alcohol which gives *S*-**15**.[17] Finally, all of the dimethylamino complexes could be obtained in high yield by the exposure of the methoxy complexes to dimethylamine.

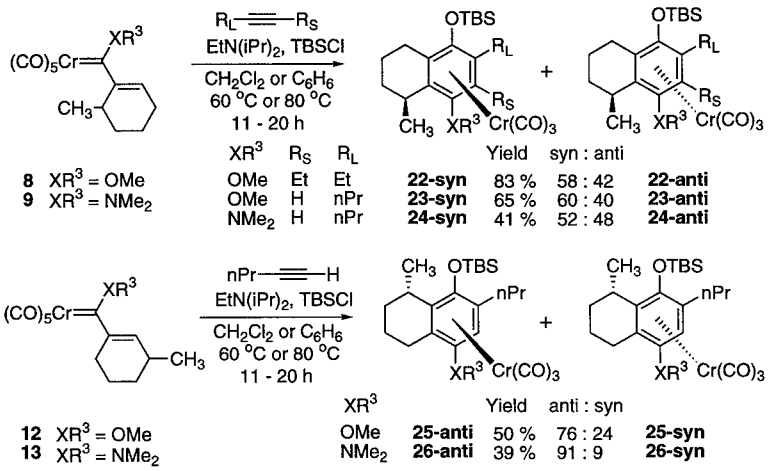


Scheme 3

a. LDA, $(n\text{-Bu})_3SnH$, CuCN, −78 °C to −40 °C, 19 h. b. Br_2, pentane, −78 °C, 3 h. c. i. *t*-BuLi (2.0 eq), Et_2O, −78 °C, 2 h.; ii. $Cr(CO)_6$, Et_2O, −78 °C to r.t., 3 h; MeOTf, −10 °C, 1 h. d. dimethylamine, THF, −78 °C, 15 min. e. i. Dibal-H, THF, −78 °C, 2.5–14 h; ii. CH_3OH, 0 °C, 2 h; iii. 2 NHCl. f. Imidazole, TBSOTf, CH_2Cl_2, r.t., 6 h. g. NaH, THF, MeI, −10 °C to r.t., 30 h. h. Dimethylamine, hexane, −78 °C, 15 min.

Stereoselective Benzannulation Reactions

The typical conditions for the reactions of the methoxy substituted carbene complexes is illustrated by the reaction of the 6-methoxycyclohexenyl complex **8** with 1.9 equivalent of pent-1-yne where the benzannulation is performed in the presence of 3.0 equivalents of diisopropylethylamine (Hünig's base) and two equivalents of *tert*-butyldimethylsilyl chloride (TBSCl) in dichloromethane at 0.05 M in the carbene complex at 60 °C. The benzannulation reaction of the corresponding amino complex **9** with pent-1-yne was conducted in benzene at 0.27 M since it is known that the benzannulations of amino complexes give substantial amounts of five-membered ring side-products in more polar and coordinating solvents and at lower concentrations.[10] The reactions of the amino complexes were carried out at higher temperature (80 °C) since the rate-limiting loss of a carbon monoxide ligand is much slower in these complexes. As indicated in Scheme 4, the generation of the 5-methyltetralin chromium tricarbonyl complexes **22–24** from the carbene complexes **8** and **9** occurs with a low but consistent preference for the formation of the *syn*-isomer. The stereo-

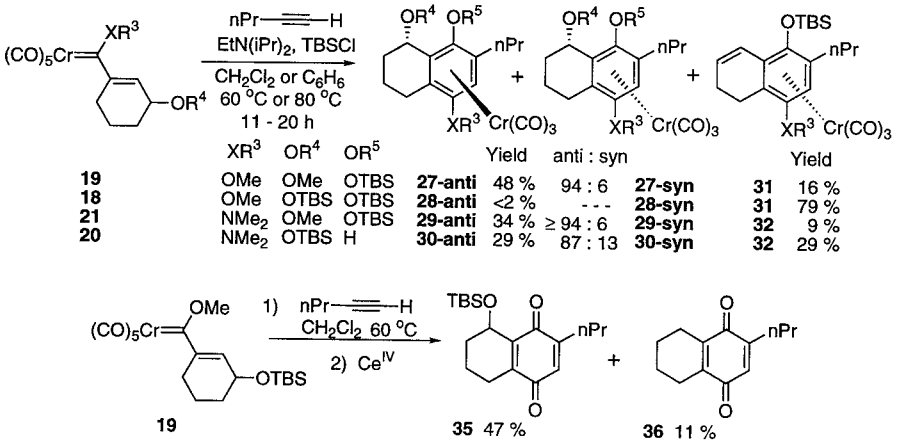


Scheme 4

chemical assignments were made by ^{1}H NMR as discussed below. No difference in the stereoselection was observed between hex-3-yne and pent-1-yne and in conjunction with the observation that the reactions of alkenyl amino carbene complexes do not give benzannulated products with internal alkynes[10] the decision was made to limit the scope of the present work to reactions with terminal alkynes. It was interesting to find that, while the 5-methyltetralin derivatives **22–24** are formed with low selectivity, the 8-methyltetralin complexes **25–26** are formed with a higher stereoselectivity which is more pronounced with the amino carbene complex **13** than with the methoxy carbene complex **12**. Most interesting of all, the sense of stereoselection is reversed with a preference for the *anti*-isomer observed for the 8-methyltetralin complexes.

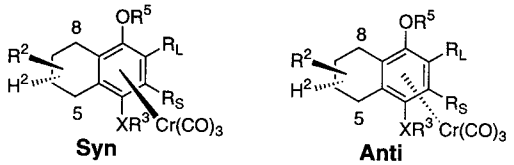
As was observed for the 3-methylcyclohexenyl carbene complex **12**, the benzannulation reaction of the 3-methoxycyclohexenyl carbene complex **19** with pent-1-yne is also *anti*-selective. The 8-methoxytetralin chromium tricarbonyl complex **27** was isolated in 48 % yield with a 94:6 selectivity and, in addition, the didehydrotetralin chromium tricarbonyl complex **31** was isolated in 16 % yield. This elimination process was more pronounced with the 3-siloxy-substituted carbene complex **18** and in fact the elimination product **31** was the only isolable product from this reaction (79 %). The elimination reaction is less prominent for the amino carbene complexes since the 8-*tert*-butyldimethylsilyloxytetralin chromium tricarbonyl complex **30** could be isolated from the reaction of amino complex **20** with pent-1-yne with an 87:13 ratio of *anti*- to *syn*-isomers. In this case it was found that the phenol function in the benzannulated product was not silylated which may be due to steric hindrance associated with the silyl group in the 8-position. This phenol chromium tricarbonyl complex **30** was somewhat sensitive and decomposed to a purple material after short periods but could be purified by silica gel chromatography and obtained as a yellow oil. If the benzannulation of complex **19** is carried out in the absence of a base and the crude products oxidized with ceric ammonium nitrate, the quinone **35** bearing the 8-*tert*-butyldimethylsiloxy group was isolated in 47 % yield. A second product isolated from this reaction is the reduced quinone **36**. We have not attempted to identify the mechanism by which either the elimination product **31** or the reduction product **36** are formed or whether their formation is mechanistically related. The formation of the elimination products **31** and **32** from the reactions shown in Scheme 5 renders the stereoselectivity of these reactions less clear. While the reaction of complex **18** with pent-1-yne demonstrates the case that both *syn*- and *anti*-isomers can suffer elimination of an oxygen substituent at the 8-position, the possibility that the *syn*- and *anti*-isomers undergo elimination at different rates calls into question the exact stereoselectivities for these reactions. The selectivity for the formation of **27** would fall to 75:25 if **31** is formed only from the *syn*-isomer and would rise to 95:5 if formed exclusively from the *anti*-isomer. In any event, it is clear that these reactions selectively give rise to the *anti*-isomers and that 8-oxygenated tetralin complexes can be isolated from these reactions with high stereoselectivities.

The stereochemical assignments for the tetralin chromium tricarbonyl complexes **22–30** were made on the basis of their ^{1}H NMR spectra. It is well established for tetralin and indane chromium tricarbonyl complexes that protons on the saturated ring that are *syn* to the metal are shifted downfield relative to their isomers in which the same proton is *anti* to the metal center.[8d,18] The chemical shifts for the protons directly attached to the chiral carbon of the tetralin ring (R^2) for both the *syn*- and *anti*-isomers are presented in Table 1 except for the *syn*-isomer of **29** whose formation could not be detected from the reaction of complex **21** with pent-1-yne. The chemical shifts are also listed for the substituent R^2 when R^2 is methyl or methoxyl. As can be seen from the data in Table 1, there is a correlation between the chemical shits of H^2 and R^2. For the *syn*-isomers H^2 is shifted upfield from same protons in the *anti*-isomers and the protons on R^2 are shifted downfield relative to the same protons in the *anti*-isomers. As indicated in the Table, the H^2 protons are deshielded by approximately $\delta = 0.3$ and the protons of the methyl and methoxy groups of R^2 are deshielded by approximately $\delta = 0.1$ when they are *syn* to the chromium tricarbonyl group.



Scheme 5

Table 1. ^{1}H NMR Chemical Shift Correlations for the *Syn* and *Anti* Chromium Tricarbonyl Complexes.[a]

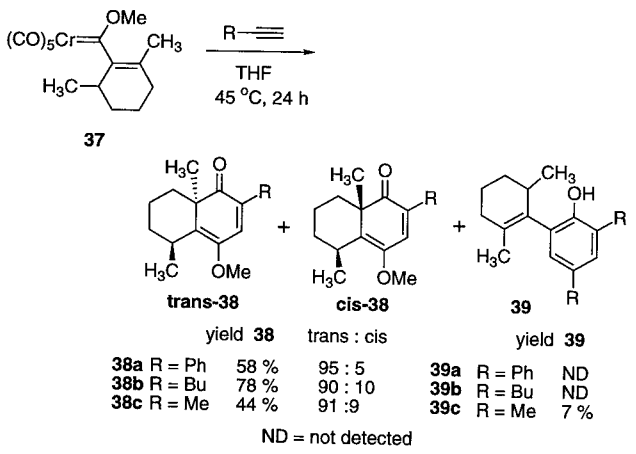


Arene Complex	R^2	XR^3	*Syn* : *Anti*	Major Isomer	*Syn* Isomer δ H^2	*Syn* Isomer δ R^2	*Anti* Isomer δ H^2	*Anti* Isomer δ R^2	δ *Syn*–δ *Anti* $\Delta\delta$ H^2	δ *Syn*–δ *Anti* $\Delta\delta$ R^2
22	5-Me	OMe	58 : 42	*Syn*	2.83	1.41	3.07	1.29	– 0.24	0.12
23	5-Me	OMe	60 : 40	*Syn*	2.86	1.30	3.13	1.21	– 0.27	0.09
24	5-Me	NMe_2	52 : 48	*Syn*	NA	1.44	NA	1.36	–	0.08
25	8-Me	OMe	24 : 76	*Anti*	3.05	1.35	3.19	1.28	– 0.14	0.07
26	8-Me	NMe_2	9 : 91	*Anti*	2.54	1.42	2.82	1.33	– 0.28	0.09
27	8-OMe	OMe	6 : 94	*Anti*	4.26	3.41	4.61	3.35	– 0.35	0.06
29	8-OMe	NMe_2	< 6 : 94	*Anti*	ND	ND	4.67	3.30	ND	ND
30	8-OTBS	NMe_2	13 : 87	*Anti*	4.87	–	5.07	–	– 0.20	–

[a] NA = not assigned. ND = not determined.

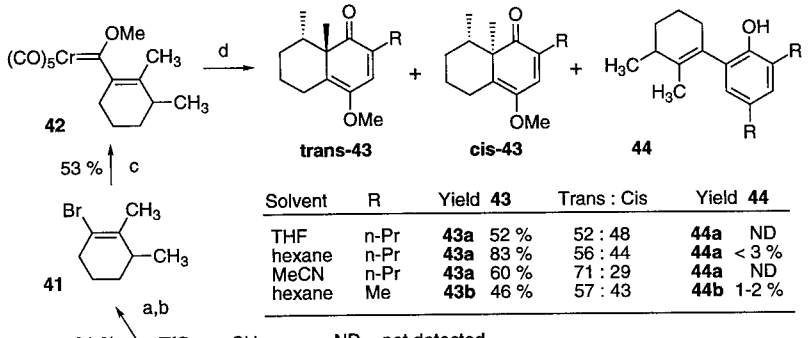
Stereoselective Cyclohexadienone Annulation

The lack of stereoselectivity observed in the benzannulation of the 6-methylcyclohexenyl carbene complexes **8** and **9** that was observed in the present work stands in contrast to the relatively high stereoselectivities that we had previously reported for the cyclohexadienone annulation of the 2,6-dimethylcyclohexenyl carbene complex **37**.[11] In this study it was found that complex **37** would react with a number of terminal alkynes to give greater than 90 % selectivity for the *trans*-isomer of the decaladienone product in all cases. This reaction also gave small amounts of the phenol **39** which results from the incorporation of two equivalents of the alkyne and which is more prevalent for those reactions with smaller alkynes. The method by which the stereochemistry of the decaladienone product **38** was assigned in these reactions has already been described.[20] The difference in selectivity observed for the 6-methyl-substituted carbene complexes **8** and **37** which differ by the presence of a methyl group in the 2-position raised the question of whether the stereoselectivity of the benzannulation of the 3-methylcyclohexenyl complex **12** would be related to the stereoselectivity of the cyclohexadienone annulation of the 2,3-dimethylcyclohexenyl carbene complex **42**. We thus set out to prepare complex **42** and evaluate the stereoselectivity of its reactions with terminal alkynes.



Scheme 6

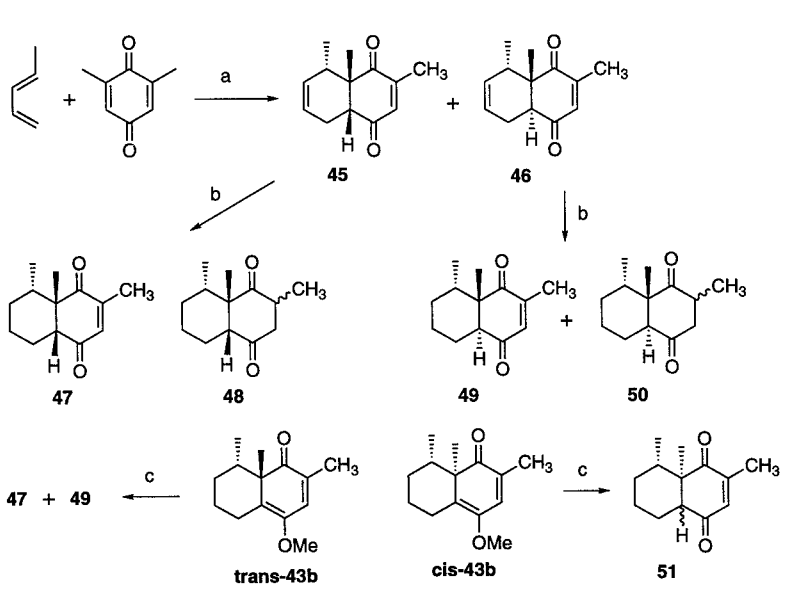
The carbene complex **42** was prepared from 1-bromo-2,3-dimethylcyclohexene as indicated in Scheme 7. This vinyl bromide was prepared from the vinyl triflate **40** by coupling with tributylstannyl higher order cuprate[13] and the vinyl triflate was made by trapping of the enolate generated from the addition of methylcuprate to 2-methylcyclohexenone.[12] The reaction of complex **42** was examined with pent-1-yne and it was found that a very low stereoselectivity was observed in noncoordinating solvents giving nearly an equal mixture of the *trans*- and *cis*-dimethyldecaladienones **43**. The reaction with propyne was also examined and under the proper conditions the yield of the two-alkyne phenol product **44b** could be minimized and a 46% yield of the decaladienone **43b** could be obtained with essentially the same selectivity as was observed with pent-1-yne. The stereoselectivity was enhanced slightly in favor of the *trans* product when the reaction of **42** with pent-1-yne was carried out in acetonitrile. We have not pursued the source of this effect nor have we carried out the reactions of complexes **37**, **8** or **9** in acetonitrile. It has been previously suggested that strongly coordinating solvents such as acetonitrile can displace the metal from vinyl ketene intemediates and thus the stereoselectivity may result from cyclizations of metal-free vinyl ketenes (vide infra).[20] No such strong differences have been observed between THF and dichloromethane as solvent for these reactions.[21]



Solvent	R	Yield 43	Trans : Cis	Yield 44
THF	n-Pr	**43a** 52 %	52 : 48	**44a** ND
hexane	n-Pr	**43a** 83 %	56 : 44	**44a** < 3 %
MeCN	n-Pr	**43a** 60 %	71 : 29	**44a** ND
hexane	Me	**43b** 46 %	57 : 43	**44b** 1-2 %

a. LDA, $(n\text{-Bu})_3SnH$, CuCN, THF, −78 to −20 °C, 2 h. b. Br_2, pentane, −78 °C, 1 h. c. *t*-BuLi (2 eq), THF, −78 °C, 20 min; ii, $Cr(CO)_6$, THF, 0 to 25 °C, 1 h; iii, MeOTf, 25 °C, 10 min. d. RC≡CH (1.5 eq), solvent, 60 °C, 24 h.

Scheme 7



a. $TiCl_4$, −78 °C, 30 min. b. $(PPh_3)_3RhCl$, H_2 (1 atm), benzene, 25 °C, 17 h. c. THF/10% aq HCl (1:1), 65 °C, 1.5 h.

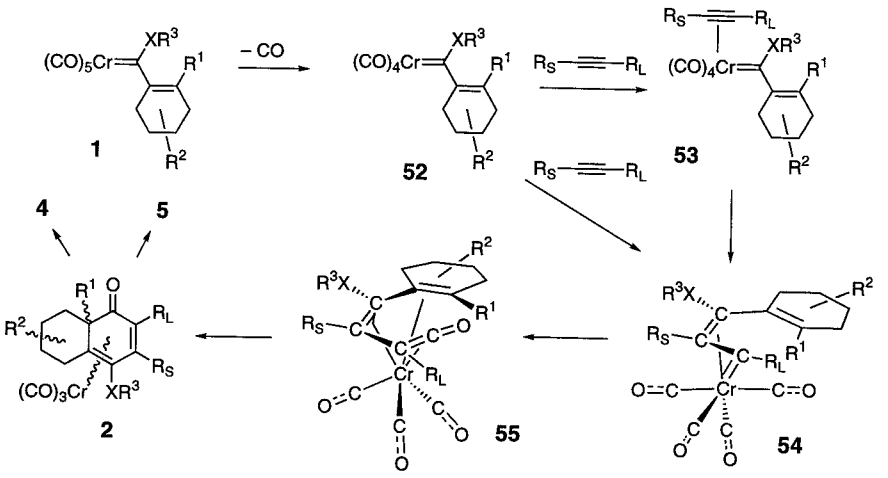
Scheme 8

The assignment of the major isomer of the decaladienone **43a** obtained from the reaction of complex **42** with pent-1-yne as the *trans*-isomer was determined by the chemical correlation outlined in Scheme 8. This correlation was made possible by the fact that titanium(IV) chloride (and not boron trifluoride–diethyl ether complex) is known to catalyze the reaction of *trans*-piperylene and 2,5-dimethylbenzoquinone to give the *endo* adduct **45** having a *trans* relationship of the two methyl groups.[22] We have found that if this reaction is carried out at −78 °C and then warmed to 0 °C and quenched immediately, a 93% yield of **45** can be obtained whereas if the mixture is warmed to 25 °C and quenched after 30 minutes that the major product is the epimer **46**. Reduction of the cycloadduct **45** with Wilkinson's catalyst gives a mixture of the mono-reduced and doubly-reduced products **47** and **48**, respectively, the latter as a mixture of diastereomers. A separate reduction of the epimer of the cycloadduct under the same conditions gave a mixture of the reduced products **49** and **50** with the overreduced product again as a mixture of diastereomers. Hydrolysis of the major isomer of the 4-methoxydecaladienone **43b** with HCl in aqueous THF gave a mixture of **47** and **49**. Hydrolysis of the major isomer of the 4-methoxydecaladienone **43b** with HCl in aqueous THF gave a mixture of **47** and **49**. Hydrolysis of the minor isomer of **43b** gave a mixture of two diastereomers neither of which was identical to **47** or **49** as determined by their NMR spectral data. Based on these observations, the major product from the reaction of complex **42** with propyne is *trans*-**43b** and thus, by inference, *trans*-**43a** is the major product with pent-1-yne.

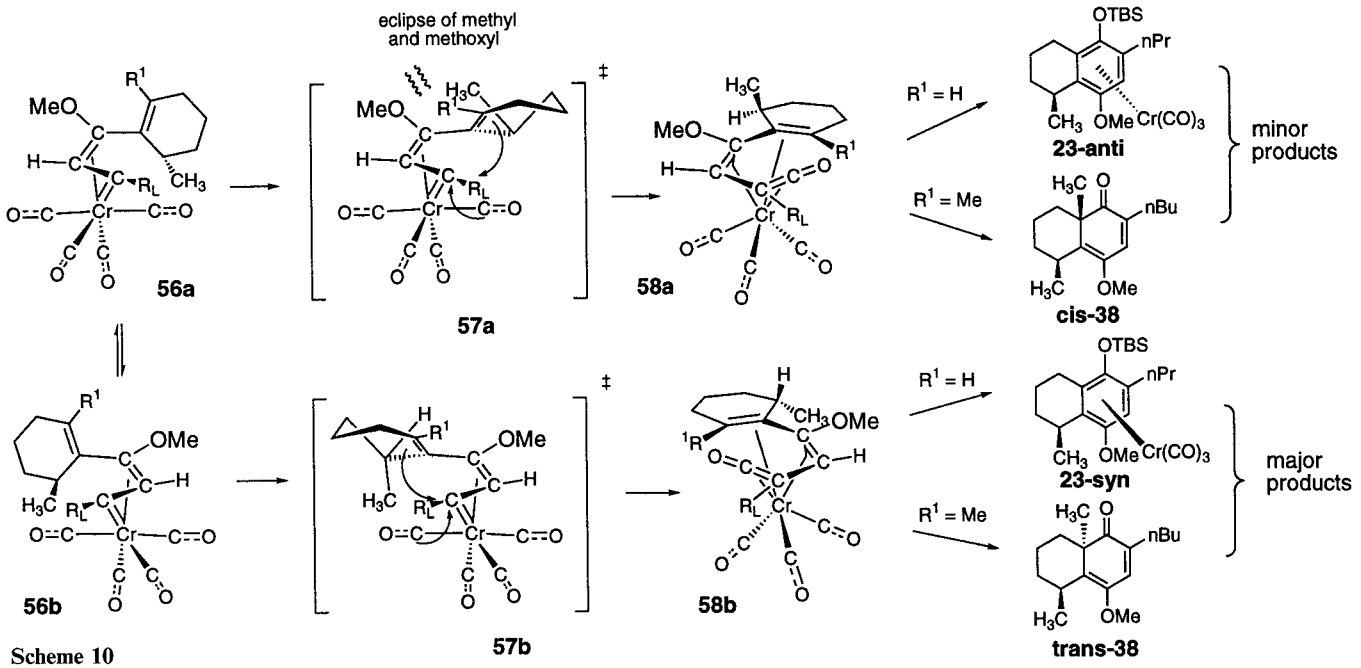
Discussion

An analysis of the source of the stereoselectivities observed in the benzannulation and cyclohexadienone annulation reactions described in this work begins with a consideration of information available concerning the mechanism of the reaction. The mechanism outlined in Scheme 9 represents the best thinking at the moment and is the result of a combination of kinetic studies,[23] theoretical calculations[24] and product analysis.[25] The overall rate-limiting step of the reaction is the initial loss of a carbon monoxide ligand from the carbene complex to give the unsaturated 16 e$^-$ complex **52**.[23a] The alkyne then is thought to react with this unsaturated carbene complex either by coordination of the alkyne to give **53** and then carbon–carbon bond formation to give the η^1,η^3-vinyl carbene complexed intermediate **54** or by a direct addition of the alkyne to **52** to give **54** directly.[24] A migratory insertion of a carbon monoxide ligand gives the vinyl ketene complex **55** which upon electrocyclic ring closure is thought to give the metal coordinated cyclohexadienone intermediate **2** as the penultimate intermediate in the reaction. Loss of the metal gives rise to the decaladienone product **4** when $R^1 \neq H$ and tautomerization when $R^1 = H$ gives the tetralin chromium tricarbonyl complex **3** (**5** upon in situ protection of the phenol).

The level of detail in the understanding of the mechanism of the reactions of carbene complexes with alkynes is not sufficient at this point in time to provide an explanation for the stereoselectivities observed in the present work. We will therefore only propose an explanation for these stereoselectivities which is consistent with the observations but not demanded by them. The premise to the proposal outlined below is a set of three assumptions. In Scheme 10, these assumptions are brought to bear on the reactions of the 6-methyl-substituted cyclohexenyl carbene complexes **8** and **37**. The first assumption is that the two diastereomers of the vinyl carbene complexed intermediates **56a** and **56b** are in equilibrium relative to product formation. This is supported by calculations by Hofmann, Hämmerle and Unfried[24] that suggest that this is possible and by indirect experimental evidence by Gross and Finn[26] in an intramolecular reaction of an aryl chromium carbene complex. More recently this assumption has been supported by direct experimental evidence from work in our laboratories[23b] on an intermolecular reaction of an aryl carbene complex with 2-phenylpropyne. The second assumption is that the migratory insertion of the carbon monoxide ligand occurs with simultaneous coordination of the double bond of the cyclohexenyl ring in **56a** to the chromium to give the vinyl ketene complex **58a** via a transition state that resembles **57a**. While this has no experimental or theoretical support, this has been suggested before because this process maintains a saturated metal center during the course of the reaction.[25b] The third assumption is that the elec-



Scheme 9

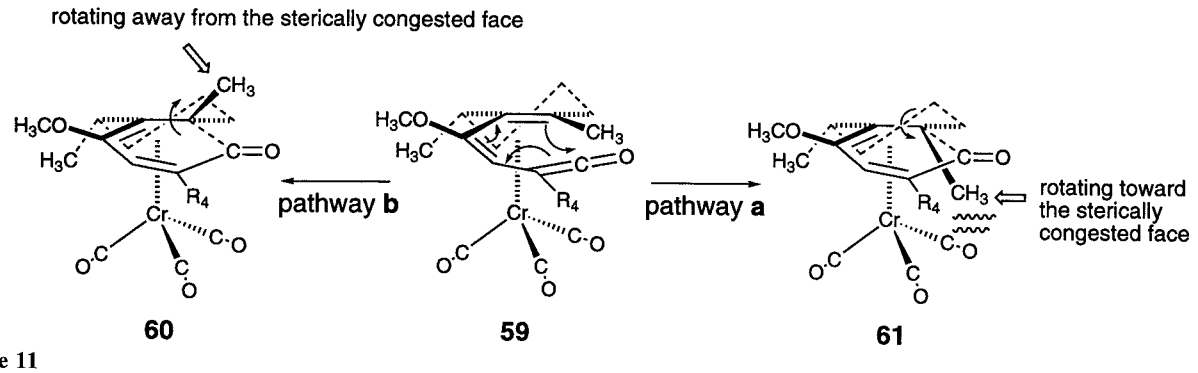


Scheme 10

trocyclic ring closure of the vinyl ketene complex occurs with rotation of the *syn* substituent on the carbon terminus of the η^6-vinyl carbene complex away from the metal center. This is illustrated in Scheme 11 by rotation of the methyl group in vinyl ketene complex **59** by pathway b rather than pathway a. This is supported by a recent experimental study in our laboratories on the stereochemistry of the cyclohexadienone annulation with chiral propargyl ethers which reveals that the electrophilic ring closure of the vinyl ketene complex is stereospecific.[27]

The reactions of the 6-methyl-substituted cyclohexenyl carbene complexes **8** and **37** will involve the two diastereomeric vinyl carbene complexed intemediates **56a** and **56b**. An examination of both mechanical and computer models (Chem 3D with coordinates taken from Hofmann's calculations[24]) suggests that the more stable conformations of the indicated rotation of the cyclohexenyl group will be those in which the cyclohexenyl plane is approximately perpendicular to the plane containing the three carbons of the vinyl carbene ligand. While we have not identified minimal energy conformations for **56a** and **56b**, there appear to be several conformations of similar energy for both of these species. The lowest energy conformations for **56a** appear to be those with the cyclohexenyl group rotated slightly inward and those for **56b** with the cyclohexenyl group rotated slightly outward (avoiding interactions of the methyl group with the metal center). While electronic factors have been proposed to have an influence of the relative energies of the conformations of vinyl carbene complexed intermediates,[6] neither electronic nor steric factors are anticipated to have an influence on the conformations of either **56a** or **56b** that could lead to any substantial energy difference between the two. Instead, the selectivity in the reactions involving these intermediates is thought to involve the transition states for carbon monoxide insertion. The transition state is proposed to be reached by a rotation of the cyclohexenyl group into a position where the double bond of the cyclohexenyl ring can begin to coordinate to the metal center as the carbon monoxide ligand migrates to the vinyl carbene ligand. In the course of the indicated rotation of the cyclohexenyl group, an eclipsing interaction between the methyl group in the 6-position of the cyclohexene ring and the methoxyl group of the vinyl carbene ligand is generated for **57a** but not for **57b**. This then leads to the preferential formation of the vinyl ketene complex **58b** and to the preferential formation of the *syn*-isomer of the tetralin complex **23** (from complex **8**) and to the preferential formation of the *trans*-isomer of the cyclohexadienone **38** (from complex **37**). As indicated by the data in Scheme 4 and 6, the cyclohexadienone **38** is formed with a much higher selectivity that the tetralin complex **23**. This could be due to an earlier transition state in the case when R^1 is a methyl group than when R^1 is a hydrogen. In the vinyl ketene complex **58a** the methoxyl group is not eclipsed with the methyl group on the 6-position on the cyclohexenyl ring. The maximum eclipsing interaction will occur substantially prior to the formation of **58a**. It is proposed that the eclipsing interaction is greater for the transition state for the complex having R^1 = methyl than for the transition state having R^1 = hydrogen due to a steric interaction between R^1 and the top part of the vinyl carbene ligand. When R^1 is methyl, a greater interaction will develop between R^1 and the vinyl carbene ligand and this will be felt at an earlier point along the path from **56a** to **58a** as the cyclohexenyl group rotates into position to coordinate to the metal.

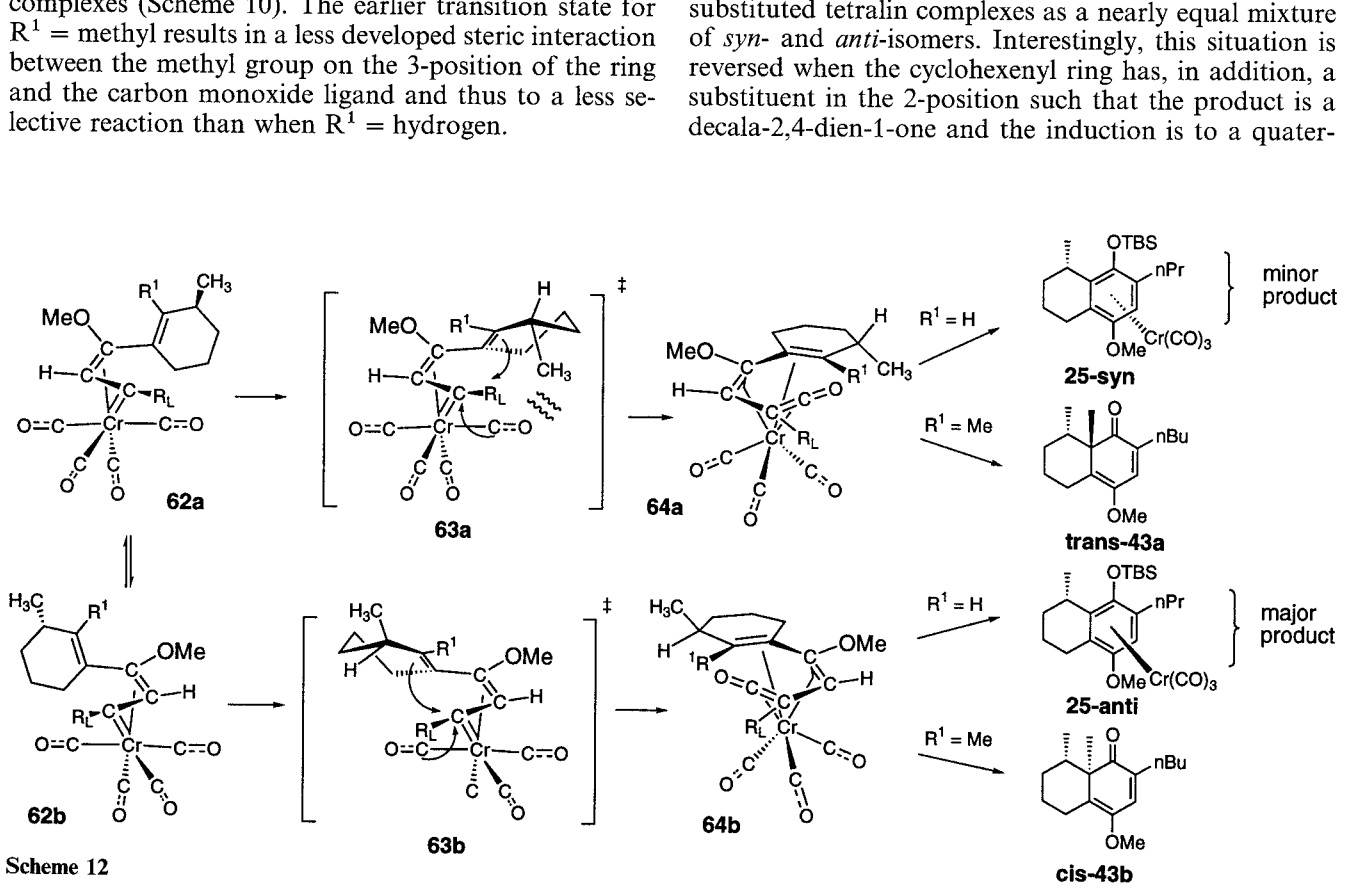
A consideration of the diastereomeric intermediates involved in the reactions of the 3-methyl-substituted cyclohexenyl complexes **12** and **42** are provided in Scheme 12. In this case the important difference between the two diastereomer transition states **63a** and **63b** is proposed to be a steric interaction between the methyl group on



Scheme 11

the 3-position on the cyclohexenyl ring and a carbon monoxide ligand on the metal center which is present in **63a** but not in **63b** (this methyl is not close to R_L which is coming out of the plane of the drawing). This would lead to the prediction of a preferential formation of the *anti*-isomer of the tetralin complex **25** and to the preferential formation of this *cis*-isomer of the cyclohexadienone **43**. The *anti*-isomer of **25** is in fact the major product, but the cyclohexadienone **43** is formed as essentially an equal mixture of isomers. Unlike the case with the 6-methyl-substituted cyclohexenyl complexes (Scheme 10), here the tetralin complexes are formed with a higher stereoselection than the cyclohexadienones. This is proposed to be due to an earlier transition state when R^1 = methyl than when R^1 = hydrogen for the reasons discussed above for the reactions of the 6-substituted complexes (Scheme 10). The earlier transition state for R^1 = methyl results in a less developed steric interaction between the methyl group on the 3-position of the ring and the carbon monoxide ligand and thus to a less selective reaction than when R^1 = hydrogen.

The present study represents the first attempt to establish the scope of the diastereoselection associated with the introduction of the planar center of chirality of an arene chromium tricarbonyl complex via the benzannulation of a carbene complex bearing a chiral center at carbon on the α,β-unsaturated carbene carbon substituent.[28] Specifically, the diastereoselectivity was examined for induction from the 3- and 6-positions of cyclohexenyl carbene complexes to the newly formed arene-chromium chiral center of the tetralin chromium tricarbonyl complexes produced from their reactions with alkynes. High inductions were observed in the reactions of the 3-substituted cyclohexenyl carbene complexes leading to *anti*-isomers of the 8-substituted tetralin chromium tricarbonyl complexes. Low inductions were observed for those complexes with substituents in the 6-position which gave 5-substituted tetralin complexes as a nearly equal mixture of *syn*- and *anti*-isomers. Interestingly, this situation is reversed when the cyclohexenyl ring has, in addition, a substituent in the 2-position such that the product is a decala-2,4-dien-1-one and the induction is to a quater-



Scheme 12

nary carbon center rather than to the arene-chromium center. High inductions are observed for the formation of the *trans*-isomer of 5,9-disubstituted decala-2,4-dienones and low inductions are observed in the formation of the 8,9-disubstituted derivatives. The results of the present study do not allow for an unambiguous detailed mechanistic accounting of the stereoselectivities of these reactions but it is hoped that the proposed mechanisms that are put forth in this work will serve to stimulate future investigations.

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Tetrahydrofuran (THF), Et_2O and benzene were distilled from benzophenone ketyl under N_2. MeCN, hexane, and CH_2Cl_2 were distilled from CaH_2 under N_2. ^1H and ^{13}C NMR data (δ, ppm) were obtained either on a University of Chicago built DS-1000 500 MHz instrument or a General Electric QE-300 MHz instrument with TMS as internal standard. HRMS were recorded on a VG 70-250 instrument or obtained from the Midwest Center for Mass Spectrometry in Lincoln, Nebraska. Elemental analyses were done by Galbraith Laboratories in Knoxville, Tennessee.

3-Methylcyclohex-1-enyl Triflate (10):
A solution of 3-methylcyclohex-2-enone (2.22 g, 20.2 mmol) in THF (120 mL) was cooled to −78 °C and L-Selectride (1 M in THF) (21.0 mL, 21.0 mmol, 1.05 equiv) was added dropwise. The mixture was stirred at −78 °C for 2 h, and then Tf_2NPh (7.22 g, 20.2 mmol, 1.0 equiv) was added as a solid. The mixture was slowly warmed to r.t. over 2 h and stirred at r.t. for 15 h. The mixture was stripped of volatiles under reduced pressure and was redissolved in pentane (300 mL). This solution was washed with 0.1 M aq NaOH (300 mL) and, after separation, the aqueous layer was extracted with pentane (100 mL). The combined pentane layers were washed with brine (300 mL) dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude oil was filtered through a short silica gel column (6.5 × 4 cm) with the aid of pentane (800 mL). After evaporating the solvent under reduced pressure, the residue oil was loaded onto a silica gel column. The vinyl triflate **10** was eluted from the column with pentane (R_f = 0.25) to give **10** as a colorless oil; yield: 629.0 mg (13%).

^1H NMR ($CDCl_3$): δ = 1.05 (d, 3H, J = 7.2 Hz), 1.21 (m, 1H), 1.69 (m, 1H), 1.77 (m, 1H), 1.88 (m, 1H), 2.28 (m, 2H), 2.41 (m, 1H), 5.58 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = 20.9, 21.3, 27.5, 29.7, 29.9, 118.5 (q, J = 320.2 Hz), 124.0, 149.2.

IR (neat): ν = 2952 m, 2936 m, 2874 w, 1684 w, 1458 w, 1418 s, 1364 w, 1246 s, 1209 s, 1144 s, 1080 m, 1058 w, 1020, 992 w, 979 s, 958 s, 883 s, 852 m, 809 cm^{-1}.

MS (EI): m/z (% rel intensity): 244 (7) M^+, 243 (27) $M^+ - H$), 229 (33), 220 (14), 205 (28), 187 (14), 163 (31), 151 (85), 137 (21), 111 (32), 95 (100); exact mass calcd for $C_8H_{10}F_3O_3S$ m/z 243.0303; found m/z 243.0286.

This procedure for the preparation of vinyl triflates by conjugate reduction follows the published method[18] but for this particular case the alternative approach involving conjugate addition would likely give superior results.[15]

1-Bromo-3-methylcyclohexene (11):
An LDA solution was prepared by the addition of BuLi (1.6 M in hexane) (5.88 mL, 9.44 mmol, 2.6 equiv) to *i*-Pr_2NH (1.58 mL, 9.44 mmol, 2.6 equiv) in THF (100 mL) at −78 °C. After the LDA solution was stirred at −78 °C for 1 h, $HSn(n\text{-}Bu)_3$ (2.15 mL, 7.99 mmol, 2.2 equiv) was added, and 1 h later, CuCN (357.7 mg, 3.99 mmol, 1.1 equiv) was added to provide a lemon yellow solution. After another hour at −78 °C, vinyl triflate **10** (886.7 mg, 3.63 mmol) was added via a cannula as a solution in THF (25 mL). The mixture was stirred at −78 °C for 8 h and at −40 °C to −35 °C for 18 h. The orange-red solution was evaporated under reduced pressure, and poured into 10% aq NH_4Cl (250 mL) overlaid with pentane (250 mL). The pentane layer was separated, washed with 10% aq NH_4Cl (2 × 250 mL) and with brine (250 mL), dried (Na_2SO_4) filtered through Celite, and evaporated under reduced pressure to provide a colorless oil which consisted of fairly pure 3-methyl-1-tributylstannylcyclohexene which used without further purification. R_f = 0.85 (pentane).

^1H NMR ($CDCl_3$): δ = 0.88 (m, 9H), 0.95 (d, 3H, J = 7.2 Hz), 1.15 (m, 1H), 1.20 (m, 1H), 1.31 (m, 6H), 1.47 (m, 6H), 1.58 (m, 7H), 1.73 (m, 1H), 2.09 (m, 2H), 2.19 (m, 1H), 5.58 (d, 1H, J = 1.3 Hz).

IR (neat): ν = 2955 s, 2928 s, 2918 s, 2871 s, 2853 s, 1464 s, 1457 s, 1418 m, 1376 s, 1357 w, 1340 m, 1071 m, 995 w, 960 w, 873 cm^{-1}.

MS (EI): m/z (% rel intensity): 329 (100, ^{120}Sn) $M^+ - n$Bu, 273 (55, ^{120}Sn), 217 (82, ^{120}Sn).

All of the above vinylstannane was dissolved in pentane (60 mL) and cooled to −78 °C and reacted with Br_2 (4.0 mL, 1.0 M in pentane) which was added dropwise. After stirring at −78 °C for 2.5 h, TLC (pentane) analysis showed the disappearance of the vinylstannane and emergence of the product. The solution should be a light yellow at this point or else overbromination may have occurred. The mixture was poured into H_2O (200 mL) overlaid with pentane (200 mL). The pentane layer was separated, washed with brine (200 mL) dried (Na_2SO_4), filtered through Celite/Na_2SO_4/silica gel mixture (~ 1:1:1), and evaporated under reduced pressure to provide a yellow oil which was chromatographed on a silica gel column with pentane to afford vinyl bromide **11** as a colorless oil; yield: 545.0 mg (86% for the two steps) R_f = 0.60 (pentane).

^1H NMR ($CDCl_3$): δ = 0.99 (d, 3H, J = 7.1 Hz), 1.29 (m, 1H), 1.50 (m, 1H), 1.65 (m, 1H), 1.77 (m, 1H), 2.27 (m, 1H), 2.37 (m, 2H), 5.88 (d, 1H, J = 1.2 Hz).

^{13}C NMR ($CDCl_3$): δ = 21.1, 23.2, 29.8, 33.1, 35.2, 132.1, 134.8.

IR (neat): ν = 2953 s, 2926 s, 1646 w, 1457 m, 1465 s, 1376 m, 1381 m, 1098 w, 737 cm^{-1}.

MS (EI): m/z (% rel intensity): 176 (21, ^{81}Br) M^+, 174 (21, ^{79}Br), M^+, 96 (100), 81 (18), 79 (18), 67 (25); exact mass calcd for $C_7H_{11}{}^{79}Br$ 174.0044; found m/z 174.0039.

1-Bromo-3-t-butyldimethylsilyloxycyclohexene (16):
Allylic alcohol **15**[15] (1.55 g, 8.76 mmol), prepared from bromoenone **14**,[16] was dissolved in CH_2Cl_2 (200 mL) at r.t. and then imidazole (715.7 mg, 10.5 mmol, 1.2 equiv) and TBSOTf (2.55 g, 9.64 mmol, 1.1 equiv) were added. The mixture was stirred at r.t. for 6 h and monitored by TLC (hexane, $KMnO_4$). When the starting alcohol was completely consumed, the mixture was evaporated under reduced pressure and chromatographed on a silica gel column with hexane as eluent to provide the pure vinyl bromide **16** as a colorless oil; yield: 2.46 g (96%). R_f = 0.20 (hexane).

^1H NMR ($CDCl_3$): δ = 0.07 (s, 3H), 0.08 (s, 3H), 0.89 (s, 9H), 1.55 (m, 1H), 1.61 (m, 1H), 1.78 (m, 1H), 1.86 (m, 1H), 2.34 (m, 1H), 2.41 (m, 1H), 4.20 (m, 1H), 5.97 (m, 1H).

^{13}C NMR ($CDCl_3$): δ = −4.7, 18.9, 20.9, 25.8, 31.2, 35.1, 68.0, 125.3, 132.6.

IR (neat): ν = 2953 s, 2930 s, 2895 w, 2858 w, 1472 m, 1257 m, 1038 s, 1025 m, 975 w, 837 s, 775 s cm^{-1}.

MS (EI): m/z (% rel intensity): 291 (6) M^+, 249 (4), 235 (10), 211 (57), 169 (13), 139 (65); exact mass calcd for $C_{12}H_{23}{}^{79}BrOSi$ m/z 290.0702; found 290.0711: calcd for $C_{12}H_{23}{}^{81}BrOSi$ m/z 292.0711; found m/z 292.0701.

Anal. calcd for $C_{12}H_{23}BrOSi$: C, 49.48; H, 7.96; Br, 27.43. Found: C, 49.08; H, 8.12; Br, 27.17.

1-Bromo-3-methoxycyclohexene (17):
NaH (313.6 mg, 60% w/w suspension in mineral oil) was washed with pentane (4 × 10 mL) to provide oil free NaH powder (190.0 mg, 7.84 mmol, 1.5 equiv) which was slurried in THF (5 mL). A solution of allylic alcohol **15** (925.0 mg, 5.23 mmol) in THF (5 mL) was added in portions to the hydride at −10 °C. After stirring for 45 min at r.t., the mixture was cooled to −10 °C and MeI (3.26 mL, 52.3 mmol, 10.0 equiv) was added. The mixture was then stirred at

r.t. for 30 h and monitored with TLC analysis (CH_2Cl_2, $KMnO_4$). Upon completion, the reaction was quenched by pouring into H_2O (50 mL). After extraction with Et_2O (3 × 50 mL), the combined Et_2O extracts were washed with brine (2 × 50 mL), dried (Na_2SO_4), filtered through Celite and evaporated under reduced pressure to provide a crude brown oil. The crude was purified on a short silica gel column with 50% CH_2Cl_2 in hexane to provide the pure vinyl bromide **17** as a colorless oil; yield: 967.3 mg (97%) $R_f = 0.53$ (CH_2Cl_2).

^{1}H NMR ($CDCl_3$): $\delta = 1.65$ (m, 2H), 1.77 (m, 1H), 1.86 (m, 1H), 2.39 (m, 1H), 2.44 (m, 1H), 3.33 (s, 3H), 3.74 (br s, 1H), 6.16 (d, 1H, $J = 3.3$ Hz).

^{13}C NMR ($CDCl_3$): $\delta = 20.6$, 26.8, 35.3, 55.8, 75.5, 127.1, 129.0.

IR (neat): $\nu = 2941$ s, 2864 w, 2820 m, 1646 m, 1355 w, 1327 m, 1101 s, 1002 m, 935 m cm^{-1}.

MS (EI): *m/z* (% rel intensity): 191 (8) M^+, 177 (11), 151 (32), 137 (19), 123 (29), 111 (83), 97 (100), 83 (61).

Methoxy Chromium Carbene Complexes 8, 12, 18, 19, and Their Corresponding Dimethylamino Carbene Complexes 9, 13, 20, 21; General Procedure:

The appropriate vinyl bromide (1.0 equiv, 2.5 mmol) was dissolved in Et_2O (50 mL) at −78 °C and 2.0 equiv of *t*-BuLi (1.7 M in pentane) was added dropwise. After stirring for 1.5 h, the vinyl anion solution was transferred dropwise via a cannula to a stirred suspension of 1.0 equiv of $Cr(CO)_6$ in Et_2O (100 mL) at −78 °C. The mixture was warmed up slowly to r.t. over 2 h and then was cooled to −10 °C and MeOTf (1.8 equiv) was added dropwise. The mixture was stirred at −10 °C for 1 h and at r.t. for 1 h. After evaporating the solvent under reduced pressure, the residue was purified by silica gel column chromatography with hexane as eluent to provide the desired corresponding methoxy carbene complex as a red oil. These complexes could be used directly or stored in a freezer under a blanket of N_2.

The above prepared methoxy carbene complex (~ 0.2 mmol) was dissolved in THF (10–20 mL, for **18** and **19**) or hexane (6–15 mL for **20** and **21**) and stirred at −78 °C for 5 min. A dry stream of $HN(Me)_2$ was gently bubbled through the mixture until the solution turned from bright red to lemon yellow. The mixture was stirred at −78 °C for another 15 min before it was warmed to r.t. and concentrated under reduced pressure and purified on a silica gel column with gradient elution in several steps from 0% to 50% CH_2Cl_2 in hexane to provide the respective dimethylamino carbene complexes.

6-Methylcyclohex-1-enyl(methoxy)methylene Pentacarbonyl Chromium **(8)**: yield (36%) from vinyl bromide **7** (2.40 mmol); red oil; $R_f = 0.37$ (pentane).

^{1}H NMR ($CDCl_3$): $\delta = 0.96$ (d, 3H, $J = 6.9$ Hz), 1.43 (m, 1H), 1.58 (m, 1H), 1.74 (m, 1H), 1.81 (m, 1H), 2.27 (m, 2H), 2.85 (m, 1H), 4.65 (s, 3H), 6.10 (m, 1H).

^{13}C NMR ($CDCl_3$): $\delta = 19.7$, 20.2, 28.9, 31.2, 31.5, 67.1, 134.4, 160.0, 217.2, 224.6, 355.7.

IR (neat): $\nu = 2960$ w, 2934 w, 2872 w, 2059 s, 1923 s, 1621 w, 1454 m, 1228 m, 1184 w, 1129 m, 1080 w, 977 w cm^{-1}.

MS (EI): *m/z* (% rel intensity): 330 (7) M^+, 316 (2), 302 (1), 288 (1), 274 (7), 260 (1), 246 (7), 232 (4), 218 (23), 204 (14), 190 (100), 175 (2), 158 (19), 143 (24); exact mass calcd for $C_{14}H_{14}CrO_6$ *m/z* 330.0195; found *m/z* 330.0218.

6-Methylcyclohex-1-enyl(dimethylamino)methylene Pentacarbonyl Chromium **(9)**: yield (92%) from methoxy complex **8** (0.127 mmol); yellow oil; $R_f = 0.49$ (50% CH_2Cl_2 in hexane).

^{1}H NMR ($CDCl_3$): $\delta = 0.86$ (d, 3H, $J = 7.2$ Hz), 1.30 (m, 1H), 1.46–1.88 (m, 3H), 2.01 (m, 1H), 2.33 (m, 1H), 3.02 (m, 1H), 3.35 (s, 3H), 3.82 (s, 3H), 4.71 (m, 1H).

^{13}C NMR (CD_2Cl_2): $\delta = 20.9$, 21.6, 25.9, 29.5, 31.1, 43.9, 51.2, 121.2, 149.7, 218.5, 224.3, 274.3.

IR (neat): $\nu = 2962$ w, 2956 w, 2934 m, 2051 s, 1904 s, 1532 m, 1402 w.

MS (EI): *m/z* (% rel intensity): 343 (2) M^+, 315 (13), 287 (3), 259 (3), 231 (18), 203 (100), 184 (4), 151 (46), 136 (74), 95 (33); exact mass calcd for $C_{15}H_{17}CrNO_5$ *m/z* 343.0512; *m/z* found 343.0490.

3-Methylcyclohex-1-enyl(methoxy)methylene Pentacarbonyl Chromium **(12)**: yield (25%) from vinyl bromide **16** (2.34 mmol); red oil; $R_f = 0.37$ (pentane).

^{1}H NMR ($CDCl_3$): $\delta = 1.11$ (d, 3H, $J = 7.2$ Hz), 1.19 (m, 1H), 1.55 (m, 1H), 1.78 (m, 2H), 2.10 (m, 2H), 2.43 (m, 1H), 4.59 (m, 3H), 6.07 (d, 1H, $J = 2.0$ Hz).

^{13}C NMR (CD_2Cl_2): $\delta = 21.1$, 21.2, 25.6, 30.5, 31.2, 66.5, 118.2, 153.6, 217.2, 224.7, 352.2.

IR (neat): $\nu = 2958$ w, 2938 m, 2932 m, 2060 s, 1921 s, 1453 m, 1231 m, 1184 w, 1132 m, 1122 w cm^{-1}.

MS (EI) *m/z* (% rel intensity): 330 (5) M^+, 302 (11), 274 (8), 246 (8), 218 (24), 190 (100), 154 (27), 138 (30), 123 (26); exact mass calcd for $C_{14}H_{14}CrO_6$ *m/z* 330.0195; found *m/z* 330.0209.

3-Methylcyclohex-1-enyl(dimethylamino)methylene Pentacarbonyl Chromium **(13)**: yield (85%) methoxy complex **12** (0.270 mmol); yellow oil; $R_f = 0.42$ (50% CH_2Cl_2 in hexane).

^{1}H MR (CD_2Cl_2): $\delta = 0.98$ (d, 3H, $J = 5.5$ Hz), 1.26 (m, 1H), 1.55–1.88 (m, 4H), 2.25 (m, 1H), 2.38 (m, 1H), 3.26 (s, 3H), 3.77 (s, 3H), 4.91 (d, 1H, $J = 11.6$ Hz).

^{13}C NMR (CD_2Cl_2): $\delta = 21.0$, 21.7, 25.5, 30.0, 30.6, 44.3, 51.3, 121.1, 150.0, 218.6, 224.2, 275.1.

IR (neat): $\nu = 2953$ m, 2930 m, 2869 w, 2052 s, 1918 s, 1532 m, 1456 w, 1402 m, 1111 w cm^{-1}.

MS (EI) *m/z* (% rel intensity): 343 (3) M^+, 315 (13), 287 (5), 259 (4), 231 (24), 203 (100), 151 (45), 136 (28), 120 (11), 105 (10), 95 (44); exact mass calcd for $C_{15}H_{17}CrNO_5$ *m/z* 343.0512; found *m/z* 343.0529.

3-tert-Butyldimethylsiloxycyclohex-1-enyl(methoxy)methylene Pentacarbonyl Chromium **(18)**: yield (60%) from vinyl bromide **16** (2.56 mmol); red oil; $R_f = 0.14$ (10% CH_2Cl_2 in hexane).

^{1}H NMR ($CDCl_3$): $\delta = 0.09$ (s, 3H), 0.10 (s, 3H), 0.89 (s, 9H), 1.55 (m, 2H), 1.83 (m, 2H), 2.07 (m, 2H), 4.37 (m, 1H), 4.57 (br s, 3H), 5.81 (m, 1H).

^{13}C NMR ($CDCl_3$): $\delta = -4.8$, 18.1, 18.9, 25.2, 25.8, 31.6, 66.0, 66.1, 131.3, 154.4, 216.4, 223.8, 353.6.

IR (neat): $\nu = 2954$ m, 2932 m, 2859 w, 2062 s, 1939 s, 1453 w, 1233 m, 1126 m, 1082 m, 1042 w, 962 w, 837 m, 775 w cm^{-1}.

MS (EI) *m/z* (% rel intensity): 446 (3) M^+, 418 (7), 306 (61), 291 (5), 270 (6), 249 (24), 233 (9), 213 (100), 197 (9), 181 (33); exact mass calcd for $C_{19}H_{26}CrO_7Si$ *m/z* 446.0853; found *m/z* 446.0842.

Anal calcd for $C_{19}H_{26}CrO_7Si$: C, 51.11; H, 5.87. Found: C, 49.44; H, 5.75.

3-tert-Butyldimethylsiloxycyclohex-1-enyl(dimethylamino)methylene Pentacarbonyl Chromium **(20)**: yield (87%) methoxy complex **18** (0.952 mmol); yellow wax; **20** contained two rotamers with ratio of 1.8:1. Rotamer **A** (major): $R_f = 0.48$; rotamer **B** (minor): $R_f = 0.62$ (50% CH_2Cl_2 in hexane).

^{1}H NMR ($CDCl_3$): δ = rotamer **A**: 0.05 (s, 6H), 0.87 (s, 9H), 1.72 (m, 2H), 1.82 (m, 2H), 2.32 (m, 2H), 3.32 (s, 3H), 3.78 (s, 3H), 4.39 (m, 1H), 5.00 (d, 1H, $J = 0.9$ Hz); rotamer **B**: 0.06 (s, 6H), 0.89 (s, 9H), 1.72 (m, 2H), 1.82 (m, 2H), 2.32 (m, 2H), 3.24 (s, 3H), 3.78 (s, 3H), 4.28 (m, 1H), 5.04 (m, 1H).

^{13}C NMR (CD_2Cl_2) δ = rotamer **A**: −4.7, 18.6, 19.0, 25.7, 26.0, 32.3, 44.6, 65.5, 118.3, 151.5, 218.3, 224.1, 256.7; rotamer **B**: −4.6, 18.4, 18.9, 24.5, 25.9, 32.1, 44.5, 65.9, 118.4, 151.2, 218.2, 224.3, 256.6.

IR (neat): $\nu = 2950$ m, 2931 m, 2858 w, 2053 s, 1971 s, 1914 s, 1534 m, 1403 w, 1255 w, 1076 s, 1006 m, 837 s, 776 m cm^{-1}.

MS (EI): *m/e* (% relative intensity): 459 (4) M^+, 431 (100), 403 (1), 388 (2), 358 (4); *m/e* calcd for $C_{20}H_{39}CrNO_6Si$ 459.1169, found 459.1160.

3-Methoxycyclohex-1-enyl(methoxy)methylene Pentacarbonyl Chromium **(19)**: yield (57%) from vinyl bromide **17** (3.93 mmol); red oil; $R_f = 0.18$ (50% CH_2Cl_2 in hexane).

^{1}H NMR ($CDCl_3$): δ = 1.63 (m, 2H), 1.84 (m, 2H), 2.12 (m, 2H), 3.39 (s, 3H), 3.94 (br s, 1H), 4.55 (br s, 3H), 5.67 (br s, 1H).

^{13}C NMR (CD_2Cl_2): δ = 19.2, 25.9, 27.8, 56.2, 66.6, 74.2, 125.5, 155.8, 216.9, 224.6, 354.4.

IR (neat): ν = 2945 w, 2062 s, 1927 s, 1452 w, 1238 m, 1190 w, 1126 m, 1092 w cm^{-1}.

MS (EI) *m/z* (% rel intensity): 346 (1) M^+, 308 (3), 290 (6), 262 (7), 234 (6), 206 (23), 174 (25), 154 (7), 124 (8), 108 (39), 80 (64), 52 (100); exact mass calcd for $C_{14}H_{14}CrO_7$ *m/z* 346.0144; found *m/z* 346.0135.

3-Methoxycyclohex-1-enyl(dimethylamino)methylene Pentacarbonyl Chromium **(21)**: yield (91%) methoxy complex **19** (0.549 mmol); yellow oil; **21** contained two rotamers with ratio of 2.0:1. Rotamer **A** (major): R_f = 0.24; rotamer **B** (minor): R_f = 0.36 (CH_2Cl_2).

^{1}H NMR ($CDCl_3$): δ = rotamer **A**: 1.76 (m, 2H), 1.85 (m, 2H), 2.34 (m, 2H), 3.31 (s, 3H), 3.34 (s, 3H), 3.78 (s, 3H), 3.91 (br s, 1H), 5.26 (br s, 1H); rotamer **B**: 1.67 (m, 2H), 1.97 (m, 2H), 2.41 (m, 2H), 3.26 (s, 3H), 3.36 (s, 3H), 3.79 (s, 3H), 3.84 (br s, 1H), 5.19 (br s, 1H).

^{13}C NMR ($CDCl_3$): δ = rotamer **A**: 18.5, 25.6, 27.4, 44.4, 56.0, 73.2, 114.6, 152.7, 217.7, 223.3, 274.9; rotamer **B**: 18.6, 25.6, 27.8, 44.1, 55.4, 73.6, 114.8, 152.5, 217.6, 223.5, 275.5.

IR (neat): ν = 2939 w, 2052 s, 1909 m, 1907 s, 1537 m, 1449 w, 1403 w, 1107 w, 1086 m cm^{-1}.

MS (EI): *m/z* (% relative intensity): 359 (4) M^+, 331 (18), 303 (4), 275 (5), 247 (8), 219 (79), 187 (38), 168 (31), 134 (100); *m/z* calcd for $C_{15}H_{17}CrNO_6$ 359.0461, found 359.0456.

Preparation of (Arene)chromium Tricarbonyl Complexes from the Benzannulation Reactions of Methoxy Chromium Carbene Complexes 8, 12, 18, 19, and Their Corresponding Dimethylamino Carbene Complexes 9, 13, 20, 21; General Procedure:

The chromium carbene complex (0.13–0.27 mmol, 1.0 equiv) and a small magnetic stir bar were placed in a flame-dried, single-necked flask that had 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 Ar. One half of the volume of anhyd CH_2Cl_2 (benzene in cases of amino carbene complexes) required for a 0.05 M solution (0.25 M in cases of amino carbene complexes) of the carbene complex, 1.9 equiv of the alkyne, 3.0 equiv of a Hunig's based (freshly distilled or filtered through a basic Al_2O_3 gel column), 2.0 equiv of *tert*-butyldimethylsilyl chloride and the remaining solvent were added via syringe. The septum was replaced with the threaded stopcock and the mixture was deoxygenated using the freeze-thaw method (three to four cycles at −196°C/25°C). Then the reaction flask was backfilled with Ar, sealed with the stopcock at 25°C heated at 60°C (80°C for amino carbene complexes) for 11–20 h or until all the carbene complex was consumed. After cooling to r.t., the mixture was analyzed by TLC (50% CH_2Cl_2 in hexane, UV/PMA), concentrated under reduced pressure and chromatographed on a silica gel column (gradient elution in several steps from 0% to 75% CH_2Cl_2 in hexane) to give the purified (arene)chromium tricarbonyl complexes. In most cases the *syn*- and *anti*-isomers of these complexes have very similar R_f values ($\Delta R_f < 0.05$). Hence, unless otherwise indicated, the *syn*- and *anti*-isomers were isolated together as one fraction, the isomeric ratios were determined using either ^{1}H NMR or ^{13}C NMR and all spectral data were collected on the mixture.

1-(tert-Butyldimethylsilyloxy)-2,3-diethyl-5,6,7,8-tetrahydro-4-methoxy-5-methylnaphthalene Tricarbonyl Chromium **(22)**: 83% yield from carbene complex **8** (0.25 mmol); yellow oil; *syn*:*anti* = 58:42; $R_{f_{syn}}$ = 0.52, $R_{f_{anti}}$ = 0.58 (50% CH_2Cl_2 in hexane).

^{1}H NMR ($CDCl_3$) δ = *syn*: 0.39 (s, 3H), 0.40 (s, 3H), 0.99 (s, 9H), 1.14–1.36 (m, 6H), 1.41 (d, 3H, J = 6.8 Hz), 1.53–1.80 (m, 4H), 2.38–2.82 (m, 6H), 2.83 (m, 1H), 3.75 (s, 3H); *anti*: 0.34 (s, 6H), 0.99 (s, 9H), 1.14–1.36 (m, 6H), 1.29 (d, 3H, J = 7.1 Hz), 1.53–1.80 (m, 4H), 2.38–2.82 (m, 6H), 3.07 (m, 1H), 3.75 (s, 3H).

^{13}C NMR ($CDCl_3$): δ = *syn*: −2.6, −2.1, 14.4, 17.8, 18.0, 18.9, 20.0, 21.2, 25.6, 26.2, 26.4, 28.0, 30.4, 61.3, 103.3, 104.7, 110.1, 111.9, 131.8, 139.7, 235.5; *anti*: −2.4, −1.8, 14.7, 17.6, 17.8, 19.1, 19.9, 21.3, 24.8, 25.9, 26.1, 26.2, 29.0, 66.8, 96.6, 106.6, 107.1, 113.7, 123.9, 136.0, 235.0.

IR (neat): ν = 2957 m, 2935 s, 2878 w, 2861 m, 1948 s, 1865 s, 1473 m, 1464 m, 1447 m, 1395 s, 1342 m, 1265 s, 1115 w, 1040 m, 1000 w, 883 w, 841 s, 826 s, 815 w, 783 m cm^{-1}.

MS (EI) *m/z* (% rel intensity): 498 (11) M^+, 470 (1), 442 (5), 414 (100), 362 (28), 347 (6), 319 (8), 305 (23), 279 (7), 248 (6), 167 (8), 149 (7); exact mass calcd for $C_{25}H_{38}CrO_5Si$ *m/z* 498.1894; found *m/z* 498.1881.

1-(tert-Butyldimethylsilyloxy)-5,6,7,8-tetrahydro-4-methoxy-5-methyl-2-propylnaphthalene Tricarbonyl Chromium **(23)**: yield (65%) from carbene complex **8** (0.25 mmol); yellow oil; *syn*:*anti* 60:40; R_f = 0.57 (50% CH_2Cl_2 in hexane).

^{1}H NMR ($CDCl_3$): δ = *syn*: 0.36 (s, 6H), 0.98 (s, 9H), 0.99 (m, 3H), 1.27 (m, 1H), 1.30 (d, 3H, J = 6.7 Hz), 1.54–1.94 (m, 3H), 2.18 (m, 2H), 2.55 (m, 1H), 2.63–2.83 (m, 3H), 2.86 (m, 1H), 3.73 (s, 3H), 4.77 (s, 1H); *anti*: 0.38 (s, 6H), 0.99 (s, 9H), 1.00 (m, 3H), 1.21 (d, 3H, J = 7.1 Hz), 1.26 (m, 1H), 1.54–1.94 (m, 3H), 2.18 (m, 2H), 2.55 (m, 1H), 2.63–2.83 (m, 3H), 3.13 (m, 1H), 3.67 (s, 3H), 4.80 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = *syn*: −2.6, −2.4, 13.9, 17.2, 18.8, 23.5, 24.5, 25.7, 26.1, 26.6, 29.7, 32.9, 55.6, 72.1, 104.2, 106.2, 108.3, 123.1, 138.7, 235.4; *anti*: −3.5, −1.8, 13.9, 16.5, 20.0, 22.1, 23.9, 26.0, 26.5, 27.4, 28.3, 32.4, 55.7, 74.2, 103.9, 105.1, 105.2, 125.7, 137.2, 235.1.

IR (neat): ν = 2959 m, 2935 m, 2861 w,1947 s, 1860 s, 1456 m, 1428 m, 1391 w, 1339 w, 1323 w, 1250 m, 1099 w, 939 w, 841 m cm^{-1}.

MS (EI): *m/z* (% rel intensity): 484 (12) M^+, 442 (1), 428 (9), 414 (18), 400 (100), 383 (2), 371 (2), 348 (6), 315 (4), 291 (6), 200 (2), 126 (21); *m/z* calcd for $C_{24}H_{36}CrO_5Si$ *m/z* 484.1737; found *m/z* 484.1727.

1-(tert-Butyldimethylsilyloxy)-4-(dimethylamino)-5,6,7,8-tetrahydro-5-methyl-2-propylnaphthalene Tricarbonyl Chromium **(24)**: yield (41%) from amino carbene complex **9** (0.13 mmol); yellow oil; *syn*:anti = 52:48; $R_{f_{syn}}$ = 0.58, $R_{f_{anti}}$ = 0.32 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ = *syn*: 0.30 (s, 3H), 0.33 (s, 3H), 1.00 (s, 9H), 0.88–1.13 (m, 3H), 1.44 (d, 3H, J = 6.7 Hz), 1.48–1.97 (m, 6H), 2.56 (s, 3H), 2.64 (s, 3H), 2.48–2.98 (m, 5H), 5.75 (s, 1H); *anti*: 0.40 (s, 3H), 0.41 (s, 3H), 1.00 (s, 9H), 0.88–1.13 (m, 3H), 1.36 (d, 3H, J = 6.7 Hz), 1.48–1.97 (m, 6H), 2.56 (s, 3H), 2.64 (s, 3H), 2.48–2.98 (m, 5H), 4.97 (s, 1H).

^{13}C NMR (CD_2Cl_2): δ = *syn*: −2.8, −2.4, 13.9, 18.6, 23.7, 25.9, 27.1, 27.6, 28.2, 28.6, 32.4, 32.7, 43.6, 80.4, 105.5, 106.8, 113.3, 131.2, 140.8, 235.3; *anti*: −3.7, −2.0, 13.9, 19.7, 24.9, 25.8, 26.5, 27.7, 28.8, 29.9, 30.3, 31.9, 43.8, 81.6, 104.8, 105.1, 111.4, 132.6, 137.4, 235.2.

IR (neat): ν = 2957 w, 2934 m, 2862 w, 1945 s, 1864 s, 1464 w, 1456 wm 1420 m, 1257 m, 840 m cm^{-1}.

MS (EI) *m/z* (% rel intensity): 497 (10) M^+, 441 (5), 413 (100), 399 (3), 383 (2), 361 (22), 346 (5), 328 (3), 304 (6), 289 (3); exact mass calcd for $C_{25}H_{39}CrNO_4Si$ *m/z* 497.2053; found *m/z* 497.2052.

1-(tert-Butyldimethylsilyloxy)-5,6,7,8-tetrahydro-4-methoxy-8-methyl-2-propylnaphthalene Tricarbonyl Chromium **(25)**: yield (50%) from carbene complex **12** (0.25 mmol); yellow oil; *syn*: anti = 24:76; $R_{f_{anti}}$ 0.62 $R_{f_{syn}}$ = 0.53 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ = *anti*: 0.41 (s, 3H), 0.44 (s, 3H), 0.98 (t, 3H, J = 6.6 Hz), 1.01 (s, 9H), 1.28 (d, 3H, J = 7.3 Hz), 1.57 (m, 3H), 1.71 (m, 4H), 2.13 (m, 1H), 2.44–2.83 (m, 2H), 3.19 (m, 1H), 3.69 (s, 3H), 4.95 (s, 1H); *syn*: 0.25 (s, 3H), 0.29 (s, 3H), 0.99 (s, 9H), 1.07 (t, 3H, J = 7.4 Hz), 1.35 (d, 3H, J = 6.7 Hz), 1.57 (m, 3H), 1.71 (m, 4H), 2.37 (m, 1H), 2.44–2.83 (m, 2H), 3.05 (m, 1H), 3.66 (s, 3H), 5.60 (s, 1H).

^{13}C NMR (CD_2Cl_2): δ = *anti*: −3.4, −1.3, 14.0, 16.5, 19.3, 20.3, 22.5, 24.7, 26.4, 28.3, 28.5, 32.7, 56.3, 74.7, 98.5, 104.9, 106.6, 113.5,

138.2, 235.6; *syn*: −2.3, −1.8, 14.5, 16.9, 19.6, 20.8, 23.7, 24.5, 26.6, 27.5, 27.7, 32.5, 57.6, 83.0, 98.2, 106.3, 108.3, 113.3, 137.5, 236.5.

IR (neat): ν = 2959 w, 2934 m, 2861 w, 1947 s, 1859 s, 1865 w, 1455 w, 1429 s, 1370 w, 1326 w, 1256 w, 1246 w, 1091 w, 840 w, 809 w, 782 w cm^{-1}.

MS (EI) *m/z* (% rel intensity) 484 (53) M^+, 428 (32), 400 (100), 348 (42), 291 (37), 234 (37), 205 (18), 126 (53); exact mass calcd for $C_{24}H_{36}CrO_5Si$ *m/z* 484.1737; found *m/z* 484.1748.

A second product was formed in this reaction (11% yield) that was tentatively identified on the basis of the following data: yellow oil; R_f = 0.58 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ = 1.04 (t, 3H, J = 7.9 Hz), 1.21 (d, 3H, J = 6.7 Hz), 1.60 (m, 4H), 1.68 (m, 2H), 1.70 (m, 4H), 1.94 (m, 1H), 3.73 (s, 3H), 6.46 (s, 1H).

^{13}C NMR (CD_2Cl_2): δ = 14.3, 17.5, 23.1, 23.8, 25.5, 30.1, 30.4, 33.0, 38.7, 56.3, 98.9, 107.2, 125.7, 130.0.

IR (neat): ν = 2959 m, 2934 s, 2861 m, 1465 w, 1429 s, 1370 m, 1326 w, 1259 w, 1246 m, 1091 m cm^{-1}.

MS (EI) *m/z* (% rel intensity): 205 (47) M^+, 191 (10), 177 (20), 159 (7), 126 (100), 112 (10), 96 (20), 70 (72), 52 (35).

1-(tert-Butyldimethylsilyloxy)-4-(dimethylamino)-5,6,7,8-tetrahydro-8-methyl-2-propylnaphthalene Tricarbonyl Chromium **(26)**: yield (39%) from amino carbene complex **13** (0.15 mmol); yellow oily wax; *anti*:syn = 91:9; R_f = 0.37 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ = *anti*: 0.27 (s, 3H), 0.29 (s, 3H), 1.04 (s, 9H), 1.05 (t, 3H, J = 7.1 Hz), 1.33 (d, 3H, J = 6.5 Hz), 1.59 (m, 2H), 1.68 (m, 4H), 1.90 (m, 1H), 2.28 (m, 1H), 2.52 (s, 6H), 2.82 (m, 1H), 2.85 (m, 2H), 5.70 (s, 1H); *syn*: 0.43 (s, 3H), 0.44 (s, 3H), 1.04 (s, 9H), 1.05 (t, 3H, J = 7.1 Hz), 1.42 (m, 3H), 1.59 (m, 2H), 1.68 (m, 4H), 1.90 (m, 1H), 2.20 (m, 1H), 2.54 (m, 1H), 2.59 (s, 6H), 2.85 (m, 2H), 4.98 (s, 1H).

^{13}C NMR (CD_2Cl_2): δ = *anti*: −2.5, −1.8, 14.5, 18.3, 24.5, 24.9, 26.4, 26.8, 27.0, 28.0, 30.7, 32.0, 45.6, 91.3, 99.5, 106.9, 113.3, 121.4, 139.6, 236.3; *syn*: −3.6, −1.5, 14.0, 19.7, 24.2, 24.7, 26.2, 26.3, 28.1, 29.7, 30.5, 32.2, 44.4, 82.1, 99.7, 104.6, 112.8, 120.4, 138.s4, 235.7.

IR (neat): ν = 2959 m, 2935 m, 2861 w, 1944 s, 1859 s, 1465 w, 1420 m, 1264 w, 1257 w, 950 w, 852 m, 841 m, 782 w cm^{-1}.

MS (EI) *m/z* (% rel intensity): 497 (13) M^+, 441 (16), 413 (100), 361 (s45), 346 (5), 304 (9), 289 (2), 231 (2), 126 (14); exact mass calcd for $C_{25}H_{39}CrNO_4Si$ *m/z* 497.2053; found *m/z* 497.2054.

1-(tert-Butyldimethylsilyloxy)-5,6,7,8-tetrahydro-4,8-dimethoxy-2-propylnaphthalene Tricarbonyl Chromium **(27)**: yield (48%) from carbene complex **19** (0.20 mmol); yellow oil; *anti*:syn = 94:6; R_f = 0.38 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ = *anti*: 0.41 (s, 3H), 0.46 (s, 3H), 0.99 (t, 3H, J = 7.6 Hz), 1.01 (s, 9H), 1.57–1.91 (m, 4H), 2.11–2.27 (m, 2H), 2.53–2.75 (m, 4H), 3.35 (s, 3H), 3.66 (s, 3H), 4.61 (t, 1H, J = 2.4 Hz), 5.02 (s, 1H); *syn*: 0.32 (s, 3H), 0.36 (s, 3H), 0.94 (t, 3H, J = 6.9 Hz), 1.00 (s, 9H), 1.57–1.91 (m, 4H), 2.11–2.27 (m, 2H), 2.53–2.75 (m, 4H), 3.41 (s, 3H), 3.72 (s, 3H), 4.26 (m, 1H), 5.08 (s, 1H).

^{13}C NMR (CD_2Cl_2): δ = *anti*: −3.2, −0.9, 14.0, 15.5, 19.3, 21.9, 24.3, 24.7, 26.3, 32.5, 56.2, 56.5, 71.1, 76.3, 100.3, 103.9, 105.2, 126.8, 137.2, 235.2; *syn*: −2.7, −1.6, 14.3, 14.8, 19.8, 21.3, 23.1, 24.2, 26.4, 32.0, 57.2, 57.3, 70.4, 76.2, 100.5, 106.3, 117.8, 120.3, 131.8, 235.6.

IR (neat): 2959 m, 2935 m, 2861 w, 1951 s, 1861 s, 1457 m, 1431 m, 1358 w, 1336, 1250 w, 1087 m, 841 m cm^{-1}.

MS (EI) *m/z* (% rel intensity): 00 (6) M^+, 416 (32), 384 (100), 326 (13), 275 (19), 233 (6), 189 (1), 126 (30); exact mass calcd for $C_{24}H_{36}CrO_6Si$ *m/z* 500.1686, found *m/z* 500.1666. This reaction also gave a 16% yield of **31**.

1-(tert-Butyldimethylsilyloxy)-4-(dimethylamino)-5,6,7,8-tetrahydro-8-methoxy-2-propylnaphthalene Tricarbonyl Chromium **(29)**: yield (34%) from carbene complex **21** (0.21 mmol); yellow oil; *anti*:*syn* ≥ 94:6 (the minor isomer could not be detected by ^{1}H NMR of crude mixture and the selectivity was estimated by integration); R_f = 0.41 (CH_2Cl_2).

^{1}H NMR (CD_2Cl_2): δ = *anti*: 0.45 (s, 3H), 0.47 (s, 3H), 0.95 (t, 3H, J = 7.5 Hz), 1.04 (s, 9H), 1.62 (m, 2H), 1.94 (m, 2H), 2.13–2.56 (m, 4H), 2.61 (s, 6H), 2.81 (m, 2H), 3.30 (s, 3H), 4.67 (br t, 1H, J = 3.2 Hz), 5.15 (s, 1H).

^{13}C NMR (CD_2Cl_2): δ = *anti*: −3.5, −1.4, 14.0, 17.8, 19.1, 23.1, 24.8, 25.5, 26.1, 32.1, 44.5, 56.0, 71.3, 83.8, 99.5, 103.1, 118.1, 129.6, 132.5, 235.3.

IR (neat): 2955 m, 2930 m, 1948 s, 1868 s, 1464 w, 1426 w, 1258 w, 1106 w, 840 m cm^{-1}.

MS (EI) *m/z* (% rel intensity): 513 (8) M^+ 481 (14), 429 (19), 397 (100), 345 (84), 288 (28), 231 (25); exact mass calcd for $C_{25}H_{39}CrNO_5Si$ *m/z* 513.2002; found *m/z* 513.2001. Also isolated from this reaction was a 9% yield of **32**.

1,8-Bis(tert-butyldimethylsilyloxy)-4-dimethylamino-5,6,7,8-tetrahydro-1-hydroxy-2-propylnaphthalene Tricarbonyl Chromium **(30)**: yield (29%) from carbene complex **20** (0.27 mmol); yellow oil; *anti*:*syn* = 87:13; R_f = 0.78 (CH_2Cl_2).

^{1}H NMR (CD_2Cl_2): δ = *anti*: 0.28 (s, 3H), 0.29 (s, 3H), 0.95 (t, 3H, J = 6.3 Hz), 0.98 (s, 9H), 1.79–2.03 (m, 2H), 2.11–2.47 (m, 4H), 2.54 (s, 6H), 2.66 (m, 4H), 5.07 (t, 1H, J = 8.9 Hz), 5.64 (s, 1H), 8.34 (s, 1H); *syn*: 0.21 (s, 3H), 0.22 (s, 3H), 0.93 (m, 3H), 0.99 (s, 9H), 1.79–2.03 (m, 2H), 2.11–2.47 (m, 4H), 2.55 (s, 6H), 2.66 (m, 4H), 4.87 (br s, 1H), 5.71 (s, 1H), 7.61 (s 1H).

^{13}C NMR (CD_2Cl_2): δ = *anti*: −3.2, −2.7, 14.2, 20.8, 23.6, 24.4, 24.8, 26.0, 26.2, 32.5, 44.1, 71.9, 82.6, 93.1, 105.4, 118.4, 129.2, 132.9, 236.6; *syn*: not determined.

IR (neat): ν = 3260 (br d) w, 2956 m, 2933 m, 2860 w, 1948 s, 1868 s, 1464 w, 1443 w, 1428 m, 1258 m, 840 s cm^{-1}.

MS (EI) *m/z* (% rel intensity) 500 (3) M^+, 483 (22), 428 (16), 399 (100), 347 (41), 290 (19), 244 (31), 200 (16), 184 (16), 156 (9). This compound was too unstable to obtain any high resolution mass analysis. Initially isolated as a yellow oil, it was observed to turn to a purple color upon standing for short periods of time. Also isolated from this reaction was a 29% yield of **32**.

1-(tert-Butyldimethylsilyloxy)-5,6-dihydro-4-methoxy-2-propylnaphthalene Tricarbonyl Chromium **(31)**: yield (79%) from carbene complex **18** (0.20 mmol); yellow oil; R_f = 0.52 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ = 0.33 (s, 3H), 0.36 (s, 3H), 1.00 (s, 9H), 1.01 (t, 3H, J = 7.3 Hz), 1.60 (m, 2H), 2.25 (m, 2H), 2.32 (m, 2H), 2.75 (m, 1H), 2.89 (m, 1H), 3.69 (s, 3H), 4.93 (s, 1H), 6.28 (m, 1H), 6.58 (m, 1H).

^{13}C NMR (CD_2Cl_2): δ = −3.1, −2.4, 14.1, 19.0, 21.1, 22.7, 24.3, 26.1, 33.0, 56.4, 75.2, 96.5, 105.3, 112.1, 121.5, 124.5, 133.6, 137.5, 235.8.

IR (neat): ν = 2958 w, 2933 w, 1949 s, 1866 s, 1454 m, 1433 m, 1369 w, 1254 m, 1097 w, 841 m cm^{-1}.

MS (EI) *m/z* (% rel intensity): 468 (8)M^+, 412 (8), 384 (54), 332 (76), 275 (100), 232 (14), 215 (10), 201 (6), 185 (4); exact mass calcd for $C_{23}H_{32}CrO_5Si$ *m/z* 468.1424; found *m/z* 468.1438. None of the expected arene complex **28** could be detected from this reaction. When 6.0 equiv of Hünig's base and 4.0 equiv of TBSCl were used, only a 29% yield of **31** was isolated from reaction in THF. With 5.0 equiv of 2,6-lutidine and 3.0 equiv of TBSOTf, the reaction in benzene led to the exclusive formation of **31** in 72%.

1-(tert-Butyldimethylsilyloxy)-4-dimethylamino-5,6-dihydro-2-propylnaphthalene Tricarbonyl Chromium **(32)**: yield (29%) from carbene complex **20** (0.27 mmol); orange oil; R_f = 0.72 (CH_2Cl_2).

^{1}H NMR (CD_2Cl_2): δ = 0.36 (s, 3H), 0.37 (s, 3H), 0.95 (t, 3H, J = 7.2 Hz), 1.04 (s, 9H), 1.65 (m, 2H), 2.23–2.50 (m, 4H), 2.60 (s, 6H), 2.95 (m, 2H), 5.10 (s, 1H), 6.21 (br t, 1H, J = 3.7 Hz), 6.54 (d, 1H, J = 10.0 Hz).

^{13}C NMR (C_6D_6): δ = −2.3, 14.1, 23.2, 23.3, 24.4, 25.9, 26.1, 32.5, 43.4, 80.7, 97.1, 113.4, 115.9, 125.9, 131.8, 122.0, 156.8, 235.6.

IR (neat): ν = 2955 m, 2930 m, 1948 s, 1868 s, 1464 w, 1426 w, 1258 w, 1106 w, 840 m cm^{-1}.

MS (EI) *m/z* (% rel intensity): 481 (6) M^+, 425 (9), 397 (100), 345 (36), 311 (12), 288 (21), 231 (14), 184 (5), 149 (10), 126 (55); exact mass calcd for $C_{24}H_{35}CrNO_4Si$ *m/z* 481.1740; found *m/z* 481.1742.

8-*tert*-Butyldimethylsilyloxy-2-propyl-1,4-naphthoquinone (35):
This compound was prepared from the reaction of carbene complex **19** with pent-1-yne carried out with the general procedure but in the absence of Hünig's base and TBSCl. The crude mixture was oxidized by stirring with an aqueous solution of ceric ammonium nitrate to give the quinone **35** in 47% yield as a yellow oil. Also isolated from this reaction was the known quinone **36**[21] in 11% yield. R_f = 0.40 (CH_2Cl_2).

^{1}H NMR ($CDCl_3$): δ = 0.07 (s, 3H), 0.20 (s, 3H), 0.85 (s, 9H), 0.95 (t, 3H, J = 7.3 Hz), 1.44 (m, 1H), 1.51 (q, 1H, J = 6.7 Hz), 1.53 (m, 1H), 1.72 (m, 1H), 1.89 (m, 2H), 2.15 (m, 1H), 2.33 (quint, 1H, J = 7.5 Hz), 2.42 (quint, 1H, J = 7.2 Hz), 2.61 (dd, 1H, J = 4.7, 20.3 Hz), 4.82 (t, 1H, J = 2.3 Hz), 6.45 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = −5.0, −4.6, 13.7, 15.3, 18.1, 21.2, 22.5, 25.5, 30.8, 31.1, 60.5, 132.2, 141.4, 142.8, 149.3, 186.7, 188.6.

IR (neat): ν = 2954 s, 2933 s, 2857 w, 1654 s, 1287 w, 1252 m, 1092 m, 1039 w, 976 w, 856 w, 837 s, 778 m cm^{-1}.

MS (EI) *m/z* (% rel intensity): 334 (1) M^+, 319 (5), 277 (100), 235 (6), 217 (3), 139 (2); exact mass calcd for $C_{19}H_{30}O_3Si$ *m/z* 334.1964; found *m/z* 334.1943.

2,3-Dimethylcyclohex-1-enyl Triflate (40):
To a solution of Me_2S–CuBr (11.29 g, 54.9 mmol) in Me_2S (36 mL) was added dropwise a 1.4 M solution of MeLi (78.4 mL, 2.41 g, 109.8 mmol) at r.t. under N_2. The solution was stirred 5 min, then 2-methylcyclohexenone (4.62 g, 41.9 mmol) was added in Et_2O (15 mL), and the mixture stirred an additional 20 min. The solution was then transferred via cannula to a solution of 59.87 g (167.7 mmol) of Tf_2NPh in Et_2O (380 mL) and the mixture stirred for 12 h at r.t. under N_2. The resulting greenish-black suspension was washed several times with sat. NH_4Cl/NH_4OH until no copper remained in the organic layer (no blue color in the NH_4OH solution). The Et_2O layer was then washed with pH 7 buffer solution (3 × 200 mL), dried ($MgSO_4$) and concentrated on a rotary evaporator. Purification on silica gel with hexanes as eluent gave 7.14 g (68%) of vinyl triflate **40**.

^{1}H NMR ($CDCl_3$): δ = 1.08 (d, 3H, J = 6.9 Hz), 1.37 (m, 1H), 1.60–1.90 (m, 3H), 1.80 (s, 3H), 2.29 (br s, 3H).

^{13}C NMR ($CDCl_3$): δ = 14.6, 18.9, 20.1, 27.9, 30.0, 34.6, 118.5 (q, J = 319.4 Hz), 130.46, 143.9.

IR (neat): ν = 2952 m, 2936 m, 2874 w, 1446 w, 1413 s, 1246 s,1208 s, 1144 s, 1042 w, 999 w, 969 s, 897 s, 803 m cm^{-1}.

MS (EI) *m/z* (% rel intensity): 258 (68) M^+, 243 (15), 125 (36), 109 (45), 97 (100), 83 (54), 69 (59).

Anal. calcd for $C_9H_{13}F_3O_3S$: C, 41.86; H, 5.07; found: C, 42.10; H, 5.25.

1-Bromo-2,3-dimethylcyclohexene (41):
The reaction of vinyl triflate **40** (3.10 mmol) with the tributylstannyl higher-order cuprate was carried out according to the procedure described for the reaction of vinyl triflate **10** in the preparation of 1-bromo-3-methylcyclohexene. Upon completion of the reaction (2 h), the solution was poured into a mixture of pentane (30 mL) and 10% aqueous NH_4Cl (30 mL), washed with H_2O (2 × 30 mL) and brine (2 × 30 mL) dried ($MgSO_4$). The volatiles were removed by a rotary evaporator to give 2,3-dimethyl-1-tributylstannylcyclohexene as an oil. The vinylstannane was dissolved in CH_2Cl_2 (or pentane) (30 mL) and cooled to −78 °C and then a 1.0 M solution of Br_2 (3.3 mL, 3.3 mmol, 1.06 equiv) (in CH_2Cl_2 or pentane) was added. The mixture was stirred for 5 minutes and then checked by GC for the disappearance of the vinylstannane. Upon completion (which is usually immediate), the solution was washed several times with H_2O (20 mL, 3–5 portions), brine, dried ($MgSO_4$) and concentrated on a rotary evaporator. The product was purified by gravity column chromatography (silica gel with hexanes or pentane) and was collected in 5 mL fractions (R_f = 0.54) which were combined and concentrated. The bromide **41** was kept away from high vacuum due to its volatility, and was obtained in 81% yield (0.477 g, 2.52 mmol) as a colorless oil.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.04 (d, 3H, J = 7.0 Hz, 3-CH_3), 1.37–1.48 (m, 1H, 3-CH), 1.52–1.70 (m, 1H, C(H)*H*), 1.70–1.85 (m, 2H, CH_2), 1.79 (s, 3H, 2-CH_3), 2.16–2.30 (m, 1H, 4-C(*H*)H), 2.45 (br s, 2H, 6-CH_2).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 19.49 (qd, J = 126.0, 3.3 Hz, 3-CH_3), 21.56 (t, J = 125.8 Hz, CH_2), 21.78 (q, J = 127.0 Hz, 2-CH_3), 30.56 (t of quint, J = 127.1, 4.8 Hz, C-5), 36.32 (d, J = 129.7 Hz, C-3), 36.87 (t, J = 130.4 Hz, CH_2), 119.90 (s, C-2), 136.19 (s, C-1).

IR (neat): ν = 2960, 2938, 2871, 2860, 1653m 1456, 1378, 1321, 1030, 943, 774 cm^{-1}.

MS, *m/z* (% rel intensity): 190 (^{81}Br) M^+ (11), 188 (^{79}Br) M^+ (10), 175 (4) 173 (4), 148 (1), 146 (1), 109 (100), 93 (36), 91 (21), 81 (21), 79 (20), 77 (24).

Anal. calcd for $C_8H_{13}Br$: C, 50.82; H, 6.93. Found: C, 50.83; H, 6.96.

In the case where the 1.0 M Br_2 solution was added until an orange color persisted, the tribrominated product was isolated as a major side product (mp = 143–144 °C). This tribromide can be reconverted to the desired bromide **41** by reduction with Zn/HOAc.

^{1}H NMR ($CDCl_3$): δ = 1.10 (d, 3H, J = 6.4 Hz), 1.48–1.61 (m, 2H), 1.61–1.75 (m, 2H), 1.85–2.16 (m, 1H), 2.10 (s, 3H), 2.52–2.66 (m, 1H), 3.00–3.15 (m, 1H).

^{13}C NMR ($CDCl_3$): δ = 14.1, 19.8, 22.4, 24.5, 30.4, 30.6, 34.1, 39.3, 46.5, 82.5, 82.7.

MS, *m/e* (% relative intensity) 269 M^+ − Br (12), 187 (23), 107 (100), 91 (17), 83 (78), 77 (12), 67 (10).

2,3-Dimethylcyclohex-1-enyl(methoxy)methylene Pentacarbonyl Chromium (42):
To a solution of 1-bromo-2,3-dimethylcyclohexene **(41)** (0.383 g, 2.03 mmol) in THF (15 mL) at −78 °C under Ar was added *t*-BuLi (2.39 mL) and the resultant mixture stirred for 20 min at −78 °C. The solution was then transferred via cannula to a solution of $Cr(CO)_6$ (0.537 g, 2.44 mmol) in THF (15 mL) at 0 °C under Ar. This mixture was stirred for 5 min at 0 °C and 1 h at r.t. Next, $MeOSO_2F$ (0.33 mL, 0.463 g, 4.06 mmol) was added and the solution stirred for an additional 10 min. The crude mixture was then diluted with hexanes (~ 25 mL) and washed with sat. $NaHCO_3$ (3 × 20 mL). The aqueous layer was then extracted with hexanes (3 × 20 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated. The carbene complex **42** was isolated in 53% yield (0.355 g) after purification on silica gel with hexanes as eluent (R_f = 0.15).

Variable temperature NMR data:

^{1}H NMR (Tol-d_8) −80 °C: δ = 0.57 (br d, J = 4.4 Hz, C(H)CH_3, sharp doublet from −60–0 °C), 0.90 (br s, C(H)CH_3, sharp doublet from −60–0 °C), 1.05 (br s, CH_3), 1.10 (br s, CH_3), 1.12–1.62 (br m), 1.60–1.80 (br s), 2.07–2.43 (br, m), 2.73 (s, OCH_3), 2.81 (s, OCH_3); +15 °C: 0.69 (br s, C(H)CH_3), 0.72–1.07 (br m), 0.90–1.35 (br m), 1.19–1.66 (br m), 2.52–2.78 (br s), 1.69–1.92 (br s), 3.17 (br s, OCH_3); +30 °C: 0.49–1.18 (br m), 1.00–1.48 (br m), 1.23 (s, CH_3), 1.30–1.71 (br s), 1.57–2.00 (br m), 2.13–2.58 (br s), 3.27 (br s, OCH_3); +80 °C: 0.88 (d, 3H, J = 5.5 Hz, C(H)CH_3), 1.04–1.48 (br m, 2H), 1.30 (s, 3H, CH_3), 1.36–1.67 (br s, 2H), 1.61–2.12 (br m, 3H), 3.49 (s, 3H, OCH_3).

^{13}C NMR (Tol-d_8) −60 °C: 17.93, 18.22, 19.29, 19.44, 26.82, 27.00, 29.83, 31.55, 32.76, 33.83, 62.87 (q, OCH_3), 63.20 (qm OCH_3), 124.03 (s, vinyl C), 124.80 (s, vinyl C), 143.12 (s, vinyl C), 143.75 (s, vinyl C), 217.17 (s, *trans* CO), 224.92 (s, *cis* CO), 225.10 (s, *cis* CO), 360.68 (s, carbene C); 0 °C: 17.59, 18.18, 19.30, 19.46, 26.91, 27.06, 30.11, 31.57, 32.97, 33.71, 62.75 (q, OCH_3),63.08 (q, OCH_3), 124.42 (s, vinyl C, other buried under solvent), 143.13 (s, vinyl C), 143.76 (s, vinyl C), 217.16 (s, *trans* CO), 224.94 (s, *cis* CO), 225.10 (s, *cis* CO), 360.70 (s, carbene C); +60 °C: 18.04 (q, CH_3), 19.25 (q, CH_3), 27.14 (t, cyclohexenyl C-4+5), 31.07 (d, cyclohexenyl

C-3), 33.60 (t, cyclohexenyl C-6), 63.19 (q, OCH_3), ~144 (very broad peak, vinyl C), 217.09 (s, *trans* CO), 224.62 (s, *cis* CO), 360.69 (s, carbene C). The vinyl carbon at ~124 does not appear at all in this spectrum.

IR (neat): ν = 2062 s, 1986 s, 1923 s, 1432, 1246, 1126, 1086, 918 cm^{-1}.

MS, *m/e* (% rel intensity): 344 (12) M^+, 316 (6), 288 (6), 260 (13), 232 (31), 204 (100), 172 (42), 157 (14), 143 (7), 131 (6).

Anal. calcd for $C_{15}H_{16}CrO_6$: C, 52.33; H, 4.68; found,C, 52.32; H, 4.72.

Reaction of the 2,3-Dimethylcyclohexenyl Carbene Complex 42 with Pent-1-yne:

A solution of complex **42** (0.128 g, 0.37 mmol) and pent-1-yne (0.07 mL, 0.051 g, 0.74 mmol) in hexanes (7.4 mL) was deoxygenated by the freeze-thaw method (3 cycles) and then stirred at 60 °C under Ar for 12 h. The crude solution was stirred in air for 1 h and then filtered through Celite. After removal of solvent on a rotary evaporator, the cyclohexadienone product was purified on silica gel with a 1:1:10 mixture of Et_2O/CH_2Cl_2/hexane as eluent to give 0.076 g (83%) of **43a** as a 44:56 mixture of *cis* and *trans* isomers (*cis*: R_f (1:1:4) = 0.53; *trans* R_f (1:1:4) = 0.48). Spectral data for **43a** (collected on the mixture).

^1H NMR ($CDCl_3$): *cis*-**43a**: δ = 0.86–0.96 (m, 6H), 1.17 (s, 3H), 1.18–1.30 (m, 1H), 1.43–1.55 (m, 5H), 1.83–1.95 (m, 2H), 2.12–2.20 (m, 1H), 2.30–2.39 (m, 1H), 2.36–2.43 (m, 1H), 3.59 (s, 3H), 6.75 (s, 1H); *trans*-**43a**: δ = 0.65 (d, 3H, J = 6.9 Hz), 0.91 (t, 3H, J = 7.5 Hz), 1.25 (s, 3H), 1.36–1.70 (m, 4H), 1.88–2.05 (m, 3H), 2.13–2.38 (m, 3H), 2.85–2.90 (m, 1H), 3.61 (s, 3H), 6.78 (s, 1H).

^{13}C NMR ($CDCl_3$): *cis*-**43a**; δ = 13.9, 15.4, 15.6, 21.7, 23.4, 27.8, 30.9, 31.2, 40.1, 53.3, 59.0, 135.3, 136.6, 137.9, 143.2, 204.3; *trans*-**43a**; δ = 13.8, 15.1, 21.5, 22.4, 22.6, 25.0, 28.0, 30.8, 40.4, 52.9, 59.2, 135.5, 136.4, 136.6, 145.2, 206.5.

IR (CCl_4): ν = 2960 s, 2932 s, 2873 m, 2859 m, 2834 w, 1663 w, 1641 s, 1462 m, 1456 m, 1440 w, 1381 s, 1365 w, 1184 m, 1088 w, 1054 w, 909 w cm^{-1}.

MS (EI) *m/z* (% rel intensity): 248 (100) M^+, 233 (30), 219 (15), 205 (15), 193 (25), 177 (22), 166 (63), 151 (14), 135 (8), 128 (6), 121 (8), 108 (15), 91 (27), 77 (15), 67 (8).

Anal. calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.43; H, 9.39. When the reaction was carried out in THF, the yield for **43a** was 52% with *trans*/*cis* ratio of 52:48, and no **44a** was found. When the solvent was MeCN, the yield was 60% and the ratio was 71:29, and no **44a** was observed.

The phenol **44a** is derived from the incorporation of two equiv of the alkyne and was isolated in yields of up to 3% in some reactions. The ^1H NMR spectrum reveals the presence of two rotational isomers at r.t.

^1H NMR ($CDCl_3$): δ = 0.93 (t, 3H, J = 7.3 Hz), 0.97 (t, 3H, J = 7.3 Hz), 1.12 (d, 3H, J = 7.4 Hz), 1.34 (d, 3H, J = 7.0 Hz), 1.51 (s, 3H), 1.52 (s, 3H), 1.54–1.77 (m, 4H), 1.74–1.86 (m, 1H), 1.81–1.96 (m, 1H), 2.02–2.17 (m, 1H), 2.12–2.33 (m, 2H), 2.48 (t, 2H, J = 7.5 Hz), 2.58 (t, 2H, J = 7.5 Hz), 5.04 (s, 1H), 5.13 (s, 1H), 6.61 (s, 1H), 6.64 (s, 1H), 6.79 (s, 1H) + upfield ring protons.

^{13}C NMR ($CDCl_3$): δ = 14.6, 14.8, 19.0, 20.3, 20.6, 21.2, 21.3, 23.8, 25.5, 31.8, 32.2, 32.7, 32.9, 33.2, 33.3, 34.8, 35.4, 38.1, 126.1, 126.8, 128.3, 128.4, 129.1, 129.2, 129.7 129.8, 134.4, 134.5, 138.7, 139.0, 147.9, 148.1.

IR (CCl_4): ν = 3519 m, 2960 s, 2932 s, 2872 s, 2837 m, 1465 s, 1456 s, 1379 m, 1331 m, 1154 w, 1120 w, 908 m cm^{-1}.

MS (EI) *m/z* (% rel intensity) 286 (85) M^+, 271 (23), 257 (100), 243 (18), 229 (20), 215 (10), 204 (53), 191 (20), 175 (42), 163 (10), 145 (8), 121 (27), 105 (12), 91 (20); exact mass calcd for $C_{20}H_{30}O$ *m/z* 286.2230, found *m/z* 286.2308.

Reaction of the 2,3-Dimethylcyclohexenyl Carbene Complex 42 with Propyne:

A solution of carbene complex **42** (0.115 g, 0.22 mmol) in hexanes (6.6 mL) was deoxygenated by the freeze-thaw method (3 cycles). To this solution was added gaseous propyne (~9 mL, 0.37 mmol at STP). The propyne was taken up in a gas syringe from a 50 mL flask that had been flushed with the acetylene for 2 min. The mixture was stirred at 50 °C under Ar and after 21 h TLC indicated starting material still present. An additional 0.5 equiv of acetylene was added and the reaction stirred a further 24 h. The crude mixture was then stirred in air for 1.5 h and filtered through Celite. After removal of the solvent on a rotary evaporator, the crude products were purified on silica gel with a 1:1:4 mixture of Et_2O:CH_2Cl_2:hexanes as eluent to give an 11.8% yield of *trans*-**43b** (R_f = 0.44), an 8.9% yield of *cis*-**43b** (R_f = 0.39) and a mixed fraction of *cis* and *trans* isomers that represented a 23.9% yield of **43b**. The total ratio of *trans*:*cis* isomers was 57:43. The *ortho*-alk-2-yne phenol **44b** (R_f = 0.66) was also isolated in a 1–2% yield. When a large excess of propyne was used, the phenol **44b** was obtained in 15.9% yield along with 19.3% of the dienones **43b**. Spectral data for **43b**:

^1H NMR ($CDCl_3$): *trans*-**43b**; δ = 0.94 (d, 3H, J = 5.9 Hz), 1.18 (s, 3H), 1.18–1.20 (m, 1H), 1.43–1.60 (m, 3H), 1.80–1.93 (m, 2H), 1.89 (s, 3H), 2.86–2.94 (m, 1H), 3.60 (s, 3H), 6.82 (s, 1H); *cis*-**43b**; δ = 0.65 (d, 3H, J = 7.0 Hz), 1.27 (s, 3H), 1.36–1.45 (m, 1H), 1.53–1.64 (m, 1H), 1.65–1.72 (m, 1H), 1.87 (s, 3H), 1.90–2.06 (m, 2H), 2.28–2.36 (m, 1H), 2.86–2.93 (m, 1H), 3.61 (s, 3H), 6.84 (s, 1H).

^{13}C NMR ($CDCl_3$) *trans*-**43b**; δ = 15.5, 15.6, 15.7, 23.4, 27.8, 31.0, 40.1, 53.0, 59.0, 132.5, 136.3, 138.07 (s, C-2 or 4a), 143.1, 204.8; *cis*-**43b**; δ = 15.2, 22.5, 22.7, 25.1, 28.1, 40.5, 52.92 (s, C-8a), 59.3 132.2, 135.5, 137.4, 145.16 (s, C-4), 207.0 , 1 C not located.

IR (CCl_4) cm^{-1} 2978 m, 2932 s, 2859 m, 2832 w, 1663 m, 1643 s, 1451 m, 1379 s, 1369 s, 1340 w, 1155 s, 1120 w, 1093 w, 1079 w, 1054 w, 1036 m, 957 w.

MS (*cis* + *trans*) (EI) *m/z* (% relative intensity) 220 (43) M^+, 205 (15), 177 (8), 165 (17), 138 (32), 121 (9), 105 (7), 91 (14), 83 (100), 77 (11), 65 (6).

Anal. (*cis* + *trans*) calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 75.90; H, 9.13.

Spectral data for **44b**: At r.t. the ^1H NMR spectrum indicates the presence of isomers due to hindered rotation about the aryl-vinyl single bond. Several of the peaks begin to broaden at about 50 °C, although most have still not fully coalesced at 84 °C. The following data were recorded at r.t.

^1H NMR ($CDCl_3$): δ = 1.12 (d, 3H, J = 7.2 Hz), 1.15 (d, 3H, J = 7.2 Hz), 1.40–1.50 (m, 1H), 1.52 (s, 3H), 1.53 (s, 3H), 1.62–1.92 (m, 3H), 2.03–2.30 (m, 3H), 5.02 (s, 1H), 5.11 (s, 1H), 6.61 (s, 1H), 6.63 (s, 1H), 6.80 (s, 1H).

IR (CCl_4): ν = 3700–3350 s, 2959 s, 2929 s, 2863 s, 1640 m, 1477 s, 1331 m, 1261 s, 1209 s, 859 s cm^{-1}.

MS (EI) *m/z* (% rel intensity): 230 (100) M^+, 215 (30), 201 (14), 187 (26), 173 (37), 159 (21), 148 (74), 135 (30), 128 (8), 115 (9), 105 (6), 91 (17), 77 (10), 65 (4); exact mass calcd for $C_{16}H_{22}O$ 230.1671, found 230.1671.

Diels–Alder Reaction of *trans*-Piperylene with 2,6-Dimethylbenzoquinone:

To a solution of 2,6-dimethylbenzoquinone (0.350 g, 2.57 mmol) in CH_2Cl_2 (10 mL) at −78 °C under Ar was added of a 1.0 M solution of $TiCl_4$ (2.57 mL, 2.57 mmol) in CH_2Cl_2 and the resulting mixture stirred 5 min at −78 °C. To this mixture was added dropwise *trans*-piperylene (0.175 g, 2.57 mmol) and the reaction stirred for 30 min. At this time the solution was warmed to 0 °C and washed with ice-cold sat. $NaHCO_3$, H_2O and brine (each 3 × 10 mL), dried ($MgSO_4$) and concentrated on a rotary evaporator. The crude mixture was filtered through a plug of silica gel to give 0.506 g (96%) of the desired *cis*-cycloadduct **45**. R_f (1:1:4, Et_2O:CH_2Cl_2:hexane) = 0.35.

^1H NMR ($CDCl_3$): δ = 0.80 (d, 3H, J = 7.3 Hz), 1.41 (s, 3H), 1.99 (s, 3H), 2.02–2.15 (m, 2H), 2.82–2.92 (m, 2H), 5.53–5.63 (m, 2H), 6.62 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = 16.3, 19.5, 20.6, 24.0, 39.4, 50.4, 50.6, 122.6, 130.1, 137.8, 149.7, 198.8, 203.8.

IR (neat): ν = 3025 m, 2973 m, 2934 m, 2875 m, 1678 s, 1628 m, 1463 m, 1426 m, 1376 s, 1324 m, 1233 s, 1196 m, 1018 m, 971 m, 916 m, 733 s, 707 m cm^{-1}.

MS (EI) *m/z* (% rel intensity) 204 (22) M^+, 189 (20), 176 (100), 161 (69), 143 (15), 133 (11), 120 (12), 105 (13); exact mass calcd for $C_{13}H_{16}O_2$ *m/z* 204.1150, found *m/z* 204.1150.

When the reaction was carried out in the same manner and then allowed to warm to r.t. for 30 min, workup gave a mixture which consisted of the cycloadduct **45** as a minor product and the epimerized cycloadduct **46** as the major product.

^1H NMR ($CDCl_3$): δ = 0.92 (d, 3H), 1.07 (s, 3H), 1.94 (s, 3H), 2.17–2.37 (m, 2H), 2.39–2.48 (m, 1H), 2.98–3.05 (m, 1H), 5.49–5.61 (m, 2H), 6.53 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = 17.1, 18.8, 22.6, 23.4, 37.9, 46.1, 51.5, 123.3, 131.6, 137.8, 148.4, 201.2, 203.6.

IR (CCl_4): 3027 s, 2988 s, 2963 s, 2932 s, 2905 s, 2874 s, 2849 m, 1691 s, 1627 m, 1460 m, 1452 m, 1436 s, 1375 s, 1333 s, 1301 s, 1284 m, 1178 m, 1166 m, 1091 w, 1061 w, 1034 w, 945 w, 908 w, 893 cm^{-1}.

MS (EI) (% rel intensity) 204 M^+ (100), 188 (50), 176 (33), 171 (6), 161 (43), 147 (8), 143 (15), 133 (13), 128 (5), 124 (6), 119 (7), 108 (18), 196 (19), 133 (13), 128 (5), 124 (6), 119 (7), 108 (18), 96 (19), 91 (35), 83 (72); exact mass calcd for $C_{13}H_{16}O_2$ *m/z* 204.1150; found *m/z* 204.1150.

Reduction of the Dihydroquinone 45 with Wilkinson's Catalyst:
To a solution of **45** (0.023 g, 0.11 mmol) in anhyd benzene (3 mL) was added $(PPh_3)_3RhCl$ (0.013 g, 0.014 mmol). H_2 gas was bubbled through the solution for 1–2 min and then the mixture was stirred at r.t. under a balloon of H_2. The reaction was checked by TLC after 17 h and determined to be complete. The crude mixture was filtered through Celite and concentrated on a rotary evaporator. Purification of the products on a silica gel column with a 1:1:4 mixture of Et_2O/CH_2Cl_2/hexanes gave 0.007 g (28%) dihydroquinone **47** and a small amount of the tetrahydroquinone **48** (yield not determined). When the reduction of **45** was allowed to run for 4 days, a 26% yield of a 6:1 mixture of the dihydroquinones **47** and **49** was obtained along with a 36% yield of the two diastereomers of the tetrahydroquinone **48**.

Spectral data for **47**: R_f (1:1:4) = 0.38.

^1H NMR ($CDCl_3$): δ = 1.21 (d, 3H, J = 7.1 Hz), 1.33 (s, 3H), 1.30–1.46 (m, 2H), 1.72–1.83 (m, 2H), 1.97 (s, 3H), 2.45–2.51 (m, 1H), 6.40 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = 16.5, 16.6, 24.5, 25.5, 29.2, 30.2, 41.6, 51.4, 59.5, 134.2, 149.6, 202.2, 204.0.

IR (neat): ν = 2965 s, 2935 s, 2861 s, 1637 s, 1625 s, 1460 s, 1446 s, 1375 s, 1335 m, 1270 s, 1199 s, 1180 s, 1022 s, 971 s, 903 m, 885 m cm^{-1}.

MS, *m/z* (% rel intensity): 206 (100) M^+, 191 (5), 178 (31), 163 (11), 151 (60), 138 (52), 124 (21), 109 (18), 96 (73), 91 (12), 81 (12), 77 (17), 68 (63).

Anal. calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.43; H, 8.90.

Spectral data for **48**: R_f (1:1:4) = 0.30.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (d, 3H, 6.1 Hz, 2 or 8-CH_3), 1.09 (d, 3H, J = 6.4 Hz, 2 or 8-CH_3), 1.20–1.60 (m, 3H), 1.32 (s, 3H, 8a-CH_3), 1.55–1.65 (m, 2H), 1.65–1.78 (m, 1H), 1.78–1.83 (m, 1H), 2.32–2.40 (m, 1H), 2.48–2.54 (m, 1H), 2.68 (dd, 1H, J = 17.0, 7.2 Hz), 2.95–3.05 (m, 1H).

IR (neat): ν = 2967 s, 2935 s, 2863 s, 1711 s, 1454 m, 1379 m, 1244 m, 1181 m, 1143 m, 1084 m, 995 m, 733 m cm^{-1}.

MS *m/z* (% rel intensity): 208 M^+ (100), 193 (13), 180 (6), 165 (16), 152 (15), 137 (17), 123 (10), 110 (66), 95 (37), 81 (33), 67 (46); exact mass calcd for $C_{13}H_{20}O_2$ *m/z* 208.1463; found *m/z* 208.1463.

Reduction of the Dihydroquinone 46 with Wilkinson's Catalyst:
The reduction of **46** (0.136 g, 0.66 mmol) was carried out as described for **45**. A 17 h reaction time gave 0.072 g (53%) of dihydroquinone **49** and 0.044 g (33%) of the tetrahydroquinone **50**. Spectral data for **49**:

^1H NMR ($CDCl_3$): δ = 0.96 (d, 3H, J = 6.9 Hz), 1.13 (s, 3H), 1.32–1.64 (m, 4H), 1.68–1.79 (m, 2H), 1.93 (s, 3H), 2.14–2.22 (m, 1H), 2.97 (dd, 1H, J = 11.4, 3.4 Hz), 6.49 (s, 1H).

^{13}C NMR ($CDCl_3$): δ = 15.9, 17.1, 19.4, 21.1, 22.2, 27.7, 34.4, 49.1, 53.0, 137.3, 147.7, 201.8, 204.2.

IR (CCl_4): ν = 2998 w, 2975 w, 2960 w, 2875 w, 1695 s, 1680 s, 1632 w, 1497 w, 1454 m, 1384 s, 1338 w, 1318 w, 1282 m, 1200 w, 1180 w cm^{-1}.

MS (EI): *m/z* (% rel intensity): 206 (100) M^+, 191 (20), 178 (15), 173 (4), 163 (22), 151 (29), 145 (5), 137 (35), 131 (3), 124 (40), 119 (4), 109 (30), 96 (92), 91 (21), 81 (28), 77 (25), 68 (87), 65 (16).

Anal. calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.43; H, 8.90.

Spectral data for **50**: R_f (1:1:4) = 0.23.

^1H NMR ($CDCl_3$): δ = 0.92 (d, 3H, J = 7.0 Hz), 0.99 (s, 3H), 1.13 (d, 3H, J = 6.4 Hz), 1.20–1.33 (m, 1H), 1.33–1.40 (m, 1H), 1.40–1.48 (m, 1H), 1.55–1.65 (m, 1H), 1.68–1.78 (m, 1H), 1.85–1.90 (m, 1H), 2.10–2.18 (m, 1H), 2.18–2.20 (m, 1H), 2.73 (dd, 1H, J = 19.4, 6.9 Hz), 2.82–2.90 (m, 1H), 3.05–3.10 (m, 1H).

IR (neat): ν = 2966 s, 2936 s, 1706 s, 1446 m, 1409 m, 1378 m, 1318 w, 1280 m, 1260 w, 1228 m 1172 m, 1154 m, 1118 m, 1098 m, 1033 w, 1004 w, 92 w,733 m cm^{-1}.

MS (EI): *m/z* (% rel intensity): 108 (85) M^+, 193 (5), 180 (10), 165 (11), 151 (6), 137 (30), 123 (8), 109 (100), 95 (35), 91 (9), 81 (33), 77 (8), 67 (24); exact mass calcd for $C_{13}H_{20}O_2$ *m/z* 208.1463; found *m/z* 208.1463.

Assignment of Stereochemistry of the Major Isomer of the Decaladienones 43b:
A sample of the major diastereomer of **43b** (0.055 g) which was completely separated from the minor diastereomer was dissolved in a 1:1 THF:10% HCl mixture (20 mL) and stirred at 60–70°C for 1.5 h. The mixture was diluted with hexane (10 mL) and the aqueous layer was then drained away. The organic layer was extracted with H_2O (2 × 20 mL) and then washed with sat. $NaHCO_3$ (20 mL) dried ($MgSO_4$) and concentrated on a rotary evaporator. The mixture was found to consist of a mixture of the dihydroquinones **47** and **49** by a comparison with the ^1H NMR and ^{13}C NMR spectrum of **47** and **49** prepared as described above. The minor isomer of **43b** was hydrolyzed in a similar manner to produce a mixture that contained one major compound tentatively assigned as **51**. There were no peaks in the ^1H NMR spectrum of the crude mixture that correlated with those for **47** and **49**. On the basis of these two experiments, the stereochemistry of the major isomer of the decaladienone **43b** was assigned as *trans*.

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