Chiral Ancillaries in the Benzannulations of Alkoxy and Amino Carbene Complexes with Alkynes

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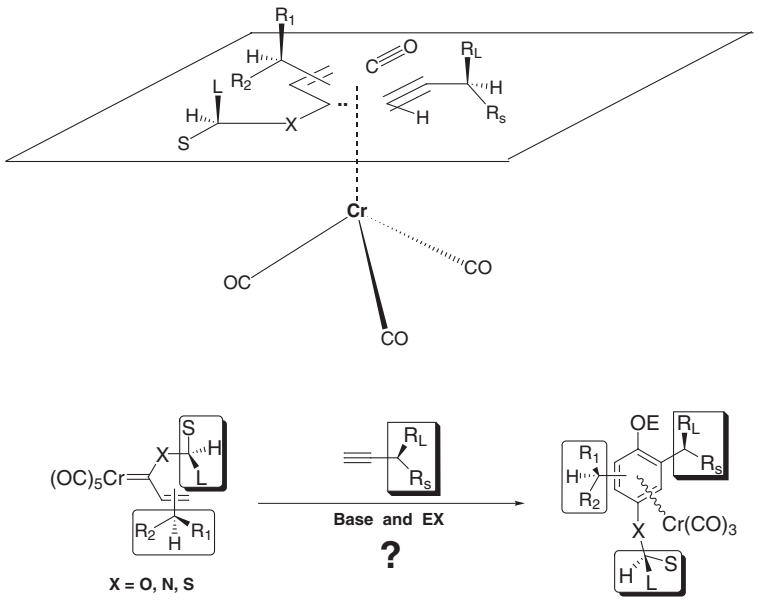
Abstract: The asymmetric benzannulation of chiral Fischer carbene complexes were investigated with a series of complexes bearing either chiral alcohols or chiral amines at the heteroatom stabilizing substituent. A set of seven alkenyl complexes and one aryl complex were prepared from five chiral alcohols; (1*S*,2*R*,5*S*)-(+)-menthol, (1*R*,2*S*)-(−)-*trans*-2-phenylcyclohexanol, (±)-*trans*-2-methylcyclopentanol, (±)-isoborneol, and (−)-8-phenylmenthol. The reaction of all seven of the alkenyl complexes with pent-1-yne and 3,3-dimethylbut-1-yne gave (arene)chromium tricarbonyl complexes with very low asymmetric inductions (0–20% de). The phenyl carbene complex derived from (+)-menthol gave good asymmetric induction with 3,3-dimethylbut-1-yne as had been previously reported, but the reaction with pent-1-yne gave lower induction and a much lower chemical yield. Alkenyl complexes bearing prolinol derivatives as the heteroatom stabilizing substituent also gave very low induction in reactions with pent-1-yne and this held true for both *E*- and *Z*-isomers of these complexes. An alkenyl carbene complex derived from the C-2 symmetrical amine, 3,5-dimethylmorpholine, reacted with pent-1-yne to give moderate yields of the (arene)chromium tricarbonyl complex but only in 10% de. High asymmetric inductions were observed for the cyclohexadienone annulation of atropisomeric 2-(*N*-methyl-3-methylindolyl) carbene complexes prepared from the chiral auxiliary, (4*R*,5*S*)-5-phenyl-4-methylimidazolidinone. Each atropisomer gives a single and different diastereomer of the same 4*H*-carbazol-4-one where it is the chiral axis of each atropisomer that controls the sense of induction and not the chirality of the auxiliary. Thus it is likely that these complexes, unlike all of the others examined in this work, react with acetylenes in a process in which the chiral auxiliary is not free to rotate about the carbene carbon in any of the reaction intermediates leading to product formation.

Key words: asymmetric benzannulation, chiral amine, chiral alcohol, chiral carbene complex, (arene)chromium tricarbonyl, planar chirality, arene complexes

The benzannulation reaction of chromium carbene complexes with alkynes is useful for the preparation of benzenoids and other aromatic compounds.[1] In its most useful version, an α,β-unsaturated carbene complex reacts with an alkyne to give a phenol product that results from the assembly of the unsaturated substituent, the carbene carbon, the alkyne and a carbon monoxide ligand in the coordination sphere of the metal. Since all of the bonds between all of the fragments are formed in the coordination sphere of the metal, the possibility exists for an asymmetric version of this reaction where an existing chiral center in one of the pieces can induce the formation of a specific stereoisomer about the center of planar chirality in the arene chromium tricarbonyl complex. As illustrated in Scheme 1, there are three possibilities for the incorporation of chiral centers into the starting materials. Neither of these possibilities have been extensively investigated as of yet and all of the studies have only recently appeared in the literature following a general method for the in-situ protection of the phenol function and the resulting production of air-stable arene chromium tricarbonyl complexes.[2] High levels of stereoselectivity for induction of the center of planar chirality has been observed with chiral alkynes that contain a chiral center at a propargyl ether function.[3] A few select examples of asymmetric induction from a chiral center on the carbon substituent of the carbene carbon have been reported and a few of those have given high stereoselectivity.[4] The same situation applies for the third option involving either chiral amines or chiral alcohols at the heteroatom stabilizing substiuent.[5] All of the known examples of the latter are somewhat limited and in the case of intermolecular reactions of complexes derived from chiral alcohols the reactions have been only reported with 3,3-dimethylbut-1-yne. In this report we describe a general study on the third option involving the benzannulation of chiral carbene complexes bearing chiral alcohols and amines as the heteroatom stabilizing carbene carbon substituent.

Nearly all benzannulations reactions in the literature have been carried out and optimized on either methoxyl or ethoxy complexes and relatively few on amino carbene complexes.[1] This is because, with the exception of alkenyl complexes with terminal alkynes,[6] the reactions of dialkylamino complexes generally give low yields of phenol products and instead give predominately five-membered ring annulated products. For this reason, we began this study on the asymmetric benzannulation with a chiral auxiliary derived from chiral alcohols. Despite the very large literature record on the chemistry of Fischer carbene complexes, very few optically active complexes have been prepared from chiral alcohols and even fewer have had their chemistry examined.[7] The set of eight chiral carbene complexes that were chosen to be examined is shown in the Figure 1. Complexes **1–5** are new and their syntheses are described below and complexes **6–8** were prepared as previously reported.[5c] This set of eight chiral carbene complexes were prepared from a set of five chiral alcohols which are; 1. (1*S*,2*R*,5*S*)-(+)-menthol (complexes **6–8**); 2. (1*R*,2*S*)-(−)-*trans*-2-phenyl-



Scheme 1

cyclohexanol (complex **1**); 3. (±)-*trans*-2-methylcyclopentanol (complex **2**); 4. (±)-isoborneol (complex **3**); and 5. (–)-8-phenylmenthol (complex **4**).

The chiral alkoxy carbene complexes **1**–**5** were prepared by the method of Connors involving the in situ generation of a mixed anhydride complex. The tetramethyl ammonium acylates **9** and **10** were treated with 1.05 equivalents of acetyl bromide in dichloromethane at −78 °C. To the resulting deep red-purple solution was added 1.0 equivalent of the chiral alcohol and the resulting mixture allowed to react for various times at temperatures between −78 °C and −20 °C to give the red carbene complexes in the yields indicated in Table 1. The success of these reactions are known to be a function of concentration, temperature and the nature of the solvent however no attempt was made to optimize these reactions.

The crystal structure of the *trans*-propenyl (–)-menthol complex **5** was determined and the ORTEP is shown in Figure 2. The *trans*-propenyl group has the *s-cis* conformation and the propenyl group is nearly co-planar with the carbene complex as the dihedral angle Cr–C(6)–C(7)–C(8) is 12°. The isopropyl group of the menthol is projected nearly perpendicular to the plane containing the *trans*-propenyl group. The dihedral angle for C(6)–O(6)–C(10)–C(11) is 81° and this is offset by the dihedral angle of C(7)–C(6)–O(6)–C(10) of 9°. This conformation thus comes very close to providing the maximum shielding of one face of the propenyl group. This of course may not be the only conformation present in solution and this structure may bear no relation to the organometallic species at which the stereogenic step in the reaction with alkynes occurs.

The benzannulation of carbene complexes **1**–**5** were screened with pent-1-yne and the results are outlined in Table 2. The one-pot in-situ protection protocol was used which involves performing the benzannulation reaction in dichloromethane in the presence of three equivalents of

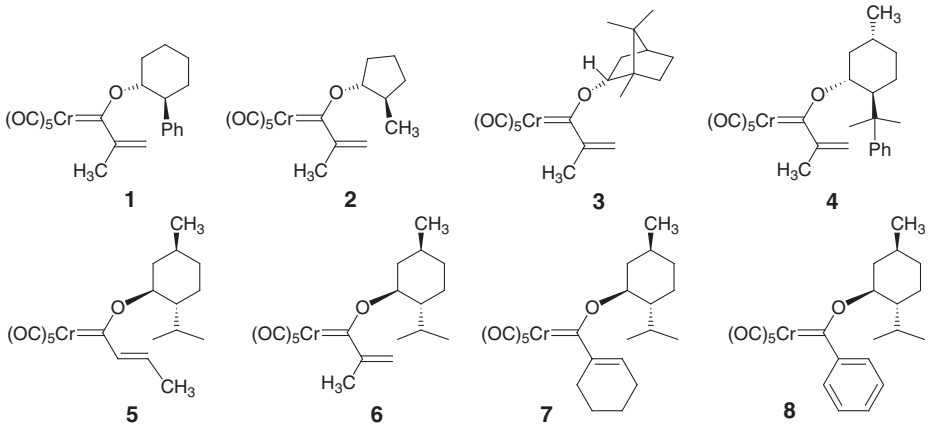


Figure 1 Structures of the eight chiral carbene complexes chosen for study

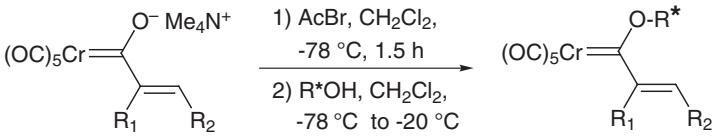


Table 1 Synthesis of Chiral Alkoxy Chromium Carbene Complexes **1–5**

Entry	Starting Salt	R_1	R_2	Time (h)	Product	Yield (%)
1	**9**	CH_3	H	24	**1**	12
2	**9**	CH_3	H	5	**2**	72
3	**9**	CH_3	H	21	**3**	45
4	**9**	CH_3	H	24	**4**	23
5	**10**	H	CH_3	21	**5**	50

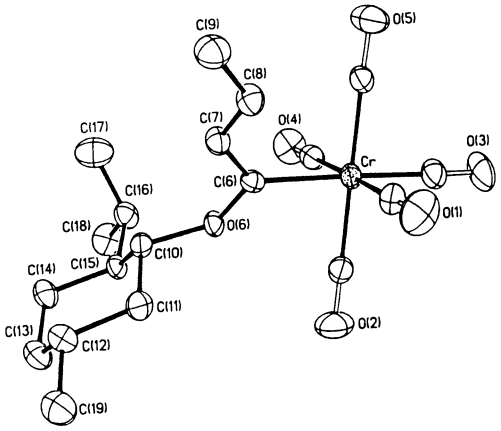


Figure 2 ORTEP of *trans*-propenyl (−)-menthol complex **5**

Hünig's base and two equivalents of *tert*-butyldimethylsilyl chloride.[2] The chromium tricarbonyl complexes **11–15** were isolated in good chemical yields, which ranged from 68–82%. The rest of the mass balance was not determined in each case but the metal-free silylated phenol was observed in only one case (Table 1, Entry 1, 23% yield). The asymmetric induction was poor in all cases with the highest at 20% de observed with complex **1** containing the *trans*-2-phenylcyclohexanol auxiliary to the lowest of 0% de observed with complex **2** containing the *trans*-2-methylcyclopentanol auxiliary.

The reaction of complexes **5–7** with 3,3-dimethylbut-1-yne gives asymmetric inductions that are in the range observed for the reaction of complexes **1–5** with pent-1-yne and the data are given in Table 3. The data in Entries 2 and 3 in Table 3 are taken from Ref. 5c and the procedure for these reactions (Method B) differs from that employed in the present work (Method A). These reactions were run in *tert*-butyl methyl ether and the silylation step was performed after the benzannulation reaction was complete and after the crude phenol chromium tricarbonyl product was partially purified by a rapid filtration through silica gel. A comparison of the two methods was made for the reaction of complex **7** and as can be seen by the first two Entries in Table 3, the asymmetric induction observed is approximately the same for each. However, the yield is higher for the procedure in which the benzannulation is carried out in the presence of the silylating agent. This

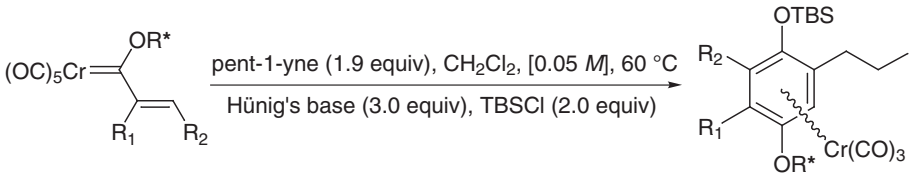


Table 2 Reactions of Chiral Alkoxy Carbene Complexes **1–5** with Pent-1-yne[a]

Entry	Starting Complex	R_1	R_2	Time (h)	Product	Yield (%)	Diastereomeric Ratio (%*de*)[b]
1	**1**	CH_3	H	19	**11**	69[c]	60 : 40 (20 %*de*)
2	**2**	CH_3	H	17	**12**	83	50 : 50 (0 %*de*)
3	**3**	CH_3	H	14	**13**	68	58 : 42 (16 %*de*)
4	**4**	CH_3	H	15	**14**	77	55 : 45 (10 %*de*)
5	**5**	H	CH_3	14	**15**	82	57 : 43 (14 %*de*)

[a] All reactions were carried out as indicated in the scheme unless otherwise indicated.
[b] All ratios were determined from ^1H NMR and/or ^{13}C NMR.
[c] Also isolated was the corresponding free arene **16** in 23 % yield.

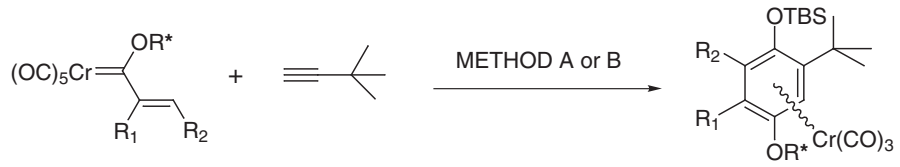


Table 3 Reactions of Chiral Alkoxy Carbene Complexes **1–5** with 3,3-Dimethylbut-1-yne

Entry	Starting Complex	R_1	R_2	Method[a]	Product	Yield (%)[b]	Diastereomeric Ratio (*%de*)
1	**7**	- (C_4H_8) -		A	**17**	90	55 : 45 (10 *%de*)
2	**7**	- (C_4H_8) -		B	**17**	59[c]	58 : 42 (16 *%de*)
3	**6**	CH_3	H	B	**18**	63[c]	57 : 43 (14 *%de*)
4	**5**	H	CH_3	A	**19**	78	52 : 48 (4 *%de*)

[a] Method A: Reaction carried out with a 0.05 M solution of carbene complex in CH_2Cl_2 with 1.9 equiv of alkyne in the presence of 3.0 equiv of Hünig's base and 2.0 equiv of TBSCl at 60 °C for 14 h. Method B: Reaction carried out with a 0.4 M solution of carbene complex in *t*-BuOMe at 55 °C for 55 min. After filtration through silica gel, the crude product was silylated with 4.0 equiv of TBSCl and 4.0 equiv of Et_3N at 25 °C for 3 h.

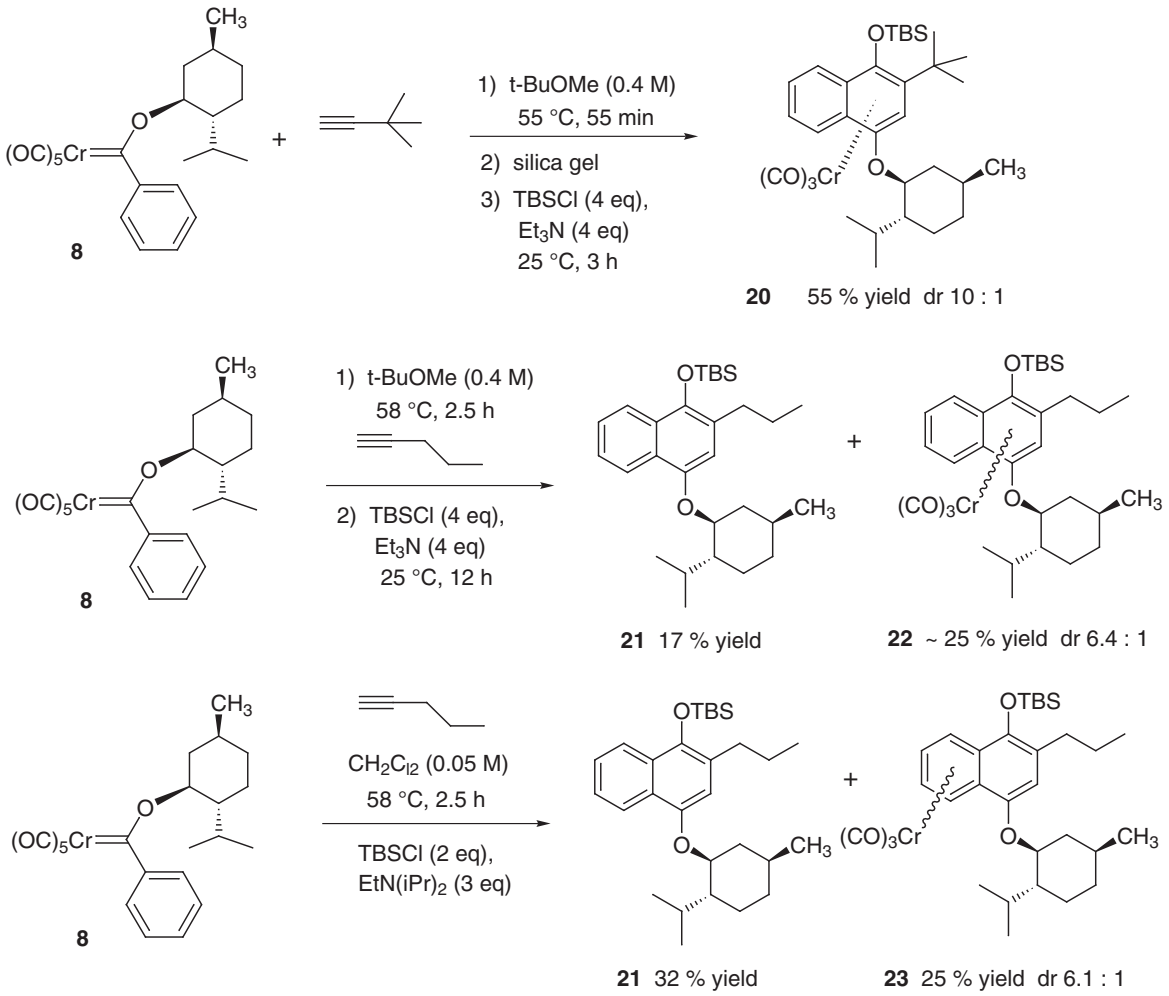
[b] After purification by chromatography on silica gel.

[c] Data taken from reference 5c.

may be due to some loses that would be anticipated when the air-sensitive chromium tricarbonyl phenol complex is filtered through silica gel in the presence of air.

Previous work by Dötz and Stinner revealed that the phenyl (–)-menthol complex **8** would react with 3,3-dimethylbut-1-yne to give the naphthol chromium tricarbonyl complex **20** with a 10:1 selectivity in favor of the diastereomer shown in Scheme 2.[5c] This is significantly higher than that seen for any of the alkenyl complexes **5**–**7** with the same alkyne (Table 3 and Ref. 5c). The menthol complex **8** gave the highest selectivity among a set of chiral phenyl complexes prepared from seven different chiral alcohols.[5c] Curiously, Dötz and Stinner did not report the reaction of complex **8** with any other alkyne. We were thus lead to investigate the reaction of complex **8** with pent-1-yne and the results are summarized in Scheme 2. This reaction was carried out with two different procedures: a sequential benzannulation/silylation process and a concurrent benzannulation/silylation process. In each case substantial amounts of the metal-free silylated phenol **21** was obtained, however, the arene chromium tricarbonyl complexes that were observed were different for the two procedures. The sequential process gives the arene complex **22** while the concurrent process gives the arene complex **23** with the chromium tricarbonyl group migrated to the other ring of the naphthalene core. Dötz and Stinner have shown that **23** is the thermodynamic product and that the isomerization will occur thermally. However, the two reactions in Scheme 2 were performed at the same temperature and with the same reaction time. Presumably, in this case the diisopropylethyl amine is accelerating this isomerization. The sizable amounts of metal free product in these reactions could be expected on the basis of previous observations that larger substituents on the alkyne produce more air-stable chromium tricarbonyl phenol complexes.[8] The *t*-butyl substituted phenol complex from the reaction of complex **8** with 3,3-dimethylbut-1-yne would be expected to be more air stable and this is indicated by the fact that it is stable to filtration through silica gel in the presence of air prior to silylation. Indeed, it is remarkable that a 55% yield of **20** was obtained. Apparently, the phenol complex from the reaction of **8** with pent-1-yne is less air-stable since substantial amounts of the metal-free arene was obtained for each procedure despite the fact that the protocol involving the exposure of the phenol complex to air during filtration through silica gel was deleted from the procedure for the sequential process. The asymmetric induction in the formation of the center of planar chirality for both complexes **22** and **23** is approximately the same (6.2:1) but it is not clear that this represents the actual stereoselectivity of the reaction since there is nearly equal amounts of metal-free product formed in each reaction. In any event, given the difficulty in retaining the metal on the benzannulated product with pent-1-yne, the low yield of arene complex **22** obtained for this reaction suggests that this reaction will not be synthetically useful in the general sense for the asymmetric synthesis of naphthalene chromium tricarbonyl complexes.

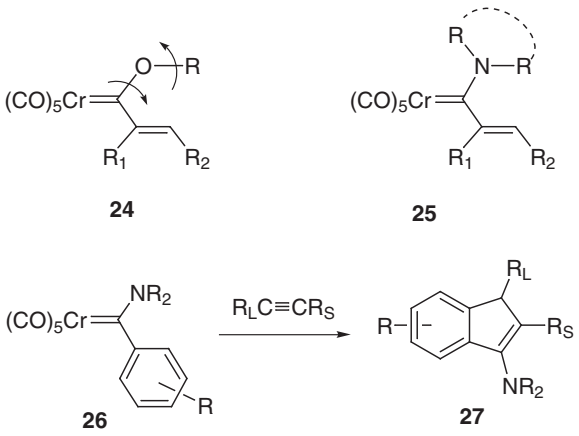
Given the failure of the asymmetric induction in the benzannulation of chiral alkoxy substituted carbene complexes attention was turned to carbene complexes that bear chiral nitrogen-based heteroatom stabilizing groups. An attractive feature of amino carbene complexes is that the rotational barrier about the nitrogen-carbene carbon bond is typically greater than 25–30 kcal/mol due to the resonance delocalization from nitrogen to the carbene carbon.[9] For the vast majority (if not all) of amino complexes this results in the complete inhibition of the interconversion of rotational isomers at room temperature. In alkoxy carbene complexes the rotational barrier is approximately 15 kcal/mol and thus one of the explanations for the low inductions observed for the benzannulation of alkoxy complex-



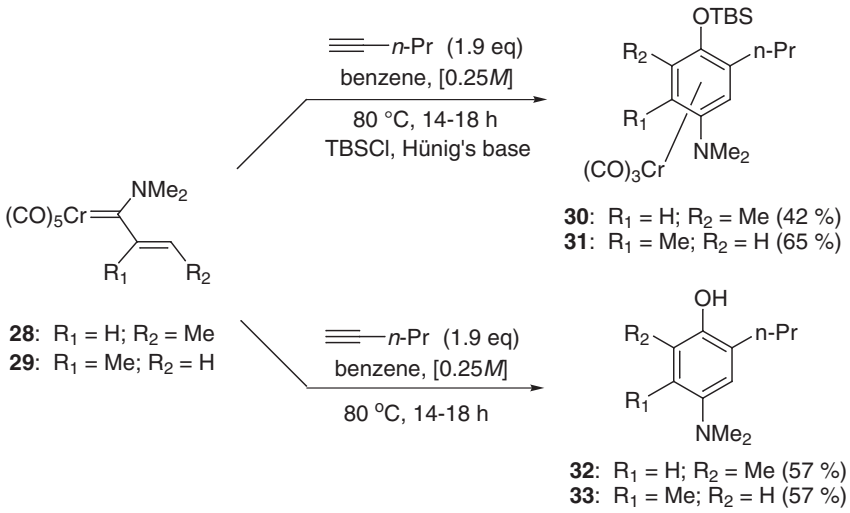
Scheme 2

es is the result of the fact that there are actually two degrees of freedom that separate the chiral center in a chiral alkoxy substituent and the metal center; the free rotations about both of the sigma bonds associated with the oxygen atom. It is possible with amino complexes to remove both of these degrees of freedom if a cyclic nitrogen substituent is used (Scheme 3).

A consultation of the literature reveals that the use of aryl carbene complexes of the type **26** derived from cyclic chiral amines may not be useful in asymmetric benzannulations since amino carbene complexes do not react with alkynes to give phenol products. It has been well documented that the reactions of aryl carbene complexes bearing amino substituents on the carbene carbon lead to the formation of indenes as the major product (Scheme 3).[6,10] However, we have found that the corresponding reactions of vinyl carbene complexes with amino substituents with terminal, but not internal, alkynes will give phenol products. An initial study of the scope of this reaction has been published,[6] and as illustrated in Scheme 4, both isopropenyl and *trans*-propenyl complexes will react with pent-1-yne to give phenol products, or performed in the presence of a silylating agent, both can give silyl protected phenol chromium tricarbonyl complexes. As a result of these findings, a number of alkenyl carbene complexes derived from chiral cyclic amines were prepared and their reactions with alkynes examined for asymmetric induc-



Scheme 3



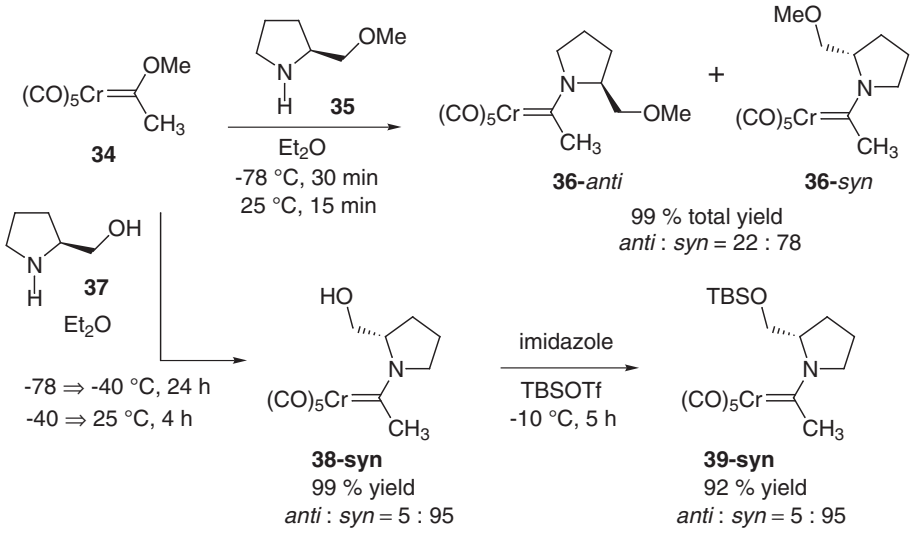
Scheme 4

tion in the formation of the center of planar chirality in the silylated phenol chromium tricarbonyl products.

The choice of chiral amine to incorporate into a Fischer carbene complex is somewhat limited because direct aminolysis of the alkenyl methoxy chromium carbene complex is successful with only a few unhindered secondary amines such as dimethylamine, pyrrolidine and morpholine. Most significantly, C-2 symmetrical *trans*-2,5-disubstituted pyrrolidines fail to react with methoxyl carbene complexes to give any substantial amount of amino carbene complexes.[11] However, carbene complexes derived from prolinol can be prepared by aminolysis and have been used in asymmetric Michael addition reactions.[12] In an effort to develop a convergent route to α,β-unsaturated Fischer carbene complexes, the chiral amino methyl carbene complexes **36** and **39** were prepared which were then converted to unsaturated complexes by a Peterson olefination reaction.[13]

The amino complex **36** was prepared in essentially quantitative yield by aminolysis of complex **34** with (*S*)-(+)-2-methoxymethyl pyrrolidine by the previously described procedure[12] to give a 78:22 mixture of isomers in which the *syn*-isomer *syn*-**36** predominates. Interestingly, the aminolysis of complex **34** with (*S*)-prolinol gives only the *syn*-isomer of complex **38** and, after silylation with *tert*-butyldimethylsilyl triflate, the chiral amino complex **39** could obtained as a exclusively the *syn*-diastereomer in 91% overall yield (Scheme 5).

The Peterson olefination of complexes **36** and **39** was accomplished according to Macomber's procedure[13] and is summarized in Table 4. Silylation of complex **36** with butyllithium and then trimethylsilyl chloride afforded complex **40** in 67% yield. The enolate of complex **40** was generated with butyllithium and then reacted with three different aldehydes in an effort to form alkenyl amino complexes. The reaction with pivaldehyde produced negligible amounts of product. The reaction with acetalde-



Scheme 5

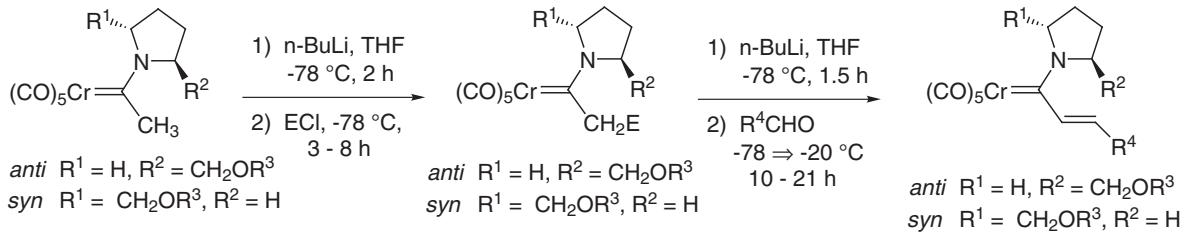


Table 4 Synthesis of Chiral Amino-Alkenyl Chromium Carbene Complexes

	methyl complex			silylmethyl complex				alkenyl complex			
Entry		R^3	*anti* : *syn*		E	Yield (%)	*anti* : *syn*		R^4	Yield (%)	*anti* : *syn*
1	**36**	CH_3	22 : 78	**40**	TMS	67	33 : 67	**43**	CH_3	47[a,b]	66 : 34
2	**36**	CH_3	22 : 78	**40**	TMS	67	33 : 67	**44**	Ph	54[c]	29 : 71
3	**36**	CH_3	22 : 78	**40**	TMS	67	33 : 67	**45**	t-Bu	<2[d,e]	
4	**36**	CH_3	22 : 78	**41**	TBS	7[f,g]	55 : 45				
5	**39**	TBS	5 : 95	**42**	TMS	91[h]	43 : 57	**46**	CH_3	42[i]	33 : 67

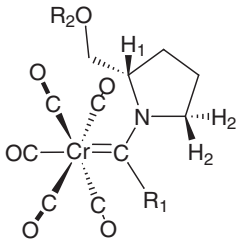
[a] The reaction was also stirred at 25 °C for 2 h.
[b] Also 8–50 % of the starting material and desilylated starting material also observed.
[c] Also isolated was 29 % of starting material.
[d] The reaction was also stirred at 25 °C for 1 h.
[e] Only 77 % of the starting material and 18 % of desilylated starting material were isolated.
[f] The reaction was stirred at –78 °C to –35 °C for 16 h and at –20 °C for 72 h.
[g] Reaction with TBSOTf and $CF_3CON(CH_3)$TBS only lead to recovery of starting material.
[h] The reaction was also stirred at –15 °C for 12 h.
[i] Also isolated was 30 % of the desilylated starting material.

hyde produced **43** in 47% yield as a 66:34 mixture of two isomers that could be painstakingly separated via silica gel chromatography. Reaction with benzaldehyde led to the desired alkenyl amino complex **44** in 54% yield as a mixture of diastereomers whose separation was also very difficult and tedious. These olefinations are difficult to drive to completion and desilylated complex **36** can often in isolated in significant amounts. The silylation of complex **39** gave **42** in high yield but the reaction produced a nearly 1:1 mixture of isomers from a single isomer of **39**. This is consistent with the observation that the deprotonation of an α-proton of an amino carbene complex will cause equilibration of their rotamers.[12,14]

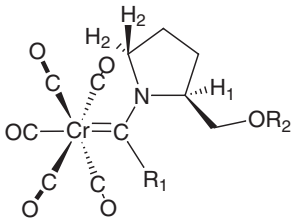
The assignment of the stereochemistry of the two rotamers for each pyrrolidine complex was determined by relative chemical shifts in the ^{1}H NMR according to the method of Fischer.[12,15,16] Accordingly, the *syn*-isomer has the alkoxymethyl group directed toward the metal and the proton H_1 would be expected to experience a downfield shift. Conversely, in the *anti*-isomer, proton H_2 would be expected to be shifted downfield since it is much closer to the metal center than in the *syn*-isomer. The chemical shifts of H_1 and H_2 for complexes **39**–**44** and **46** are given in Table 5. A clear assignment of the stereochemistry of these complexes would be expected to provide a basis for mechanistic interpretation of the stereochemistry of the benzannulation reactions involving each rotamer.

The benzannulation of a sample of complex **43** that was predominately the *syn*-isomer with pent-1-yne in the presence of Hünig's base and *tert*-butyldimethylsilyl chloride in benzene at 80 °C for 16 hours gave the desired amino (arene)chromium tricarbonyl complex **47** in 49% yield with 10% de. Although this is the first benzannulation reaction of a chiral amino carbene complex and the yield is within the range expected for amino alkenyl complexes with a terminal alkyne, the diastereoselectivity reveals that there is not a significant asymmetric induction in the center of planar chirality. Interestingly, the same level of asymmetric induction in the chromium tricarbonyl complex **47** was observed for the reaction of a sample of complex **43** that was predominately the *anti*-isomer. The *trans*-styryl complex **44** does not give any significant difference in induction than does the *trans*-crotyl complex **43**. Disappointingly, it was found that increasing the size of the chiral auxiliary from a prolinol methyl ether to a prolinol *tert*-butyldimethylsilyl ether did not result in increased induction as illustrated for the reaction of complex **46**. In this case, the *anti*-isomer gives a slightly higher induction that the *syn*-isomer. Although small, this difference is not understood since it would be expected that the rotamer with the chiral center closest to the metal would be the most capable of inducing the newly formed center of planar chirality comprised of the chromium complexed arene of the benzannulation reaction.

The low levels of induction observed for the reactions summarized in Table 6 could in principle be the result of isomerization of the *E*- and *Z*-isomers of the amino complexes **43**, **44** and **46** to give nearly equal mixtures of the



syn-rotomer



anti-rotomer

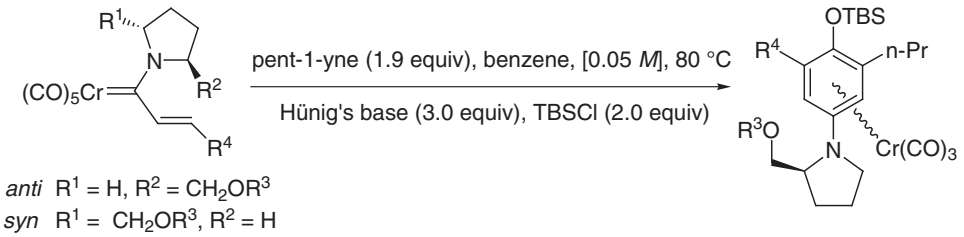
Table 5 Assignment of Rotomers using Proton Chemical Shifts of H_1 and H_2

		syn-Rotomer		*anti*-Rotomer			
Entry	Complexes	δ H_1	δ H_2	δ H_2	δ H_1	Δ (δ H_1)[a]	Δ (δ H_2)[b]
1	**39**	4.66	3.59, 3.64	4.41	4.12, 4.27	+0.25	–0,.58
2	**40**	4.72	3.57	4.31	4.08, 4.14	+0.41	–0.54
3	**41**	4.89	3.57, 3.67	4.50	4.04, 4.23	+0.39	–0.52
4	**42**	4.67	3.82	4.13	4.24	+0.54	–0.42
5	**43**	4.69	3.58, 3.64	4.55	4.12, 4.21	+0.14	–0.56
6	**44**	4.76	3.74, 3.81	4.63	4.19, 4.63	+0.13	–0.64
7	**46**	4.63	3.63, 3.81	4.24	4.14, 4.52	+0.39	–0.61

[a] The chemical shift differences were calculated from *syn* (δ H_n) - *anti* (δ H_n).
[b] The chemical shift differences were calculated from the average values.

E- and *Z*-isomers of each, followed by highly asymmetric benzannulation reactions that occur with high but opposite stereoselectivity for the two isomers. This was considered unlikely at the outset since although the *E*- and *Z*-enolates of amino carbene complexes readily undergo isomerization (Table 6),[12,14] the barrier to rotation about the carbon–nitrogen bond of an amino carbene is quite high and examples of thermal isomerization of amino carbene complexes are quite rare.[9] The data in Table 7 reveal that in fact the isomers of the amino carbene complexes **43** and **46** do slowly isomerize under the reaction conditions (80 °C). This complicates the interpretation of the low asymmetric inductions of the benzannulation of complexes **43**, **44** and **46** (Table 6). If these complexes isomerize under the reaction conditions to give a mixture of isomers whose asymmetric inductions cancel to some degree, then a solution would be to employ a C_2 symmetrical pyrrolidine complex.

The preparation of *trans*-2,5-dimethyl substituted pyrrolidine analogs of the methyl complex **36** has proven to be quite difficult[11] and has been reported in only 8% yield.[11a] We thus turned our attention to complex **51** which is the

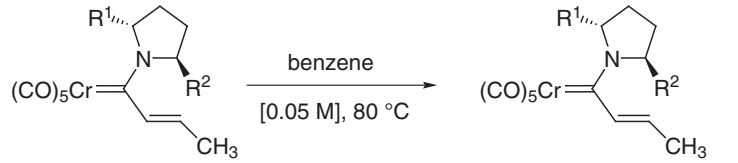


anti $R^1 = H$, $R^2 = CH_2OR^3$
syn $R^1 = CH_2OR^3$, $R^2 = H$

Table 6 Benzannulation Reactions of Chiral Amino Carbene Complexes **43, 44** and **46**[a]

Starting Complex	R^3	R^4	*anti* : *syn*	Time (h)	Product	Yield (%)	Diastereomeric Ratio (% de)[b]
43	CH_3	CH_3	≤17 : 83	16	**47**	49	55 : 45 (10 % de)
43	CH_3	CH_3	≥83 : 17	14	**47**	34	55 : 45 (10 % de)
44	CH_3	Ph	26 : 74	18	**48**	40[c]	52 : 48 (4 % de)
46	TBS	CH_3	14 : 86	16	**49**	51	55 : 45 (10 % de)
46	TBS	CH_3	86 : 14	14	**49**	48	59 : 41 (18 % de)

[a] All reactions were carried out as indicated unless otherwise indicated.
[b] All ratios were determined from 1H NMR and/or ^{13}C NMR.
[c] Also isolated was the metal free arene **50** in 13 % yield.



anti $R^1 = H$, $R^2 = CH_2OR^3$ *anti* $R^1 = H$, $R^2 = CH_2OR^3$
syn $R^1 = CH_2OR^3$, $R^2 = H$ *syn* $R^1 = CH_2OR^3$, $R^2 = H$

Table 7 Isomerization of the *ayn* and *anti* Rotomers of **43** and **46**

Starting Complex	R^3	initial *anti* : *syn*[a]	Time (h)	Recovery (%)	final *anti* : *syn*[a]
43	CH_3	≤83 : 17	15	68	62 : 38
43	CH_3	≥83 : 17	15	60	62 : 38
43	CH_3	68 : 32	30	85	58 : 42
43	CH_3	80 : 20	48	93	58 : 42
43	CH_3	48 : 52	48	57	57 : 43
46	TBS	14 : 86	16	91	50 : 50
46	TBS	86 : 14	22	91	75 : 25
46	TBS	75 : 25	37	73	64 : 36

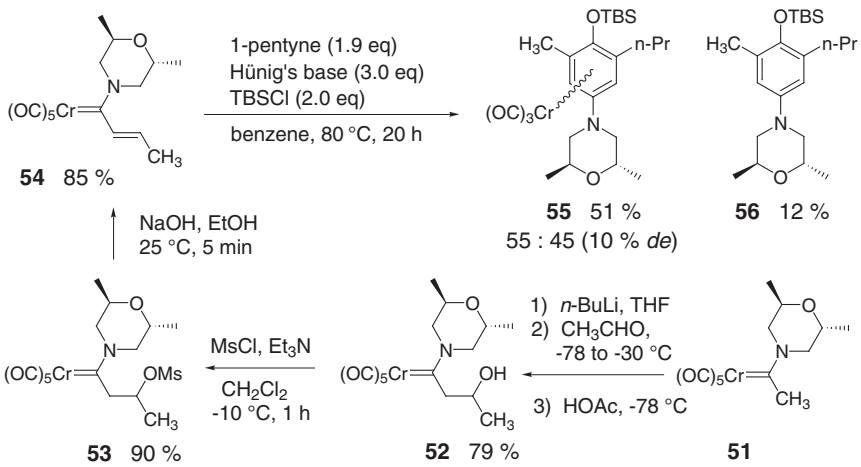
[a] All ratios were determined by ^1H NMR.
[b] Hünig's base was also present in this reaction.

only known carbene complex that contains a C_2 symmetrical chiral amine.[11b] The aldol reaction complex **51** with acetaldehyde proceed with complete lack of asymmetric induction to give the adduct **52** in 79% yield as a 1:1 mixture of diastereomers. The mesylation of **52** and subsequent elimination with sodium hydroxide in ethanol[17] gave the desired vinyl carbene complex **54** in 77% yield for the two steps. The benzannulation of complex **54** with 1-pentyne in the presence of Hünig's base and *tert*-butyldimethylsilyl chloride in benzene gave the (arene)chromium tricarbonyl complex **55** in 51% yield and in addition a 12% yield of the metal free benzannulated product **56** (Scheme 6). The diastereomeric excess in the formation of **55** was only 10%. The failure to observe significant asymmetric induction in this reaction can either be attributed to free rotation of the chiral amine in an intermediate that has no predominant low energy conformation or to the fact that the chiral groups on the chiral amine are too far removed from the newly formed arene ring to effect any facial selectivity in the installation of the chromium tricarbonyl group.

An opportunity to investigate the asymmetric induction in a complex where free rotation of the chiral amine substituent can not occur was presented when we prepared the indole carbene complex **59** and found that they could be separated into two atropisomers **59a** and **59b**.[5d] These complexes were prepared by the reaction of the lithium salt **58** generated from (4*R*,5*S*) 5-phenyl-4-methylimidazolidinone with the 1,3-dimethyl-2-indolyl carbene complex **57** in 48% yield. The atropisomers of **59** can be completely separated by a single pass on a silica gel column (R_f 0.43 and 0.30 in 1:1 EtOAc/hexane) to give each compound as lustrous black crystals. These isomers could not be interconverted thermally. When complex **59a** was heated in a deoxygenated benzene solution for 24 hours at 80 °C it was recovered in essentially quantitative yield with no detectable isomerization to **59b** or no detectable decomposition. However, when heated at 110 °C in deoxygenated toluene-d_8 for prolonged periods, only substantial decomposition of **59a** was observed.

The reactions of 1,3-disubstituted 2-indolyl pentacarbonyl chromium carbene complexes with alkyne are known to occur to give substituted a 2,4-cyclohexadienone unit embedded in a 4*H*-carbazol-4-one.[18] As illustrated by the reaction of complex **60** with hex-3-yne, the reaction occurs to give the 4-carbazol-4-one **62** in 79% along with the tetracarbonyl chromium dienyl complex **61** in 21% yield (Scheme 7). The metal complex is usually not isolated from these reactions but, nonetheless, the asymmetric induction from a chiral center on the heteroatom-stabilizing group can be monitored as the diastereomeric ratio with respect to the newly formed center of chirality at the carbon in position 6 in the cyclohexadienone ring.

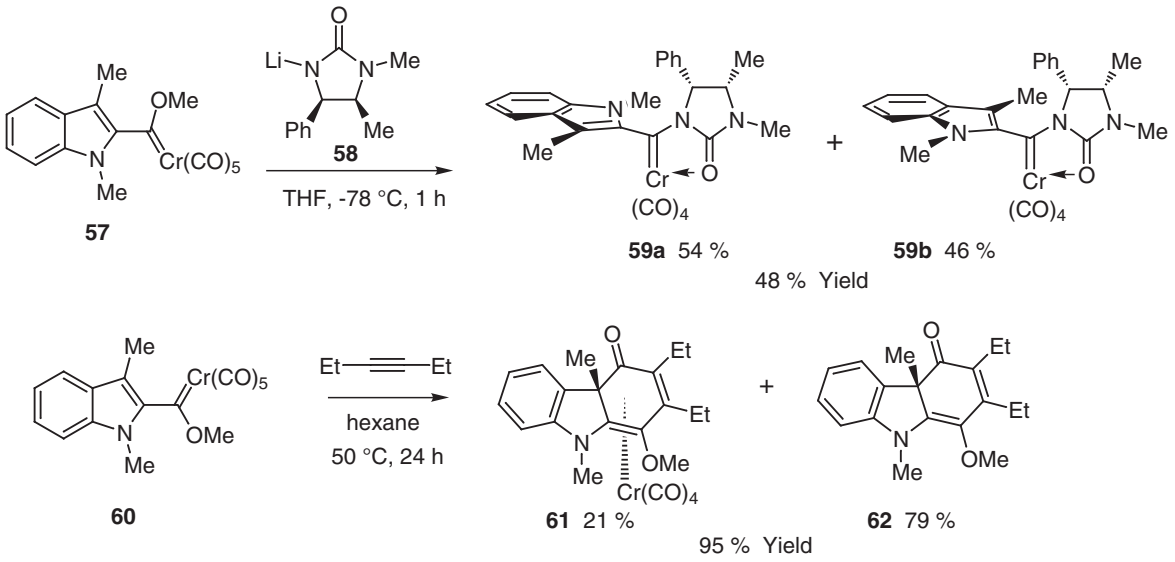
The cyclohexadienone annulation reactions of atropisomeric carbene complexes **59a** and **59b** were carried out independently and the results are summarized in Table 8. All of these reactions produce the cyclohexadienone product as the only compound, which is mobile on silica gel. The yield of the 4*H*-carbazol-4-one increases with decreasing concentration suggesting that multiple alkyne incorporation is a competing pathway as has been seen in the other examples.[19] The yields in Table 8 for Entries 3 and 6 are the average of several runs, where for example, the range in the yield of **63** is 54–70% at 0.005 M. In every reaction in Table 8 only a single diastereomer of the product could be observed within the limits of detection



Scheme 6

by ^{1}H NMR. Interestingly, it was found that the reaction is stereospecific with each atropisomer giving a different diastereomer one of which was dark orange and the other dark red. The diastereomeric 4*H*-carbazol-4-ones **63** and **64** do not exist as atropisomers although hindered rotation is evident in their ^{1}H NMR spectra at room temperature. The assignment of the stereochemistry of the diastereomeric 4*H*-carbazol-4-ones **63** and **64** and the atropisomeric carbene complexes **59a** and **59b** were determined by x-ray diffraction as previously described.[5d]

One possible explanation for the stereospecificity of the reactions of complexes **59a** and **59b** is shown in Scheme 8. Rotation about the indole-carbene carbon bond does not occur in the carbene complex **59** under the reaction conditions and if this is also the case for the vinyl carbene complexed intermediate **65** and the vinyl ketene complexed intermediate **66** then the stereochemistry of **63** can be predicted from **59a** according to the stereochemistry of the intermediates in Scheme 8. Reaction of **59a** with the alkyne would be expected to occur with the chromium and its ligands remaining on the same face of the indole ring to give the vinyl carbene intermediate **65**. Insertion of CO would then give the ketene complex **66**. If the electrocyclic ring-closure of the ketene complex **66** were to occur with a migration of the methyl group away from the chromium, then the stereochemistry of the observed product **63** could be accounted for. Evidence for this stereochemistry in the electrocyclic ring-closure can be found in our earlier observation of the η^4-cyclohexadienone chromium tetracarbonyl complex **61**.[18] Complex **61** is the only example of a complex of this type from the cyclohexadienone annulation. It was isolated as a single diastereomer with the methyl anti to the chromium although it is not clear that this is the only isomer produced since substantial amounts of the demetallated material was also produced in this reaction. Additional evidence for the anti-rotation of the methyl group in the cyclization of **66** comes from our recent studies on 1,4-induction in the cyclohexadienone annulation of chiral alkynes.[3b]



Scheme 7

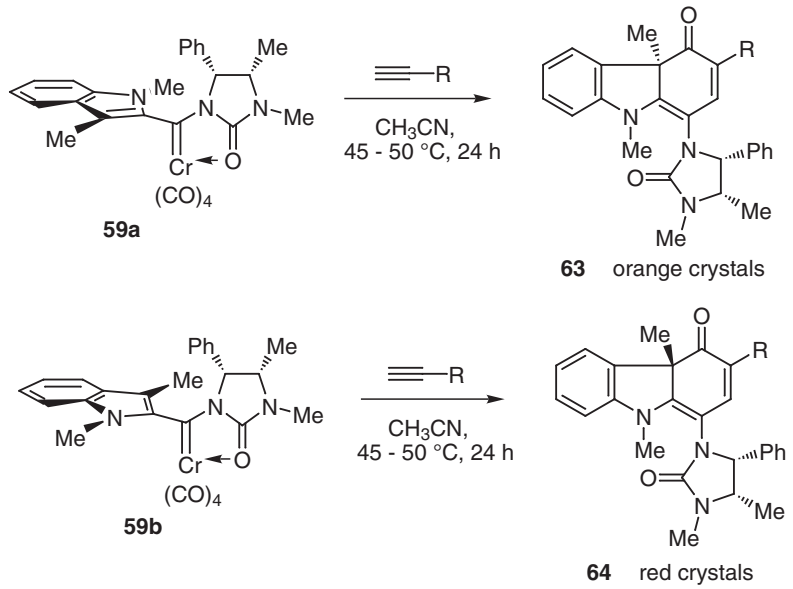


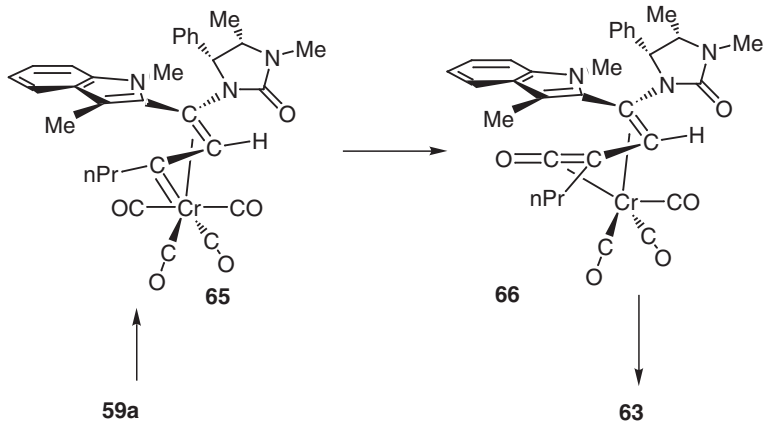
Table 8 Asymmetric Induction in Cyclohexadienone Annulation of Indole Complexes[a]

Entry	Carbene Complex	Mb	R	Yield **63**[c] (%)	Yield **64**[c] (%)	% de
1	**59a**	0.05	*n*-Pr	40	0.8	96
2	**59a**	0.01	*n*-Pr	50	1.0	96
3	**59a**	0.005	*n*-Pr	61[d]	1.2	96
4	**59b**	0.05	*n*-Pr	0.6	22	95
5	**59b**	0.01	*n*-Pr	0.9	35	95
6	**59b**	0.005	*n*-Pr	0.9	33[e]	95
7	**59b**	0.01	Ph	1.0	40	95

[a] Reactions carried out in acetonitrile at the indicated concentration in carbene complex with 1.5 equivalents of alkyne.
[b] Concentration of carbene complex.
[c] Isolated yield after purification on silica gel (hexane:EtOAc, 1:1). Upper limit on minor product determined by ^{1}H NMR.
[d] Yields for this reaction ranged from 54–70 %.
[e] Yields for this reaction ranged from 26–48 %.

The development of an asymmetric benzannulation reaction with a removal chiral auxiliary on the heteroatom-stabilizing group of the Fischer carbene complexes has proven to be an elusive goal with the present work being no exception. The series of chiral alcohols shown in Figure 1 all failed to give significant induction in the chromium tricarbonyl arene complexes produced from their reaction with n-propyl acetylene and 3,3-dimethylbut-1-yne with the exception of the reaction of the aryl complex **8** with 3,3,-dimethylbut-1-yne. This is certainly an outcome that was not anticipated given the complexity of the mechanism of this reaction[1] and from a consideration of the fact that whichever intermediate involved in the stereogenic step, it will be attached to the chiral auxiliary by two carbon–oxygen single bonds. Neither of these bonds is likely to be perturbed in a way to energetic favor a particular conformation. One of these degrees of freedom is removed with the cyclic amino complexes of the type **43–46,** however, these complexes also failed to give even modest induction. This failure may be due to the presence of *syn* and *anti* isomers, however, this cannot be the case for the cyclic amino complex **54** which is C-2 symmetrical. High asymmetric induction was only observed for the indole carbene complexes **59a** and **59b** with (4*R*,5*S*) 5-phenyl-4-methylimidazolidinone as the chiral auxiliary. These complexes are atropisomeric due to hindered rotation about the carbon–carbon bond connecting the indole to the carbene carbon. It is suspected that high induction observed for these complexes is a result of hindered rotation about this same bond in the stereogenic intermediate in the reaction pathway. Nonetheless, this tactic will not led to a general solution for either the benzannulation or cyclohexadienone annulation reactions since the substrate must be highly sterically substituted in positions close to the carbene carbon. While still not realized, the goal of finding a generally effective asymmetric benzannulation of Fischer carbene complexes that are chiral at the heteroatom should continue to spur future effort since its solution would have great impact on the chemistry of (arene)chromium tricarbonyl complexes.

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. THF and Et_2O were distilled from benzophenone ketyl under N_2. CH_2Cl_2 and



Scheme 8

benzene were distilled from CaH_2 under N_2. MeOH was dried over activated Molecular Sieves 4 Å prior to use. Chromatographic purifications were performed on EM Science silica gel (230–400 mesh) under gravity or by flash technique. High resolution mass spectra were recorded on a VG 70-250 instrument or obtained from the Midwest Center for Mass Spectrometry in Lincoln, Nebraska. Elemental analysis were done by Galbraith Laboratories in Knoxville, Tennessee. Optical rotations were obtained on a Perkin-Elmer 141 Polarimeter. All reactions were carried out under either argon or N_2 and for the reactions involving carbene complexes the reaction mixtures were deoxygenated by the freeze-thaw method (–196 °C/ 25 °C, 3 cycles).

Chiral Alkoxy Carbene Complexes; *trans*-Propenyl Complex 5; Typical Procedure

The ammonium salt **10** (134.1 mg, 0.40 mmol) was dissolved in CH_2Cl_2 (5 mL) at −78 °C, and freshly distilled AcBr (31.0 µL, 0.42 mmol, 1.05 equiv) was added dropwise. After stirring at −78 °C for 1−1.5 h, a solution of (1*S*,2*R*,5*S*)-(+)-menthol (65.6 mg, 0.42 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added dropwise. After stirring at −78 °C for 6 h, and −20 °C for 15 h, the mixture was concentrated under reduced pressure and subjected to silica gel column chromatography (size: 2 × 35cm, eluent: hexane) to provide 80.1 mg of the pure complex **5** (50%) as a red solid; R_f 0.35 (hexane); maroon needles from hexane at −78 °C, mp 102.0–103.0 °C.

^{1}H NMR (CD_2Cl_2): δ = 0.82 (d, 3 H, *J* = 6.6 Hz), 0.98 (d, 3 H, *J* = 6.5 Hz), 0.99 (d, 3 H, *J* = 6.8 Hz), 1.01 (m, 2 H), 1.21 (m, 1 H), 1.33 (q, 1 H, *J* = 11.6 Hz), 1.62 (m, 1 H), 1.81 (m, 1 H), 1.86 (d, 3 H, *J* = 6.2 Hz), 1.97 (m, 2 H), 2.08 (m, 1 H), 4.90 (br s, 1 H), 6.56 (br s, 1 H), 7.12 (br s, 1 H).

^{13}C NMR (CD_2Cl_2): δ = 17.4, 18.8, 21.5, 22.0, 22.1, 24.2, 27.0, 31.7, 34.5, 42.2, 48.7, 104.8, 144.6, 217.7, 225.2, 360.1.

IR (neat): ν = 2933w, 2069s, 1919s, 1639m, 1472w, 1170w cm^{-1}.

MS (EI): *m/z* (%) = 400 (3) M$^+$, 372 (10), 344 (3), 316 (2), 288 (21), 260 (84), 206 (16), 122 (54), 83 (76), 55 (100).

HRMS: *m/z* calcd for $C_{19}H_{24}CrO_6$ 400.0978, found 400.0982.

Anal calcd for $C_{19}H_{24}CrO_6$: C, 57.00; H, 6.04; found C, 56.77; H, 6.22;

Crystal Structure of Complex 5

The structure of **5** was solved by heavy atom methods which located the chromium atom of **5**. The remaining non-hydrogen atoms were located through subsequent difference Fourier and least squares syntheses. All hydrogens were included as idealized isotropic contributions (*d*CH = 0.960 Å, U = 1.2U for attached C). Crystal data for $C_{19}H_{24}CrO_6$; fw = 400.39, monoclinic, $P2_1$ (no. 4), *a* = 7.929(4), *b* = 12.116(5), *c* = 11.017(4) Å, *V* = 1012.4(8) Å, Z = 2, 3750 data collected; 2756 observed from 3750 independent reflections. *R*(*F*) = 4.87% and *R*(*wF*) = 4.93%. SHELXTL (4.2) software was used for refinement (G. Sheldrick, Siemens XRD, Madison, WI). Lists of the atomic coordinates, thermal parameters, bond distances and bond angles have been deposited with the Cambridge Crystallographic Database, Cambridge, England.

Carbene Complex 1

The ammonium salt **9** (134.1 mg, 0.40 mmol) was used to generate the acetoxy complex which was subsequently reacted with (1*R*,2*S*)-(−)-*trans*-2-phenylcyclohexan-1-ol (74.0 mg, 0.42 mmol, 1.05 equiv) for 31 h at −78 °C to −60 °C and 24 h at −20 °C in the same manner as described for **5** to provide 20.8 mg of the desired complex **1** (12%) as an orange red oil; R_f 0.74 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ = 1.46 (br d, 3 H, *J* = 12.5 Hz), 1.72 (m, 2 H), 1.87 (m, 2 H), 1.94 (m, 2 H), 2.04 (m, 2 H), 3.10 (br t, 1 H, *J* = 9.6 Hz), 4.56 (br s, 1 H), 4.61 (m, 2 H), 7.14–7.24 (m, 5 H).

^{13}C NMR (CD_2Cl_2): δ = 19.3, 24.9, 25.8, 32.1, 32.7, 34.1, 50.1, 95.1, 106.3, 127.5, 128.5, 128.9, 142.1, 216.7, 225.0, 352.2.

IR (neat): ν = 2937w, 2061s, 1986m, 1919s, 1280w, 1216m, 975m, 701m cm^{-1}.

MS (EI): *m/z* (%) = 420 (31) M$^+$, 392 (81), 364 (2), 336 (100), 308 (99), 280 (100), 252 (9), 227 (100), 211 (100), 198 (28), 170 (56), 159 (100).

HRMS: *m/z* calcd for $C_{21}H_{20}CrO_6$ 420.0665, found 420.0645.

Carbene Complex 2

The ammonium salt **9** (134.1 mg, 0.40 mmol) was used to generate the acetoxy complex which was subsequently reacted with (±)-*trans*-2-methylcyclopentanol (42.1 mg, 0.42 mmol, 1.05 equiv) for 5 h at −78 °C in the same manner as described for **5** to provide 98.9 mg of the desired complex **2** (72%) as a red oil; R_f 0.27 (hexane).

^{1}H NMR (CD_2Cl_2): δ = 1.05 (d, 3 H, *J* = 4.1 Hz), 1.39 (m, 2 H), 1.85 (m, 2 H), 1.91 (s, 3 H), 2.14 (m, 2 H), 2.40 (m, 1 H), 4.68 (m, 1 H), 4.99 (br s, 1 H), 5.05 (m, 1 H).

^{13}C NMR (CD_2Cl_2): δ = 17.5, 19.6, 19.7, 22.8, 32.1, 33.0, 41.4, 99.3, 106.5, 217.0, 225.0, 351.8.

IR (neat): ν = 2968w, 2964w, 2062s, 1929s, 1282m, 1222m, 1170w, 979m, 708w cm^{-1}.

MS (EI): *m/z* (%) = 344 (4) M$^+$, 316 (13), 288 (3), 260 (8), 232 (18), 204 (100), 178 (4), 150 (9).

HRMS: *m/z* calcd for $C_{15}H_{16}CrO_6$ 344.0352, found 344.0338.

Carbene Complex 3

The ammonium salt **9** (134.1 mg, 0.40 mmol) was used to generate the acetoxy complex which was subsequently reacted with (±)-isoborneol (64.8 mg, 0.42 mmol, 1.05 equiv) for 15 h at –78 °C and 6 h at –60 °C to –30 °C in the same manner as described for **5** to provide 71.7 mg of the desired complex **3** (45%) as a red oil; R_f 0.37 (hexane).

^{1}H NMR (CD_2Cl_2): δ = 0.96 (br s, 6 H), 0.99 (s, 3 H), 1.28 (m, 2 H), 1.66 (m, 1 H), 1.76 (m, 2 H), 1.90 (s, 3 H), 2.05 (m, 2 H), 4.64 (m, 1 H), 4.86 (m, 1 H), 5.12 (m, 1 H).

^{13}C NMR (CD_2Cl_2): δ = 11.8, 19.8, 20.1, 20.2, 20.3, 27.2, 33.8, 40.2, 45.8, 48.0, 50.5, 115.3, 155.5, 216.9, 224.9, 335.5.

IR (neat): ν = 2959w, 2016s, 1927s, 1282w, 1210m, 1166w, 977m, 707w cm^{-1}.

MS (EI): *m*/*z* (%) = 398 (3) M$^+$, 370 (6), 286 (6), 258 (44), 137 (100);

HRMS: *m*/*z* calcd for $C_{19}H_{22}CrO_6$ 398.0821, found 398.0811.

Carbene Complex 4

The ammonium salt **9** (1.00 g, 2.98 mmol) was used to generate the acetoxy complex which was subsequently reacted with (–)-8-phenyl-menthol (727.1 mg, 3.13 mmol, 1.05 equiv) for 24 h at –78 to –40 °C in the same manner as described for **5** to provide 322.0 mg of the desired complex **4** (23%) as a red oil. The complex **4** was not too stable and was handled with great care at each stage of isolation and purification using cold temperature and inert atmosphere when drying and storing; R_f 0.21 (hexane).

^{1}H NMR ($CDCl_3$): δ = 0.90 (d, 3 H, *J* = 6.0 Hz), 1.24 (s, 3 H), 1.33 (s, 6 H), 1.38–1.70 (m, 4 H), 1.80–2.10 (m, 3 H), 2.49 (m, 1 H), 4.66 (m, 1 H), 4.92 (s, 1 H), 5.63 (s, 1 H), 7.08–7.37 (m, 5 H).

^{13}C NMR (CD_2Cl_2): δ = 14.2, 19.3, 23.1, 24.8, 25.7, 29.7, 30.0, 31.8, 32.3, 34.0, 50.1, 95.0, 127.4, 127.9, 128.5, 128.9, 142.0, 216.7, 225.1, 352.0.

IR (neat): ν = 2927w, 2924w, 2061s, 1941s cm^{-1}.

MS (EI): *m*/*z* (%): = 476 (3) M$^+$, 448 (18), 414 (5), 392 (7), 364 (7), 336 (100), 282 (24), 262 (37), 214 (41), 199 (26), 186 (12), 164 (66).

HRMS: *m*/*z* calcd for $C_{25}H_{28}CrO_6$ 476.1291, found 476.1304.

Formation of (Arene)chromium Tricarbonyl Complexes Using Benzannulation Reactions Carried Out in the Presence of Base and Silylating Reagent; General Procedure

The chromium carbene complex (typically 0.10–1.00 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 argon. One half of the volume of anhyd CH_2Cl_2 or benzene (unless otherwise indicated) required for 0.05 M (for CH_2Cl_2) or 0.25 M (for benzene) (unless otherwise indicated) solution of the carbene complex, 1.9 equiv of the alkyne, 2.0–6.0 equiv of a base (freshly distilled or passed through a pipette size basic Al_2O_3 gel column), 1.0–5.0 equiv of a silyl triflate or silyl chloride (freshly distilled) and the remaining solvent were added via syringes. The septum was replaced with the threaded stopcock, and the reaction mixture was degassed using freeze-thaw method (three to four cycles). Then the reaction flask was backfilled with argon, sealed with the stopcock at r.t. and the reaction mixture was heated at 60 °C for CH_2Cl_2 or 80 °C for benzene (unless otherwise indicated) for 6–24 h or until all the carbene complex was consumed. After cooling to r.t., the reaction mixture was analyzed by TLC (50% CH_2Cl_2 in hexane or 5% MeCN in CH_2Cl_2, UV/PMA or $KMnO_4$), concentrated under reduced pressure and subjected to column chromatography (gradient elution from 0% to 75% CH_2Cl_2 in hexane or pentane, or 0% to 25% MeCN in CH_2Cl_2, column size 1.5 × 30 cm or 2 × 30 cm) for isolation and purification of (arene)chromium tricarbonyl complexes and related products. Most of diastereomeric isomers (**A**: the major isomer, **B**: the minor isomer) of (arene)chromium tricarbonyl complexes have very similar R_f values (ΔR_f <0.05). Hence, unless otherwise indicated they were isolated together as one fraction from which the isomeric ratios were determined using either ^{1}H NMR or ^{13}C NMR spectroscopy. All diastereomers were well resolved from ^{1}H NMR and ^{13}C NMR whether they were separated or isolated as one fraction by column chromatographic technique, and thus ^{1}H NMR and ^{13}C NMR were recorded for each isomer. IR and low resolution mass (EI) spectra were mostly recorded for the diastereo-meric mixture because both isomers provided virtually identical IR absorption and low resolution mass fragmentation patterns. The exact mass analysis was also done for the isomeric mixture unless they were separated by chromatographic technique, in which case the more crystalline isomer was submitted for the elemental combustion analysis, and the less crystalline isomer was submitted for the exact mass analysis.

(Arene)chromium Tricarbonyl Complex 11A and 11B

The chiral alkoxy carbene complex 1 (20.0 mg, 0.048 mmol) was reacted with pent-1-yne (8.9 μL, 0.090 mmol, 1.9 equiv) in the presence of Hünig's base (24.9 μL, 0.143 mmol, 3.0 equiv) and TBSCl (14.3 g, 0.164 mmol, 2.0 equiv) in CH_2Cl_2 at 60 °C for 19 h according to the general procedure to provide 19.0 mg of the desired arene complex **11** (69%) as a yellow oil with a diastereomeric ratio of 60:40 along with 4.7 mg of the free arene **16** (23%) as a yellow oil.

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R_{fA} 0.66; R_{fB} 0.72 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ (**A**) = 0.30 (s, 3 H), 0.31 (s, 3 H), 0.91 (m, 3 H), 0.93 (s, 9 H), 1.26–1.58 (m, 6 H), 1.93 (s, 3 H), 1.61–2.05 (m, 4 H), 2.40 (m, 2 H), 2.56 (m, 1 H), 3.94 (m, 1 H), 4.84 (s, 1 H), 5.11 (s, 1 H), 7.15–7.74 (m, 5 H); δ (**B**) = 0.20 (s, 3 H), 0.23 (s, 3 H), 0.89 (m, 3 H), 0.94 (s, 9 H), 1.26–1.58 (m, 6 H), 1.83 (s, 3 H), 1.61–2.05 (m, 4 H), 2.49 (m, 1 H), 2.71 (m, 2 H), 3.94 (m, 1 H), 4.87 (s, 1 H), 4.96 (s, 1 H), 5.15–7.74 (m, 5 H).

^{13}C NMR (CD_2Cl_2): δ (**A**) = –4.0, –4.1, 14.1, 16.2, 18.4, 23.2, 24.6, 25.1, 25.6, 26.1, 32.6, 33.2, 34.1, 51.0, 84.7, 85.6, 100.4, 102.4, 126.9, 128.8, 128.9, 132.9, 143.6, 150.6, 235.4; δ (**B**) = –4.4, –4.3, 14.2, 16.3, 18.5, 22.9, 24.5, 25.6, 26.0, 26.2, 32.9, 33.1, 34.3, 51.1, 84.3, 86.5, 100.2, 116.6, 127.0, 128.2, 128.5, 134.1, 145.1, 147.3, 235.8.

IR (neat): ν = 2956w, 2930m, 2958w, 1954s, 1869s, 1499w, 1472m, 1370w, 1203m, 911w, 828m, 781m cm^{-1}.

MS (EI): *m*/*z* (%) = 574 (4) M$^+$, 490 (46), 438 (40), 280 (100), 223 (56), 193 (21).

HRMS: *m*/*z* calcd for $C_{31}H_{42}CrO_5Si$ 574.2207, found 574.2221.

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R_f 0.70 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ = 0.13 (s, 3 H), 0.14 (s, 3 H), 0.96 (m, 3 H), 0.97 (s, 9 H), 1.26–1.58 (m, 6 H), 1.85 (s, 3 H), 1.61–2.05 (m, 4 H), 2.25 (m, 1 H), 2.79 (m, 2 H), 4.12 (m, 1 H), 6.41 (br s, 2 H), 7.15–7.34 (m, 5 H).

^{13}C NMR (CD_2Cl_2): δ = –4.1, 14.3, 16.1, 19.2, 22.2, 23.9, 25.3, 25.6, 26.5, 32.9, 33.0, 34.3, 51.4, 121.0, 126.3, 126.4, 128.3, 128.4, 130.9, 132.6, 133.2, 144.0, 146.4.

IR (neat): ν = 2956m, 2930s, 2858m, 1499m, 1472s, 1370m, 1203s, 911w, 840m, 828s, 781s cm^{-1}.

MS (EI): *m*/*z* (%) = 438 (40) M$^+$, 280 (100), 223 (56), 193 (21).

HRMS: *m*/*z* calcd for $C_{28}H_{42}O_2Si$ 438.2954, found 438.2950.

(Arene)chromium Tricarbonyl Complexes 12A and 12B

The chiral alkoxy carbene complex **2** (70.0 mg, 0.20 mmol) was reacted with pent-1-yne (138.1 μL, 0.39 mmol, 1.9 equiv) in the presence of Hünig's base (106.2 μL, 0.61 mmol, 3.0 equiv) and TBSCl (60.3 mg, 0.40 mmol, 2.0 equiv) in CH_2Cl_2 at 60 °C for 17 h according to the general procedure to provide 83.1 mg of the desired arene complex **12** (83%) as a yellow oil with a diastereomeric ratio of 50:50; $R_{fA,B}$ 0.68 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ (**A**) = 0.38 (s, 6 H), 0.99 (s, 9 H), 1.02 (m, 3 H), 1.05 (d, 3 H, *J* = 7.1 Hz), 1.23 (m, 2 H), 1.56–1.84 (m, 4 H), 1.85–2.23 (m, 4 H), 2.13 (s, 3 H), 2.69 (m, 1 H), 4.04 (m, 1 H), 5.22 (s, 1 H), 5.25 (s, 1 H); δ (**B**) = 0.30 (s, 6 H), 0.99 (s, 9 H), 1.02 (m, 3 H), 1.08 (d, 3 H, *J* = 6.9 Hz), 1.23 (m, 2 H), 1.56–1.84 (m, 4 H), 1.85–2.23 (m, 4 H), 2.13 (s, 3 H), 2.69 (m, 1 H), 3.98 (m, 1 H), 5.22 (s, 1 H), 5.31 (s, 1 H).

^{13}C NMR (CD_2Cl_2): δ (**A**) = –4.3, –4.1, 14.1, 16.2, 18.0, 18.4, 18.5, 23.0, 24.6, 25.6, 31.9, 32.1, 32.8, 40.8, 82.6, 87.7, 98.2, 102.9, 131.9, 134.8, 235.8; δ (**B**) = –4.2, –4.0, 14.0, 16.2, 18.1, 18.3, 18.4, 22.8, 24.5, 25.5, 31.0, 32.0, 32.8, 40.7, 82.4, 87.6, 98.1, 102.8, 131.6, 134.4, 235.7.

IR (neat): ν = 2960s, 2932m, 2862w, 1953s, 1869s, 1479s, 1389w, 1371m, 1259w, 1231m, 1208m, 911w, 841m, 826m cm^{-1}.

MS (EI): *m*/*z* (%) = 498 (21) M^+, 442 (13), 414 (100), 362 (13), 331 (16), 280 (24), 223 (22), 126 (16).

HRMS: *m*/*z* calcd for $C_{25}H_{38}CrO_5Si$ 498.1894, found 498.1902.

(Arene)chromium Tricarbonyl Complex 13A and 13B

The chiral alkoxy carbene complex **3** (50.0 mg, 0.13 mmol) was reacted with pent-1-yne (16.3 μL, 0.24 mmol, 1.9 equiv) in the presence of Hünig's base (65.8 μL, 0.38 mmol, 3.0 equiv) and TBSCl (36.2 mg, 0.24 mmol, 2.0 equiv) in CH_2Cl_2 at 60 °C for 14 h according to the general procedure to provide 47.1 mg of the desired arene complex **13** (68%) as a yellow oil with a diastereomeric ratio of 58:42; $R_{fA,B}$ 0.74 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ (**A**) = 0.28 (s, 3 H), 0.36 (s, 3 H), 0.97 (s, 9 H), 0.99 (s, 3 H), 1.00 (s, 3 H), 1.01 (s, 3 H), 1.02 (m, 3 H), 1.49–1.66 (m, 4 H), 1.72–1.92 (m, 4 H), 2.12 (s, 3 H), 2.07–2.19 (m, 2 H), 2.67 (m, 1 H), 3.85 (m, 1 H), 5.15 (s, 1 H), 5.28 (s, 1 H); δ (**B**) = 0.26 (s, 3 H), 0.36 (s, 3 H), 0.86 (s, 3 H), 0.87 (s, 3 H), 0.92 (s, 3 H), 0.97 (s, 9 H), 1.03 (m, 3 H), 1.49–1.66 (m, 4 H), 1.72–1.92 (m, 4 H), 2.13 (s, 3 H), 2.07–2.19 (m, 2 H), 2.67 (m, 1 H), 3.78 (m, 1 H), 5.27 (s, 1 H), 5.28 (s, 1 H).

^{13}C NMR (CD_2Cl_2): δ (**A**) = –4.4, –4.3, 12.0, 13.9, 16.0, 18.1, 20.1, 20.2, 20.3, 24.5, 25.6, 25.7, 27.4, 32.8, 34.1, 38.3, 45.3, 49.6, 81.0, 86.2, 86.4, 87.7, 97.2, 102.6, 235.5; δ (**B**) = –4.4, –4.0, 11.8, 14.1, 16.1, 18.2, 20.2, 20.3, 20.4, 24.7, 25.4, 25.5, 27.2, 33.0, 33.9, 40.1, 45.7, 47.0, 80.4, 86.5, 86.6, 86.8, 96.3, 101.2, 235.4.

IR (neat): ν = 2957m, 2932w, 1952s, 1871s, 1474m, 1388w, 1371m, 1238m, 1206m, 916m, 841m cm^{-1}.

MS (EI): *m*/*z* (%) = 552 (14) M^+, 496 (9), 468 (100), 332 (56), 280 (60), 223 (19).

HRMS: *m*/*z* calcd for $C_{29}H_{44}CrO_5Si$ 552.2363, found 552.2373.

(Arene)chromium Tricarbonyl Complex 14A and 14B

The chiral alkoxy carbene complex **4** (95.3 mg, 0.20 mmol) was reacted with pent-1-yne (37.5 μL, 0.38 mmol, 1.9 equiv) in the presence of Hünig's base (104.5 mg, 0.60 mmol, 3.0 equiv) and TBSCl (60.3 mg, 0.40 mmol, 2.0 equiv) in CH_2Cl_2 at 60 °C for 15 h according to the general procedure to provide 97.6 mg of the desired arene complex **14** (77%) as a yellow waxy with a diastereomeric ratio of 55:45; $R_{fA,B}$ 0.57 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ **A** = 0.27 (s, 3 H), 0.35 (s, 3 H), 0.92 (m, 3 H), 0.98 (s, 9 H), 1.01 (d, 3 H, *J* = 6.9 Hz), 1.30 (s, 6 H), 1.23–1.80 (m, 7 H), 1.96 (s, 3 H), 1.80–2.10 (m, 2 H), 2.23 (m, 1 H), 2.60 (m, 1 H), 2.76 (m, 1 H), 3.96 (m, 1 H), 4.88 (s, 1 H), 5.12 (s, 1 H), 7.18–7.35 (m, 5 H); δ **B** = 0.24 (s, 3 H), 0.34 (s, 3 H), 0.92 (m, 3 H), 0.97 (s, 9 H), 1.01 (d, 3 H, *J* = 6.9 Hz), 1.30 (s, 6 H), 1.23–1.80 (m, 7 H), 1.86 (s, 3 H), 1.80–2.10 (m, 2 H), 2.17 (m, 1 H), 2.51 (m, 1 H), 2.76 (m, 1 H), 3.96 (m, 1 H), 4.86 (s, 1 H), 4.97 (s, 1 H), 7.18–7.35 (m, 5 H).

^{13}C NMR (CD_2Cl_2): δ **A** = –4.5, –4.1, 14.1, 16.1, 23.1, 24.6, 25.0, 25.5, 25.9, 26.0, 30.1, 32.3, 32.6, 32.8, 33.1, 34.0, 51.0, 84.2, 84.5, 86.6, 100.4, 101.2, 127.0, 128.2, 128.7, 132.5, 134.1, 235.8; δ **B** = –4.4, –4.1, 14.3, 16.3, 22.8, 24.8, 24.9, 25.4, 26.1, 26.5, 29.7, 32.4, 32.7, 33.0, 33.2, 34.2, 51.1, 84.6, 85.5, 86.2, 100.1, 104.3, 126.9, 128.4, 128.8, 132.8, 133.0, 235.3.

IR (neat): ν = 2951m, 2931s, 2860m, 1955s, 1876s, 1474m, 1369w, 1228w, 1205m, 907w, 828m, 783w cm^{-1}.

MS (EI): *m*/*z* (%) = 630 (1) M^+, 602 (1), 574 (86), 492 (100), 438 (83), 375 (45), 330 (88), 247 (57), 193 (89).

Anal calcd for $C_{35}H_{50}CrO_5Si$: C, 66.64; H, 7.99; Cr, 8.24. Found C, 65.94; H, 7.77; Cr, 7.26.

(Arene)chromium Tricarbonyl Complex 15A and 15B

The chiral alkoxy carbene complex **5** (32.5 mg, 0.082 mmol) was reacted with pent-1-yne (15.4 mg, 0.156 mmol, 1.9 equiv) in the presence of Hünig's base (42.9 mL, 0.25 mmol, 3.0 equiv) and TBSCl (24.7 mg, 0.164 mmol, 2.0 equiv) in CH_2Cl_2 at 60 °C for 14 h according to the general procedure to provide 37.5 mg of the desired arene complex **15** (82%) as a yellow waxy foam with a diastereomeric ratio of 57:43; $R_{fA,B}$ 0.72 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ (**A**) = 0.34 (s, 6 H), 0.77 (d, 3 H, *J* = 6.6 Hz), 0.90 (d, 6 H, *J* = 7.2 Hz), 1.00 (s, 9 H), 1.03 (t, 3 H, *J* = 6.9 Hz), 1.20–1.75 (m, 8 H), 2.03–2.34 (m, 3 H), 2.22 (s, 3 H), 2.72 (m, 2 H), 3.81 (m, 1 H), 5.07 (br s, 1 H), 5.32 (br s, 1 H); δ (**B**) = 0.33 (s, 6 H), 0.76 (d, 3 H, *J* = 6.9 Hz), 0.94 (d, 6 H, *J* = 6.3 Hz), 1.00 (s, 9 H), 1.03 (t, 3 H, *J* = 6.9 Hz), 1.20–1.75 (m 8 H), 2.03–2.34 (m, 3 H), 2.22 (s, 3 H), 2.72 (m, 2 H), 3.81 (m, 1 H), 5.07 (br s, 1 H), 5.32 (br s, 1 H).

^{13}C NMR (CD_2Cl_2): δ (**A**) = –2.6, –2.4, 14.1, 16.6, 16.7, 18.4, 19.0, 21.0, 22.2, 23.7, 23.9, 26.0, 26.1, 31.8, 33.1, 34.6, 40.3, 48.4, 80.3, 81.1, 102.5, 107.9, 127.9, 138.8, 235.6; δ (**B**) = –2.7, –2.5, 14.2, 16.5, 16.8, 18.3, 19.1, 20.9, 22.1, 23.6, 23.8, 25.9, 26.2, 31.7, 33.0, 34.5, 42.2, 48.3, 79.6, 82.2, 102.3, 107.6, 128.0, 138.9, 235.5.

IR (neat): ν = 2957m, 2931m, 2863w, 1945s, 1864s, 1602w, 1540w, 1464m, 1386w, 1250m, 1225w, 902m, 840m cm^{-1}.

MS (EI): *m*/*z* (%) = 554 (10) M^+, 470 (100), 419 (19), 332 (14), 280 (54), 223 (44), 193 (18).

HRMS: *m*/*z* calcd for $C_{29}H_{46}CrO_5Si$ 554.2520, found 554.2534.

(Arene)chromium Tricarbonyl Complex 17

Carbene complex **7**[5c] (0.1 g, 0.22 mmol) was reacted with 3,3-dimethylbut-1-yne (0.05 mL, 0.418 mmol, 1.9 equiv) in the presence of Hünig's base (0.115 mL, 0.66 mmol, 3 equiv) and *tert*-butyldimethylsilyl chloride (0.0663 g, 0.44 mmol, 2 equiv) in CH_2Cl_2 (45 mL) at 60 °C for 14 h utilizing the procedure described below for the formation of **19**. Purification on silica gel with a 1: 1 mixture of $CHCl_3$ and hexanes (R_f 0.56) gave complex **17** (90%) as a yellow oil with a diastereomeric ratio of 1.2:1. The spectral data for this compound were found to be identical with those previously reported.[5c]

(Arene)chromium Tricarbonyl Complex 19

A solution of chiral alkoxyl carbene complex **5** (1.1066 g, 2.76 mmol) in CH_2Cl_2 (50 mL) was reacted with 3,3-dimethylbut-1-yne (0.646 mL, 5.244 mmol, 1.9 eauiv), Hünig's base (1.442 mL, 8.28 mmol, 3.0 equiv) and *tert*-butyldimethylsilyl chloride (0.832 g, 5.52 mmol) according to the general procedure at 60 °C for 14 h. After cooling to r.t. and concentration, the mixture was loaded onto

a silica gel column and eluted with a 1:1 mixture of CH_2Cl_2 and hexane (R_f 0.56) to give 1.228 g (78%) of complex **19** as a yellow foam which was found to be a 1.1:1 mixture of diastereomers. Spectral data for **19** was obtained on the mixture.

^{1}H NMR ($CDCl_3$): δ = 0.34 (s, 3 H), 0.39 (s, 3 H), 0.8–1.2 (m, 2 H), 0.80 (d, *J* = 7 Hz, 1.5 H), 0.82 (d, *J* = 7 H, 1.5 H), 0.91 (d, *J* = 7 Hz, 3 H), 0.94 (d, *J* = 7 Hz, 1.5 H), 0.95 (d, *J* = Hz, 1.5 H), 1.03 (s, 9 H), 1.2–1.6 (m, 3 H), 1.44 (s, 9 H), 1.68 (m, 2 H), 2.19 (m, 2 H), 2.26 (s, 3 H), 3.68 (td, *J* = 10.5, 4.1 Hz, 1 H), 5.32 (t, *J* = 2.2 Hz, 1 H), 5.44 (d, *J* = 2.6 Hz, 0.5 H), 5.46 (d, *J* = 2.6 Hz, 0.5 H).

^{13}C NMR ($CDCl_3$): δ = –0.90, –0.16, 16.12, 16.19, 19.55 (2 C), 19.84, 19.91, 20.75, 20.83, 21.98 (2 C), 22.93, 23.04, 25.19, 25.33, 26.83 (2 C), 31.09, 31.14, 31.22, 31.27, 34.02 (2 C), 35.04 (2 C), 39.63, 39.73, 47.79, 47.84, 78.70, 79.06, 83.28, 83.69, 84.86, 85.45, 96.08, 96.70, 112.77, 112.88, 133.36, 133.55, 134.39, 134.67, 235.70 (2 C).

IR (neat): ν = 2957m, 2931m, 2869m, 1952s, 1871s, 1544w, 1465m, 1415m, 1256m, 1208m, 1041m, 901w cm^{-1}.

MS (FAB): *m*/*z* (%) = 569 (M^+ + 1) (16), 484 (9), 432 (56), 375 (4), 310 (18), 294 (23), 237 (30), 180 (33), 155 (69), 119 (100).

HRMS (FAB): *m*/*z* calcd for $C_{30}H_{48}O_5CrSi$ 569.2754, found 569.2756.

Anal calcd for $C_{30}H_{48}O_5CrSi$: C, 63.35; H, 8.51; Cr, 9.14. Found: C,63.61; H, 8.77; Cr, 9.32.

Formation of Phenol 67 and its Conversion to a mixture of Diastereomers of Arene Complex 19

A solution of the carbene complex **5** (0.8771 g, 2.19 mmol) in CH_2Cl_2 (30 mL) was reacted with 3,3-dimethylbut-1-yne (0.646 mL, 4.997 mmol, 1.9 equiv) at 60 °C for 14 h according to the general procedure. After cooling to r.t. and concentrating, residue was taken up in Et_2O (10 mL) and stirred open to the air for 3 h at r.t. After removal of the Et_2O, the crude mixture was loaded onto a silica gel column and eluted with a 1:1 mixture of CH_2Cl_2 and hexane (R_f 0.46) to give 0.46 g (66%) of phenol **67** as a light yellow solid.

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^{1}H NMR ($CDCl_3$): δ = 0.81 (d, *J* = 6.9 Hz, 3 H), 0.91 (d, *J* = 6.5 Hz, 3 H), 0.94 (d, *J* = 7.0 Hz, 3 H), 1.0–1.29 (m, 3 H), 1.33 (m, 1 H), 1.40 (s, 9 H), 1.50 (m, 1 H), 1.70 (m, 2 H), 2.12 (m, 1 H), 2.22 (s, 3 H), 2.26 (m, 1 H), 3.85 (td, *J* = 10.5, 3.9 Hz, 1 H), 4.38 (s, 1 H), 6.56 (d, *J* = 2.8 Hz, 1 H), 6.73 (d, *J* = 2.9 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 16.46, 20.94, 22.19, 23.49, 25.80, 29.71, 31.42, 31.57, 34.58, 40.52, 48.16, 78.48, 114.51, 123.73, 137.08, 146.64, 151.30.

IR (neat): ν = 3583b, 2956s, 2925s, 2870m, 1591w, 1480m, 1434m, 1310m, 1210s, 1130m, 1036m cm^{-1}.

MS (EI): *m*/*z* (%) = 319 (42), 318 (M^+, 100), 317 (29), 303 (34), 181 (26), 180 (96), 165 (24), 163 (28), 139 (62), 137 (30), 83 (22), 57 (46).

Anal calcd for $C_{21}H_{34}O_2$: C, 79.19; H, 10.76. Found: C,78.55; H, 10.86.

To a solution of **67** (0.335 g, 1.05 mmol) and 2,6-lutidine (0.18 mL) in anhyd CH_2Cl_2 (2 mL) under N_2 at –10 °C was added dropwise *tert*-butyldimethylsilyl chloride (237 mg, 1.575 mmol) and upon completion of addition the resulting solution was stirred at 25 °C for 36 h. The mixture was concentrated and purified by chromatography on silica gel with a 1:3 mixture of CH_2Cl_2 and hexanes (R_f 0.46) to give 0.2588 g (57%) of the aryl silyl ether as a white solid. A mixture of this compound (0.25 g, 0.58 mmol) and chromium carbonyl (0.38 g, 1.73 mmol) in 1,4-dioxane (15 mL) was added to a flask equipped with an air condensor and which was topped with a three-way stopcock. The system was deoxygenated by the freeze-thaw method and backfilled with argon. The stopcock was closed and the system heated at 100 °C for 18 h. After cooling to r.t. and removal of solvent, the residue was loaded onto a silica gel column and eluted with 1:3 mixture of CH_2Cl_2 and hexanes to give 0.2259 g (86%) of **19** as a yellow sticky solid. The spectra of this material reveals the presence of two diastereomers in a 1:1 ratio which have the same spectral properties as those prepared from the reaction of **5** described above.

Reaction of the Phenyl Mentholoxy Complex 8 with Pent-1-yne

A solution of the complex **8**[5c] (0.493 g, 1.13 mmol) and pent-1-yne (4.53 mmol) in *tert*-butyl methyl ether (3 mL) was deoxygenated by the freeze-thaw method. The flask was back-filled with argon at r.t. and then was sealed and heated to 58 °C for 2.5 h. After addition of *tert*-butyldimethylsilyl chloride (0.687 g, 4.56 mmol) and Et_3N (4.52 mmol) the mixture was allowed to stir overnight at r.t. The solvent was removed and the residue was purified by silica gel chromatography with a 5:1 mixture of hexanes and CH_2Cl_2 to give the metal-free naphthalene **21** (17% yield) and the arene complex **22** in 25% yield. Complex **22** was obtained as a 6.4:1 mixture of diastereomers and the follow data were collected on the mixture. The diastereomeric ratio was determined by integration of the singlets at δ = 5.15 and 5.26.

21

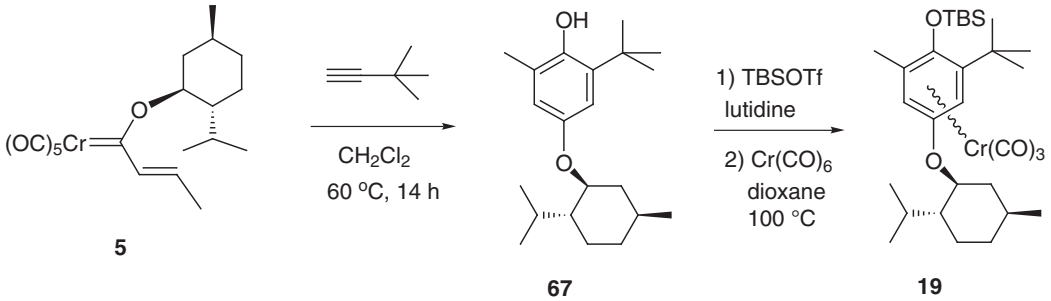
R_f (CH_2Cl_2/hexanes, 1:5) 0.68.

^{1}H NMR ($CDCl_3$): δ = 0.16 (s, 3 H), 0.16 (s, 3 H), 0.80 (d, 3 H, *J* = 6.9 Hz), 0.92 (d, 3 H, *J* = 6.6 Hz), 0.9–1.2 (m, 9 H), 1.12 (s, 9 H), 1.52 (m, 1 H), 1.64 (m, 3 H), 1.75 (m, 2 H), 2.21 (d, 1 H, *J* = 12 Hz), 2.33 (m, 1 H), 2.70 (t, 2 H, *J* = 7.8 Hz), 4.18 (td, 1 H, *J* = 10, 4.0 Hz), 6.63 (s, 1 H), 7.36 (t, 1 H, *J* = 7.5 Hz), 7.41 (t, 1 H, *J* = 7.5 Hz), 7.98 (d, 1 H, *J* = 8.4 Hz), 8.17 (d, 1 H, *J* = 8.1 Hz).

^{13}C NMR ($CDCl_3$): δ = –3.20, 14.06, 16.78, 18.67, 20.93, 22.25, 23.73, 23.79, 26.16, 26.22, 31.49, 33.05, 34.66, 40.32, 48.36, 77.74, 108.44, 122.14, 122.79, 124.08, 125.05, 126.26, 127.10, 128.88, 141.14, 148.21.

IR (film): ν = 1596 s, 1458 s, 1260 s cm^{-1}.

MS (EI): *m*/*z* (%) = 454 (M^+, 22), 316 (94), 259 (28), 217 (28), 216 (26), 174 (47), 132 (100).



5 **67** **19**

22

R_f (CH_2Cl_2/hexanes, 1:5) 0.25.

^{1}H NMR ($CDCl_3$): δ (major isomer) = 0.47 (s, 3 H), 0.51 (s, 3 H), 0.71 (d, 3 H, *J* = 6.8 Hz), 0.9–1.8 (m, 18 H), 1.10 (s, 9 H), 2.05 (m, 1 H), 2.44 (m, 1 H), 2.62 (m, 1 H), 2.84 (m, 1 H), 4.06 (t, 1 H, *J* = 6.7 Hz), 5.15 (s, 1 H), 7.41 (t, 1 H, *J* = 6.7 Hz), 7.48 (t, 1 H, *J* = 7.5 Hz), 7.92 (d, 1 H, *J* = 8.3 Hz), 8.09 (d, 1 H, *J* = 8.8 Hz).

^{13}C NMR ($CDCl_3$): δ (major isomer) = –3.57, –1.93, 13.96, 16.79, 18.84, 20.70, 22.17, 23.80, 24.23, 25.90, 26.30, 31.54, 32.62, 34.22, 39.50, 48.11, 75.12, 79.48, 97.51, 101.81, 103.14, 124.25, 124.59, 124.96, 126.71, 128.16, 132.84, 234.01.

IR (film): ν = 1950 s, 1870 vs, 1262 m cm^{-1}.

MS (EI): *m*/*z* (%) = 590 (M^+, 15), 534 (5), 506 (100), 454 (11), 368 (19), 316 (46), 259 (15), 73 (16).

When the reaction was repeated in CH_2Cl_2 in the presence of Hünig's base and *tert*-butyldimethylsilyl chloride according to the general procedure two products were obtained which were identified as the naphthalene **21** (32% yield) and the (arene)chromium tricarbonyl complex **23** (25% yield). Complex **23** was obtained as a 6.1:1 mixture of diastereomers and the follow data were collected on the mixture. The diastereomeric ratio was determined by integration of the singlets at δ = 6.34 and 6.41.

23

R_f (CH_2Cl_2/hexanes, 1:5) 0.36.

^{1}H NMR ($CDCl_3$): δ (major isomer) = 0.21 (s, 3 H), 0.26 (s, 3 H), 0.80 (d, 3 H, *J* = 6.9 Hz), 0.9-1.8 (m, 18 H), 1.13 (s, 9 H), 2.19 (m, 1 H), 2.24 (m, 1 H), 2.41 (m, 1 H), 2.80 (m, 1 H), 4.18 (td, 1 H, *J* = 10, 3.7 Hz), 5.37 (t, 1 H, *J* = 6.4 Hz), 5.51 (t, 1 H, *J* = 6.5 Hz), 6.26 (d, 1 H, *J* = 6.9 Hz), 6.34 (s, 1 H), 6.50 (d, 1 H, 6.9 Hz).

^{13}C NMR ($CDCl_3$): δ (major isomer) = –3.32, –3.00, 13.56, 17.03, 18.64, 20.71, 22.10, 23.27, 24.05, 25.99, 26.57, 31.50, 32.82, 34.50, 39.48, 47.96, 77.18, 85.37, 86.64, 90.66, 91.65, 97.02, 104.06, 107.22, 129.62, 138.73, 148.07, 232.37.

IR (film): ν = 1963 s, 1896 s, 1876 s, 1251 s cm^{-1}.

MS (EI): *m*/*z* (%) 590 (M^+, 1), 506 (8), 454 (12), 367 (8), 316 (31), 258 (12), 229 (22), 216 (12), 83 (100).

Chiral Amino Carbene Complex 38

The methoxy carbene complex **34**[20] (143.3 mg, 0.57 mmol) was dissolved in Et_2O (5 mL) at –78 °C and (*S*)-(+)-2-hydroxymethylpyrrolidine (58.2 μL, 0.59 mmol, 1.03 equiv) was added. The reaction mixture was stirred at –78 °C for 6 h, at –40 °C for 18 h and at r.t. for 4 h, and monitored with TLC analysis (CH_2Cl_2, PMA). When all the starting material was consumed as indicated by TLC analysis, the mixture was concentrated under reduced pressure and purified using silica gel column chromatography (size: 1.5 × 35cm, eluent: CH_2Cl_2) to afford 211.2 mg of the pure amino complex **38** (99%) as a yellow solid. **38** was found as a single rotamer with rotameric ratio ≥95:5. The other rotamer was never isolated or characterized; R_f 0.33 (CH_2Cl_2); mp 56.8–58.0 °C; tiny yellow needles from CH_2Cl_2 in hexane.

^{1}H NMR ($CDCl_3$): δ = 1.75 (br s, 1 H), 2.16 (m, 2 H), 2.30 (m, 2 H), 2.68 (s, 3 H), 3.62 (br t, 2 H, *J* = 6.7 Hz), 3.68 (d, 1 H, *J* = 9.3 Hz), 3.87 (d, 1 H, *J* = 9.3 Hz), 4.67 (m, 1H).

^{13}C NMR ($CDCl_3$): δ = 22.4, 25.5, 41.6, 51.7, 63.8, 71.8, 218.4, 223.0, 271.1.

IR (neat): ν = 3419(brd)w, 2930w, 2916w, 2870w, 2053s, 1900s, 1492m, 1450w, 1041w cm^{-1}.

MS (EI): *m*/*z* (%) = 319 (5) M^+, 291 (10), 263 (5), 235 (3), 207 (23), 179 (100), 169 (6), 149 (69), 140 (7), 126 (69), 112 (77).

HRMS: *m*/*z* calcd for $C_{12}H_{13}CrNO_6$ 319.0148, found 319.0172.

Chiral Amino Carbene Complex 39

The amino complex **38** (300.0 mg, 0.942 mmol) was dissolved in CH_2Cl_2 (15 mL) at –10 °C (dry ice in acetone), and imidazole (96.2 mg, 1.41 mmol, 1.5 equiv) and 259.4 uL of TBSOTf (259.4 μL, 1.13 mmol 1.2 equiv) were added. The mixture was stirred at –10 °C for 5 h and monitored with TLC analysis (50% CH_2Cl_2 in hexane, PMA). When all the starting material was consumed as indicated by TLC analysis, the mixture was concentrated under reduced pressure and purified using silica gel column chromatography (size: 3 × 30cm, gradient eluent: 0% to 25% CH_2Cl_2 in hexane) to afford 376.2 mg of the pure amino complex **39** (92%) as a yellow oil. This preparation yielded a single rotamer (rotameric ratio ≥95:5) which was characterized and later identified as the rotamer **A** when rotamer **B** was found in subsequent reactions; R_{fA} 0.32, R_{fB} 0.29 (20% CH_2Cl_2/hexane).

^{1}H NMR ($CDCl_3$): δ (**A**) = 0.05 (s, 3 H), 0.06 (s, 3 H), 0.89 (s, 9 H), 2.10 (m, 2 H), 2.21 (m, 1 H), 2.24 (m, 1 H), 2.67 (s, 3 H), 3.59 (m, 1 H), 3.64 (m, 1 H), 3.81 (m, 2 H), 4.66 (m, 1 H); δ (**B**) = 0.06 (s, 6 H), 0.89 (s, 9 H), 2.01–2.17 (m, 4 H), 2.81 (s, 3 H), 3.58 (m, 2 H), 4.12 (m, 1 H), 4.27 (m, 1 H), 4.41 (m, 1 H).

^{13}C NMR (CD_2Cl_2): δ (A) = –6.1, –5.2, 18.5, 23.1, 25.9, 26.3, 41.9, 52.7, 65.3, 71.9, 218.7, 224.0, 268.0; δ (**B**) ($CDCl_3$) = –5.6, –5.5, 17.9, 22.4, 25.8, 27.7, 40.4, 52.3, 60.8, 63.5, 218.2, 223.4, 270.4.

IR (neat): ν = 2957m, 2930m, 2858w, 2052s, 1912s, 1491m, 1472m, 1448w, 1254w, 1104m, 837m, 779m cm^{-1}.

MS (EI): *m*/*z* (%) = 433 (4) M^+, 405 (1), 377 (3), 349 (3), 321 (8), 293 (100), 241 (67), 226 (30), 200 (11), 184 (38), 156 (11), 126 (25).

HRMS: *m*/*z* calcd for $C_{18}H_{27}CrNO_6Si$ 433.1013, found 433.1013.

Chiral Amino Carbene Complex 40[13]

The amino carbene complex **36**[12] (239.3 mg, 0.72 mmol) (rotameric ratio **A**/**B** = 3.6:1) was dissolved in THF (10 mL) at –78 °C, and BuLi (1.6 M, 450 μL, 0.72 mmol, 1.0 equiv) was carefully added dropwise as the solution turned from golden yellow to brilliant orange red. After stirring at –78 °C for 2 h, freshly distilled TMSCl (120.6 μL, 0.95 mmol, 1.3 equiv) was slowly added dropwise as the solution turned from brilliant orange red to dark yellow and then to yellow. The mixture was stirred at –78 °C for 8 h before it was warmed up to r.t. After concentration under reduced pressure and silica gel column chromatography (size: 2 × 27cm, gradient eluent: 10–20% CH_2Cl_2 in hexane), 193.9 mg of the desire amino complex **40** (67%) was isolated as an orange yellow oil with rotameric ratio of **A**/**B** = 2.0:1; R_f 0.52 (50% CH_2Cl_2/hexane).

^{1}H NMR ($CDCl_3$): δ (rotamer **A**) = 0.20 (s, 9 H), 2.03–2.30 (m, 4 H), 2.93 (br d, 1 H, *J* = 11.4 Hz), 3.07 (d, 1 H, *J* = 11.4 Hz), 3.33 (s, 3 H), 3.57 (m, 4 H), 4.72 (m, 1 H); δ (rotamer **B**) 0.20 (s, 9 H), 2.03–2.30 (m, 4 H), 3.29 (m, 1 H), 3.33 (m, 1 H), 3.34 (s, 3 H), 3.67 (m, 2 H), 4.08 (m, 1 H), 4.14 (m, 1 H), 4.31 (m, 1 H).

^{13}C NMR (CD_2Cl_2): δ (rotamer **A**) = 0.7, 23.7, 26.9, 51.0, 53.2, 59.3, 70.5, 74.6, 219.3, 223.7, 269.5; δ (rotamer **B**) = 0.7, 23.0, 28.1, 49.2, 59.6, 60.8, 62.7, 73.4, 219.3, 224.2, 272.5.

IR (neat): ν = 2960w, 2956w, 2049s, 1897s, 1476m, 1448m, 1253m, 1122m, 1100w, 846s cm^{-1}.

MS (EI): *m*/*z* (%) = 405 (2) M^+, 377 (7), 349 (2), 321 (1), 293 (23), 265 (100), 250 (5), 225 (2), 213 (53), 198 (34), 182 (10).

HRMS: *m*/*z* calcd for $C_{16}H_{23}CrNO_6Si$ 405.0700, found 405.0677.

Chiral Amino Carbene Complex 43

The amino carbene complex **40** (217.4 mg, 0.58 mmol) (rotameric ratio **A**:**B** = 2.0:1) was dissolved in THF (10 mL) at –78 °C, and BuLi (1.6 M, 400.0 μL, 0.64 mmol, 1.1 equiv) was carefully added dropwise. After stirring at –78 °C for 1 h, freshly distilled and pre-

chilled (–78 °C) acetaldehyde (65.1 μL, 1.16 mmol, 2.0 equiv) was slowly added dropwise. The mixture was stirred at –78 °C for 5 h, at –20 °C for 16 h and at r.t. for 2 h. After concentration of the mixture under reduced pressure, purification on the silica gel column chromatography (size: 1.5 × 35 cm, eluent: hexane, then 50% CH_2Cl_2 in hexane) provided 98.3 mg of the desired product **43** (47%) as a yellow oil with rotameric ratio of **A**:**B** ranging from 1:1.7 to 1:2.2; R_{fA} 0.43, R_{fB} 0.40 (50% CH_2Cl_2/hexane).

^{1}H NMR ($CDCl_3$): δ (rotamer **A**) = 1.80 (d, 3 H, *J* = 6.8 Hz), 1.97 (m, 1 H), 2.09–2.23 (m, 3 H), 3.37 (s, 3 H), 3.58–3.64 (m, 2 H), 3.67 (m, 1 H), 3.75 (m, 1 H), 4.69 (m, 1 H), 5.11 (dq, 1 H, *J* = 6.8, 16.1 Hz), 6.50 (d, 1 H, *J* = 16.1 Hz); δ (rotamer **B**) = 1.82 (d, 3 H, *J* = 6.7 Hz), 2.09–2.23 (m, 4 H), 3.30 (s, 3 H), 3.58–3.68 (m, 2 H), 4.12–4.21 (m, 2 H), 4.55 (m, 1 H), 5.20 (dq, 1 H, *J* = 6.7, 16.6 Hz), 6.54 (d, 1 H, *J* = 16.6 Hz).

^{13}C NMR (CD_2Cl_2): δ (rotamer **A**) = 22.7, 26.6, 28.5, 52.4, 59.5, 69.0, 74.0, 120.6, 142.3, 215.7, 224.5, 268.1; δ (rotamer) = 23.0, 26., 28.2, 55.2, 60.0, 63.7, 72.6, 120.2, 143.7, 218.6, 224.6, 265.0.

IR (neat): ν = 2935w, 2050s, 1903s, 1487w, 1452m, 1415w, 1123w, 1111w cm^{-1}.

MS (EI): *m*/*z* (%) = 359 (2) M^+, 331 (34), 303 (6), 275 (8), 247 (49), 219 (100), 214 (44), 198 (31).

HRMS: *m*/*z* calcd for $C_{15}H_{17}CrNO_6$ 359.0461, found 359.0466.

The rotamers **43A** and **43B** could separated via silica gel column chromatography (size: 3 × 35 cm, eluent: 10%CH_2Cl_2 in hexane). In general, 5–50% of the starting material **40** and desilylated product **36** were also isolated and could be painstakingly separated from the desired product via silica gel column chromatography.

Chiral Amino Carbene Complex 44

The chiral amino carbene complex **44** was prepared from **40** (0.46 mmol) in 54% along with 29% of the starting material using the same procedure described above for **43** except 2.0 equiv of benzaldehyde was used. The rotameric ratio of **A**:**B** ranged from 1.8:1 to 2.9:1; R_f 0.34 (50% CH_2Cl_2/hexane); orange oil.

^{1}H NMR ($CDCl_3$): δ (rotamer **A**) = 1.99–2.82 (m, 4 H), 3.41 (s, 3 H), 3.69 (d, 2 H, *J* = 3.5 Hz), 3.74 (m, 1 H), 3.81 (m, 1 H), 4.76 (m, 1 H), 5.83 (d, 1 H, *J* = 16.7 Hz), 7.17 (d, 1 H, *J* = 16.7 Hz), 7.22 (t, 1 H, *J* = 8.3 Hz), 7.30 (t, 2 H, *J* = 7.4 Hz), 7.36 (d, 2 H, *J* = 8.5 Hz); δ (rotamer **B**) = 1.99–2.82 (m, 4 H), 3.28 (s, 3 H), 3.67 (d, 2 H, *J* = 3.4 Hz), 4.19 (m, 1 H), 4.24 (m, 1 H), 4.63 (m, 1 H), 5.94 (d, 1 H, *J* = 16.7 Hz), 7.21 (d, 1 H, *J* = 16.7 Hz), 7.22 (t, 1 H, *J* = 8.3 Hz), 7.30 (t, 2 H, *J* = 7.4 Hz), 7.36 (d, 2 H, *J* = 8.5 Hz).

^{13}C NMR (CD_2Cl_2): δ (rotamer **A**) = 23.4, 26.7, 55.9, 59.6, 69.1, 74.4, 121.8, 127.0, 128.4, 129.3, 136.9, 140.1, 218.5, 224.3, 265.4; δ (rotamer **B**) = 23.3, 28.4, 59.5, 60.1, 64.6, 73.2, 121.5, 126.9, 128.2, 129.2, 137.1, 139.3, 218.4, 224.5, 268.3.

IR (neat): ν = 2934w, 2929w, 2923w, 2051s, 1905s, 1506w, 1496w, 1488m, 1447w cm^{-1}.

MS (EI): *m*/*z* (%) = 421 (<1) M^+, 393 (14), 363 (2), 337 (3), 309 (18), 281 (100), 266 (18), 245 (10), 229 (17), 213 (15), 200 (72), 184 (98), 165 (39).

When, 2,2'-dimethylpropanal was used, only 3.4 mg of a yellow oil was isolated and found to possibly contain the desired product **45** (<2%) which was not further characterized. Also isolated was 77% of **40** and 18% of **36**.

Chiral Amino Carbene Complex 41

The chiral amino complex **41** was prepared from **36** (1.34 mmol) in 7% yield using the same procedure as described for the preparation of **40** except 1.3 equiv of TBSCl was used. The rotameric ratio of **A**:**B** was 1:1.2; R_{fA} 0.50, R_{fB} 0.39 (50% CH_2Cl_2/hexane); yellow oil.

^{1}H NMR ($CDCl_3$): δ (rotamer **A**) = 0.34 (s, 6 H), 0.89 (s, 9 H), 2.02 (m, 1 H), 2.13 (m, 3 H), 2.66 (m, 1 H), 2.83 (m, 1 H), 3.34 (s, 3 H), 3.32–3.53 (m, 2 H), 3.57 (m, 1 H), 3.67 (m, 1 H), 4.89 (m, 1 H); δ (rotamer **B**) = 0.20 (s, 6 H), 0.97 (s, 9 H), 2.02 (m, 1 H), 2.13 (m, 3 H), 3.22 (m, 1 H), 3.29 (s, 3 H), 3.32–3.53 (m, 3 H), 4.04 (m, 1 H), 4.23 (m, 1 H), 4.50 (m, 1 H).

^{13}C NMR (CD_2Cl_2): δ (rotamer **A**) = –4.4, –3.4, 22.8, 25.3, 25.9, 26.1, 59.26, 59.34, 71.9, 74.1, 101.6, 219.0, 224.4, 260.2; δ (rotamer **B**) = –4.3, –4.2, 23.5, 25.7, 25.8, 28.6, 60.8, 64.3, 70.1, 73.5, 100.9, 218.8, 224.6, 260.6.

IR (neat): ν = 2956w, 2933m, 2860w, 2048s, 1915s, 1603w, 1472m, 1449w, 1258m, 1226w, 840s, 789m cm^{-1}.

MS (EI): *m*/*z* (%) = 447 (11) M^+, 419 (22), 391 (22), 363 (11), 335 (11), 307 (33), 242 (100), 195 (74).

When TBSOTf or $CF_3C(O)NMeTBS$ was used, only the starting material **36** was recovered.

Chiral Amino Carbene Complex 42

The amino carbene complex **42** was prepared from **39** (0.726 mmol) in 91% yield using the same procedure as described for the preparation of **40**. The rotameric ratio of **A**:**B** was 1.3:1; R_f 0.33 (20% CH_2Cl_2/hexane); yellow oil.

^{1}H NMR ($CDCl_3$): δ (rotamer **A**) = 0.07 (s, 6 H), 0.20 (s, 9 H), 0.90 (s, 9 H), 2.01–2.30 (m, 4 H), 3.08 (d, 1 H, *J* = 10.7 Hz), 3.41 (d, 1 H, *J* = 10.7 Hz), 3.43 (m, 1 H), 3.68 (m, 1 H), 3.82 (m, 2 H), 4.67 (m, 1 H); δ (rotamer **B**) = 0.08 (s, 6 H), 0.19 (s, 9 H), 0.89 (s, 9 H), 2.01–2.30 (m, 4 H), 2.96 (br d, 1 H, *J* = 14.5 Hz), 3.21 (br d, 1 H, *J* = 14.5 Hz), 3.59 (m, 2 H), 4.13 (br t, 2 H, *J* = 7.8 Hz), 4.24 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ (rotamer **A**) = –5.4, –5.5, 0.69, 18.5, 23.6, 26.0, 26.3, 48.7, 61.1, 64.3, 71.9, 219.2, 223.7, 267.9; δ (rotamer **B**) = –5.4, –5.5, 0.73, 18.1, 23.1, 26.1, 27.6, 50.8, 53.4, 64.5, 65.5, 219.1, 223.9, 270.6.

IR (neat): ν = 2956m, 2049s, 1922s, 1472m, 1440w, 1254m, 1121w, 843s cm^{-1}.

MS (EI): *m*/*z* (%) = 505 (3) M^+, 477 (3), 449 (3), 421 (3), 393 (6), 365 (50), 313 (100), 298 (75), 240 (75).

HRMS: *m*/*z* calcd for $C_{21}H_{35}CrNO_6Si_2$ 505.1408, found 505.1404.

Chiral Amino Carbene Complex 46

The amino carbene complex **46** was prepared from **42** (0.675 mmol) in 28% yield of rotamer **46A** and 14% of the rotamer **46B** using the same procedure as described for the preparation of **43**. The rotameric ratio of **A**:**B** was 2.0:1. Also isolated was 30% of the desilylated product **39**.

Complex **46**

R_{fA} = 0.35, R_{fB} = 0.30 (20% CH_2Cl_2/hexane); yellow oil.

^{1}H NMR (CD_2Cl_2): δ (rotamer **A**) = 0.11 (s, 3 H), 0.12 (s, 3 H), 0.93 (s, 9 H), 1.83 (d, 3 H, *J* = 6.6 Hz), 1.99 (m, 1 H), 2.13–2.25 (m, 3 H), 3.63 (m, 1 H), 3.81 (m, 1 H), 3.89 (dd, 1 H, *J* = 2.4, 10.0 Hz), 3.97 (dd, 1 H, *J* = 5.5, 10.0 Hz), 4.63 (m, 1 H), 5.13 (dq, 1 H, *J* = 6.6, 15.9 Hz), 6.55 (d, 1 H, *J* = 15.9 Hz); δ (rotamer **B**) = 0.10 (s, 6 H), 0.95 (s, 9 H), 1.85 (d, 3 H, *J* = 6.5 Hz), 2.13–2.25 (m, 4 H), 3.64–3.72 (m, 2 H), 4.14 (m, 1 H), 4.24 (m, 1 H), 4.52 (m, 1 H), 5.27 (dq, 1 H, *J* = 6.5, 16.0 Hz), 6.59 (d, 1 H, *J* = 16.0 Hz).

^{13}C NMR (CD_2Cl_2): δ (rotamer **A**) = –5.4, –5.3, 17.9, 23.5, 26.1, 26.2, 27.6, 55.8, 65.8, 70.3, 120.3, 143.9, 218.7, 224.5, 264.6; δ (rotamer **B**) = –5.5, –5.4, 18.1, 23.3, 26.0, 26.4, 27.8, 60.7, 63.5, 72.1, 120.6, 142.3, 218.6, 224.6, 267.1.

IR (neat): ν = 2956w, 2929w, 2857w, 2051s, 1911s, 1491w, 838m cm^{-1}.

MS (EI): *m*/*z* (%) = 459 (2) M^+, 431 (3), 403 (10), 375 (7), 347 (13), 319 (100), 303 (30), 267 (79), 249 (23).

HRMS: *m*/*z* calcd for $C_2H_{29}CrNO_6Si$ 459.1169, found 459.1171.

(Arene)chromium Tricarbonyl Complexes 47A and 47B

The chiral amino complex **43A** (17.2 mg, 0.048 mmol) was reacted with pent-1-yne (9.00 μL, 0.091 mmol, 1.9 equiv) in the presence of Hünig's base (25.0 μL, 0.144 mmol, 3.0 equiv) and TBSCl (14.5 mg, 0.096 mmol, 2.0 equiv) in benzene at 80 °C for 16 h according to the general procedure to yield 12.1 mg of the desired arene complexes **47A** and **47B** (49%) as a yellow oil with diastereomeric ratio of 55:45; R_f 0.34 (50% CH_2Cl_2/hexane).

^{1}H NMR ($CDCl_3$): δ (**A**) = 0.375 (s, 3 H), 0.380 (s, 3 H), 0.91 (t, 3 H, *J* = 6.4 Hz), 1.03 (s, 9 H), 1.29 (m, 2 H), 1.68 (m, 2 H), 1.98 (m, 4 H), 2.23 (s, 3 H), 2.80 (m, 2 H), 3.29 (m, 2 H), 3.34 (s, 3 H), 3.68 (m, 1 H), 4.59 (d, 1 H, *J* = 2.5 Hz), 4.75 (d, 1 H, *J* = 2.5 Hz); δ (**B**) = 0.378 (s, 3 H), 0.380 (s, 3 H), 1.03 (s, 9 H), 1.05 (m, 3 H), 1.29 (m, 2 H), 1.87 (m, 2 H), 2.19 (m, 4 H), 2.25 (s, 3 H), 3.04 (m, 2 H), 3.29 (m, 2 H), 3.35 (s, 3 H), 3.74 (m, 1 H), 4.59 (d, 1 H, *J* = 2.3 Hz), 4.81 (d, 1 H, *J* = 2.3 Hz).

^{13}C NMR (CD_2Cl_2): δ (**A**) = –2.6, 14.2, 18.5, 19.0, 23.95, 26.1, 26.4, 29.1, 33.7, 49.7, 59.3, 74.2, 75.0, 76.1, 78.4, 104.9, 109.4, 112.3, 138.9, 236.7; δ (**B**) = –3.0, 14.1, 18.7, 18.9, 24.00, 24.2, 26.2, 29.4, 33.6, 49.5, 59.2, 74.3, 74.5, 77.4, 77.6, 104.7, 111.6, 124.7, 129.7, 236.6.

IR (neat): ν = 2958m, 2930m, 2885w, 2859w, 1942s, 1852s, 1555m, 1465s, 1437m, 1255s, 921m, 839m cm^{-1}.

MS (EI): *m*/*z* (%) = 513 (5) M$^+$, 429 (41), 377 (19), 332 (100), 260 (6).

HRMS: *m*/*z* calcd for $C_{25}H_{39}CrNO_5Si$ 513.2003, found 513.2001.

The chiral amino complex **43B** (12.0 mg, 0.033 mmol) was reacted with 6.20 uL of pent-1-yne (6.20 μL, 0.063 mmol, 1.9 equiv) in the presence of Hünig's base (17.2 μL, 0.099 mmol, 3.0 equiv) and TBSCl (9.95 mg, 0.066 mmol, 2.0 equiv) in benzene at 80 °C for 14 h according to the general procedure I to yield 5.8 mg of the desired arene complex **47A** and **47B** (34%) as a yellow oil with diastereomeric ratio of 55:45.

(Arene)chromium Tricarbonyl Complexes 48A and 48B

The chiral amino complex **44** (95.3 mg, 0.23 mmol) (rotameric ratio **A**:**B**: 2.9:1) was reacted with pent-1-yne (44.6 μL, 0.45 mmol, 1.9 equiv) in the presence of Hünig's base (118.1 μL, 0.68 mmol, 3.0 equiv) and TBSCl (68.1 mg, 0.45 mmol, 2.0 equiv) in benzene at 80 °C for 18 h according to the general procedure to yield 52.1 mg of the desired arene complex **48A** and **48B** (40%) as a yellow foam with diastereomeric ratio of 52:48. Also isolated was the corresponding free arene in 13% yield; R_f = 0.33 (50% CH_2Cl_2/hexane).

^{1}H NMR (CD_2Cl_2): δ (**A**) = 0.01 (s, 3 H), 0.03 (s, 3 H), 0.93 (s, 9 H), 1.11 (t, 3 H, *J* = 7.6 Hz), 1.68 (m, 2 H), 2.34 (m, 2 H), 2.79 (m, 2 H), 3.09 (m, 2 H), 3.29 (s, 3 H), 3.32 (m, 2 H), 3.76 (br t, 2 H, *J* = 6.4 Hz), 3.82 (m, 1 H), 4.81 (d, 1 H, *J* = 2.7 Hz), 4.97 (d, 1 H, *J* = 2.7 Hz), 7.39 (m, 3 H), 7.62 (d, 2 H, *J* = 7.2 Hz); δ (**B**) = –0.39 (s, 3 H), –0.37 (s, 3 H), 0.94 (s, 9 H), 1.10 (t, 3 H, *J* = 7.2 Hz), 1.76 (m, 2 H), 1.90 (m, 2 H), 2.79 (m, 2 H), 3.09 (m, 2 H), 3.34 (m, 2 H), 3.36 (s, 3 H), 3.40 (m, 2 H), 3.74 (m, 1 H), 4.73 (d, 1 H, *J* = 2.7 Hz), 4.95 (d, 1 H, *J* = 2.7 Hz), 7.39 (m, 3 H), 7.62 (d, 2 H, *J* = 7.2 Hz).

^{13}C NMR (CD_2Cl_2): δ (A) = –4.2, 14.3, 18.92, 23.9, 24.1, 26.1, 29.18, 33.3, 49.93, 59.4, 59.43, 74.7, 75.3, 79.3, 108.6, 126.9, 128.4, 130.7, 131.4, 131.6, 134.3, 143.4, 236.5; δ (**B**) = –4.0, 14.2, 18.91, 24.0, 24.2, 26.2, 29.24, 33.2, 49.87, 59.3, 59.45, 74.4, 77.0, 80.4, 108.7, 126.9, 128.5, 130.7, 131.4, 131.8, 135.6, 141.8, 236.6.

IR (neat): ν = 2957m, 2930m, 2858w, 1944s, 1855s, 1551m, 1461s, 1432s, 1254s, 921w, 839m, 783w cm^{-1}.

mass spectrum (EI): m/z (% relative intensity) 575 (15) M$^+$, 518 (3), 491 (100), 476 (5), 459 (3), 439 (39), 394 (98), 336 (9), 308 (5), 246 (7), 169 (14);

HRMS: *m*/*z* calcd for $C_{30}H_{41}CrNO_5Si$ 575.2159, found 575.2134.

Free Arene

R_f 0.44 (50% CH_2Cl_2/hexane); yellow foam.

^{1}H NMR (CD_2Cl_2): δ = –0.49 (s, 3 H), –0.47 (s, 3 H), 0.94 (s, 9 H), 1.02 (t, 3 H, *J* = 7.3 Hz), 1.68 (m, 2 H), 2.00 (m, 4 H), 2.60 (br t, 2 H, *J* = 7.8 Hz), 3.24 (m, 2 H), 3.36 (s, 3 H), 3.43 (t, 2 H, *J* = 7.7 Hz), 3.50 (m, 1 H), 6.40 (d, 1 H, *J* = 2.9 Hz), 6.45 (d, 1 H, *J* = 2.9 Hz), 7.25 (br t, 1 H, *J* = 8.7 Hz), 7.33 (t, 2 H, *J* = 7.7 Hz), 7.50 (d, 2 H, *J* = 7.4 Hz).

^{13}C NMR (CD_2Cl_2): δ = –4.1, 14.2, 18.9, 24.1, 24.4, 26.3, 29.5, 33.9, 49.66, 59.0, 59.4, 78.2, 109.7, 109.8, 112.6, 113.3, 128.3, 128.5, 128.7, 128.8, 137.2, 141.7.

IR (neat): ν = 2957m, 2930s, 2858w, 1551s, 1461s, 1431s, 1254s, 921m, 839s, 782w cm^{-1}.

MS (EI): *m*/*z* (%) = 439 (41) M$^+$, 394 (100), 378 (3), 364 (2), 350 (5), 336 (9), 322 (3), 308 (5), 294 (3), 278 (3), 246 (8), 169 (15).

HRMS: *m*/*z* calcd for $C_{21}H_{41}CrNO_2Si$ 439.2907, found 439.2892.

Arene Chromium Tricarbonyl Complexes 49A and B

The chiral amino complex **46A** (11.2 mg, 0.026 mmol) was reacted with pent-1-yne (4.76 mL, 0.048 mmol, 1.9 equiv) in the presence of Hünig's base (13.3 mL, 0.076 mmol, 3.0 equiv) and TBSCl (7.7 mg, 0.051 mmol, 2.0 equiv) in benzene at 80 °C for 16 h according to the general procedure to yield 7.9 mg of the desired arene complex **49A** and **49B** (51%) as a yellow oil with diastereomeric ratio of 55:45. R_f = 0.58 (50% CH_2Cl_2/hexane).

^{1}H NMR (CD_2Cl_2): δ (rotamer **A**) = 0.08 (s, 6 H), 0.38 (s, 6 H), 0.92 (s, 9 H), 1.03 (s, 9 H), 1.04 (m, 3 H), 1.49–1.78 (m, 6 H), 2.24 (s, 3 H), 2.82 (m, 2 H), 3.06 (m, 2 H), 3.64 (m, 2 H), 4.56 (d, 1 H, *J* = 2.6 Hz), 4.78 (d, 1 H, *J* = 2.6 Hz), 6.25 (m, 1 H); δ (rotamer **B**) = 0.08 (s, 6 H), 0.38 (s, 6 H), 0.92 (s, 9 H), 1.03 (s, 9 H), 1.07 (m, 3 H), 1.49–1.78 (m, 6 H), 2.23 (s, 3 H), 2.52 (m, 2 H), 3.30 (m, 2 H), 3.50 (m, 2 H), 4.57 (d, 1 H, *J* = 2.6 Hz), 4.68 (d, 1 H, *J* = 2.6 Hz), 5.36 (m, 1 H).

^{13}C NMR (CD_2Cl_2): δ (rotamer **A**) = –5.3, –5.1, –2.8, –2.7, 14.1, 18.5, 19.0, 23.7, 24.1, 26.0, 26.1, 28.5, 28.6, 33.7, 49.7, 61.0, 64.2, 75.9, 77.0, 78.9, 109.5, 113.4, 129.7, 236.6; δ (rotamer **B**) = –5.4, –5.2, –3.1, –2.5, 14.3, 18.7, 18.9, 23.8, 23.9, 25.9, 26.2, 26.3, 28.4, 33.6, 49.6, 60.9, 64.8, 75.8, 76.9, 78.8, 111.5, 112.3, 124.6, 236.7.

IR (neat): ν = 2956w, 2930w, 2858w, 1945s, 1858s, 1465m, 1255m, 839m cm^{-1}.

MS (EI): *m*/*z* (%) = 613 (2) M$^+$, 529 (18), 477 (15), 332 (100), 243 (8), 115 (30).

HRMS: *m*/*z* calcd for $C_{30}H_{51}CrNO_5Si_2$ 613.2711, found 613.2701.

The chiral amino complex **46A** (20.0 mg, 0.044 mmol) was reacted with pent-1-yne (8.12 μL, 0.083 mmol, 1.9 equiv) in the presence of Hünig's base (22.7 μL, 0.130 mmol, 3.0 equiv) and TBSCl (13.1 mg, 0.087 mmol, 2.0 equiv) in benzene at 80 °C for 14 h according to the general procedure to yield 12.7 mg of the desired arene complex **49A** and **49B** (48%) as a yellow oil with diastereomeric ratio of 59:41.

Isomerization of the Rotamers of Chiral Alkenyl Carbene Complexes; General Procedure

The alkenyl carbene complex with certain rotameric ratio was dissolved in benzene to make up a 0.25 M solution. Additives such as Hünig's base could be added. The mixture was deoxygenated using freeze-pump-thaw method (4 cycles at –196 °C/25 °C) before being heated at 80 °C for 15–48 h. At the end of the reaction, the mixture was usually purified using a small pipette size silica gel column eluted with 0% to 50% CH_2Cl_2 in hexane. A recovery yield was recorded and the final ratio was determined using ^{1}H NMR analysis.

Chiral (Alkenyl)chromium Carbene Complex 54
Alcohol 52

The amino carbene complex **51** (333.3 mg, 1.00 mmol) was dissolved in THF (15 mL) at –78 °C, and BuLi (1.6 M, 687.5 μL,

1.00 mmol, 1.0 equiv) was carefully added dropwise. After stirring at –78 °C for 1 h, freshly distilled and prechilled (–78 °C) acetaldehyde (139.8 μL, 2.50 mmol, 2.5 equiv) was slowly added dropwise. The reaction mixture was stirred at –78 °C for 2 h, at –30 °C for 12 h before it was quenched with AcOH (57.2 μL, 1 equiv) at –78 °C. After concentration of the mixture under reduced pressure, purification by silica gel column chromatography (size: 1.5 × 35cm, gradient eluent: 0% to 75% CH_2Cl_2 in hexane) provided 297.5 mg of the desired product **52** (79%) as a yellow waxy solid. Also isolated was 66.6 mg of the starting material **51** (20%). $R_{fA,B}$ 0.08 (CH_2Cl_2).

^{1}H NMR ($CDCl_3$): δ (**A**) = 1.21 (d, 3 H, *J* = 6.1 Hz), 1.31 (d, 3 H, *J* = 6.5 Hz), 1.34 (d, 3 H, *J* = 6.1 Hz), 1.59 (br s, 1 H), 3.17 (dd, 1 H, *J* = 2.7, 12.6 Hz), 3.46 (m, 1 H), 3.65 (dd, 1 H, *J* = 6.8, 13.2 Hz), 4.12 (m, 3 H), 4.27 (m, 1 H), 4.45 (br t, 2 H, *J* = 6.6 Hz); δ (**B**) = 1.18 (d, 3 H, *J* = 6.7 Hz), 1.28 (d, 3 H, *J* = 6.1 Hz), 1.38 (d, 3 H, *J* = 6.7 Hz), 1.59 (br s, 1 H), 3.10 (dd, 1 H, *J* = 11.4, 13.8 Hz), 3.44 (m, 1 H), 3.80 (dd, 1 H, *J* = 3.8, 11.6 Hz), 4.09 (m, 3 H), 4.22 (m, 1 H), 4.33 (m, 2 H).

IR (neat): ν = 3446 (brd)w, 2980w, 2976m, 2934w, 2052s, 1965s, 1902s, 1899s, 1808m, 1508w, 1448w, 1384w, 1253m, 1128m, 1088w, 1032w cm^{-1}.

MS (EI): *m*/*z* (%) = 377 (5) M^+, 349 (5), 321 (3), 293 (2), 265 (13), 237 (44), 193 (25), 167 (100), 154 (81), 141 (70).

The elimination of the alcohol **52** to yield **54** using phenyl isocyanate was not successful and gave only decomposition of the starting material.

Mesylate 53[17]

The alcohol **52** (145.5 mg, 0.386 mmol) was dissolved in CH_2Cl_2 (10 mL) at 0 °C, and Et_3N (113.0 μL, 0.81 mmol, 2.1 equiv) and MsCl (60.0 μL, 0.77 mmol, 2.0 equiv) were added in that order. After stirring at 0 °C for 1 h, the reaction mixture was concentrated under reduced pressure and subjected to silica gel column chromatography (size: 5 × 5cm, eluent: CH_2Cl_2) to provide 157.6 mg of the pure mesylate **53** (90%) as a pale yellow waxy solid; R_{fA} 0.22, R_{fB} 0.28 (CH_2Cl_2).

^{1}H NMR ($CDCl_3$): δ (**A**) = 1.21 (d, 6 H, *J* = 6.8 Hz), 1.23 (d, 3 H, *J* = 7.2 Hz), 3.00 (s, 3 H), 3.34 (dd, 1 H, *J* = 9.4, 14.1 Hz), 3.73 (dd, 1 H, *J* = 9.4, 13.1 Hz), 3.92 (m, 1 H), 4.09 (m, 1 H), 4.17 (m, 2 H), 4.21 (m, 1 H), 4.68 (br d, 1 H, *J* = 13.2 Hz), 5.10 (m, 1 H); δ (**B**) = 1.26 (d, 6 H, *J* = 6.3 Hz), 1.29 (d, 3 H, *J* = 7.0 Hz), 3.61 (dd, 1 H, *J* = 3.5, 10.3 Hz), 3.65 (s, 3 H), 3.84 (dd, 1 H, *J* = 3.5, 13.4 Hz), 3.95 (m, 1 H), 4.06 (m, 1 H), 4.17 (m, 2 H), 4.23 (m, 1 H), 4.59 (br d, 1 H, *J* = 12.6 Hz), 5.03 (m, 1 H).

IR (neat): ν = 2977w, 2924m, 2054s, 1969s, 1908s, 1903s, 1515m, 1354m, 1333m, 1173s, 918m cm^{-1}.

MS (EI): *m*/*z* (%) = 455 (2) M^+, 427 (1), 399 (1), 371 (1), 343 (3), 315 (4), 294 (3), 243 (3), 219 (19), 169 (40), 154 (100), 140 (16).

Elimination of 53 to Give 54[17]

The mesylate **53** (137 mg, 0.301 mmol) prepared above was eliminated using 0.50 M NaOH solution (2 equiv) in EtOH and EtOH (10 mL) at r.t. Silica gel column chromatography (size: 5 × 5 cm, eluent: 50% CH_2Cl_2 in hexane) provided 92.4 mg of the pure alkenyl complex **54** (85%) as an orange yellow oil; R_f 0.72 (CH_2Cl_2).

^{1}H NMR ($CDCl_3$): δ = 1.17 (d, 3 H, *J* = 6.5 Hz), 1.30 (d, 3 H, *J* = 6.5 Hz), 1.82 (d, 3 H, *J* = 6.7 Hz), 3.82 (m, 2 H), 3.98 (dd, 1 H, *J* = 4.2, 12.8 Hz), 4.07 (m, 1 H), 4.20 (m, 1 H), 4.57 (d, 1 H, *J* = 12.5 Hz), 4.95 (dq, 1 H, *J* = 16.2, 6.7 Hz), 6.40 (d, 1 H, *J* = 16.2 Hz).

^{13}C NMR ($CDCl_3$): δ = 16.9, 17.8, 30.1, 58.6, 65.0, 67.2, 68.0, 118.8, 141.2, 218.1, 222.4, 269.9.

IR (neat): ν = 2979w, 2975w, 2053s, 1974m, 1907s, 1646m, 1507m, 1248w, 966m, 806m cm^{-1}.

MS (EI): *m*/*z* (%) = 359 (3) M^+, 331 (52), 303 (4), 275 (8), 247 (63), 219 (100), 167 (64), 154 (26).

HRMS: *m*/*z* calcd for $C_{15}H_{17}CrNO_6$ 359.0461, found 359.0469.

(Arene)chromium Tricarbonyl Complex 55

The chiral amino complex **54** (65.6 mg, 0.18 mmol) was reacted with pent-1-yne (34.3 μL, 0.34 mmol, 1.9 equiv) in the presence of Hünig's base (95.6 mL, 0.55 mmol, 3.0 equiv) and TBSCl (55.2 mg, 0.37 mmol, 2.0 equiv) in benzene at 80 °C for 20 h according to the general procedure to yield 47.9 mg of the desired arene complexes **55A** and **55B** (51%) as a yellow oil with diastereomeric ratio of 55:45. Also isolated was 8.8 mg of the corresponding free arene **56** (12%) as a yellow oil; $R_{fA,B}$ 0.17 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ (**A**) = 0.38 (s, 6 H), 1.00 (s, 9 H), 1.02 (t, 3 H, *J* = 7.2 Hz), 1.22 (d, 6 H, *J* = 6.5 Hz), 1.58 (m, 2 H), 2.20 (s, 3 H), 2.70 (m, 2 H), 2.74 (m, 2 H), 3.04 (m, 2 H), 4.04 (m, 2 H), 4.76 (d, 1 H, *J* = 3.4 Hz), 4.83 (d, 1 H, *J* = 3.4 Hz); δ (**B**) = 0.34 (s, 6 H), 0.99 (s, 9 H), 1.01 (t, 3 H, *J* = 7.2 Hz), 1.22 (d, 6 H, *J* = 6.5 Hz), 1.58 (m, 2 H), 2.19 (s, 3 H), 2.70 (m, 2 H), 2.74 (m, 2 H), 3.04 (m, 2 H), 4.04 (m, 2 H), 4.76 (d, 1 H, *J* = 2.8 Hz), 4.84 (d, 1 H, *J* = 2.8 Hz).

^{13}C NMR (CD_2Cl_2): δ (**A**) = –3.3, 17.4, 17.6, 23.3, 23.4, 25.2, 25.4, 32.6, 32.9, 51.4, 55.1, 65.2, 66.0, 76.6, 78.4, 107.7, 126.2, 129.7, 144.8, 235.4; δ (**B**) = –3.6, 13.4, 17.7, 18.1, 25.0, 25.1, 25.3, 29.2, 32.7, 51.3, 55.0, 65.1, 65.3, 77.1, 77.7, 102.8, 128.3, 133.1, 145.6, 235.4.

IR (neat): ν = 2956m, 2932m, 1946s, 1864s, 1471m, 1254s, 915m, 840m cm^{-1}.

MS (EI): *m*/*z* (%) = 513 (1) M^+, 429 (2), 391 (1), 377 (100), 320 (9), 291 (9), 234 (34), 176 (9).

HRMS: *m*/*z* calcd for $C_{25}H_{39}CrNO_5Si$ 513.2002, found 513.1987.

Free arene 56

R_f = 0.17 (50% CH_2Cl_2 in hexane).

^{1}H NMR (CD_2Cl_2): δ = 0.16 (s, 6 H), 0.88 (t, 3 H, *J* = 6.6 Hz), 1.01 (s, 9 H), 1.26 (d, 6 H, *J* = 6.2 Hz), 1.51 (m, 2 H), 2.16 (s, 3 H), 2.50 (m, 2 H), 2.74 (m, 2 H), 3.04 (m, 2 H), 4.04 (m, 2 H), 6.47 (br s, 2 H).

IR (neat): ν = 2956m, 2932s, 1471s, 1254s, 915m, 840s cm^{-1}.

MS (EI): *m*/*z* (%) = 377 (100) M^+, 362 (4), 320 (9), 291 (9), 277 (5), 262 (8), 234 (31), 204 (34), 176 (9), 149 (4), 117 (9).

HRMS: *m*/*z* calcd for $C_{22}H_{39}NO_2Si$ 377.2750, found 377.2743.

Indole Carbene Complex 57

A solution of *t*-BuLi (45 mL of a 1.7 M solution in pentane, 76.5 mmol) was added to a solution of 1,3-dimethylindole (10.02 g, 69 mmol) in THF (45 mL) cooled to –78 °C over a 45 min period. The resulting bright yellow slurry was stirred cold for 30 min and then allowed to warm to r.t. The slurry was re-cooled to –78 °C and $Cr(CO)_6$ (16 g, 73 mmol) was added as a solid in a single portion. The reaction was again allowed to stir for 30 min cold and then warmed to r.t. The dark brown mixture was then stirred for 22 h. The solution was cooled to 0 °C and methyl triflate (8.2 mL, 72 mmol) was added. The mixture was stirred for 20 min cold, warmed to r.t. and stirred an additional hour. The deep red solution was filtered through silica gel and concentrated. The red oily residue was dissolved in hexane and allowed to stand in the freezer. The chromium carbene complex was collected as deep red crystals (19.9 g, 73%).

57

Deep red crystals; mp 102–104 °C, R_f 0.61 (80:20 hexane/EtOAc).

^{1}H NMR ($CDCl_3$): δ = 2.26 (s, 3 H), 3.60 (s, 3 H), 4.22 (s, 3 H), 7.12 (m, 2 H), 7.24 (d, 1 H, *J* = 3.5 Hz), 7.53 (d, 1 H, *J* = 8.0 Hz).

^{13}C NMR ($CDCl_3$): δ = 9.5, 31.6, 65.9, 105.5, 109.5, 120.0, 120.2, 123.7, 128.0, 138.0, 145.7, 215.8, 224.9, 348.41.

IR (neat): ν = 2063m, 1933br s, 1432w, 1355w, 1251m, 1182w, 1144m, 932m, 748m, 698m cm^{-1}.

MS (EI): *m/z* (%) = 379 (M^+, 7), 351 (57), 323 (65), 295 (25), 267 (84), 239 (100), 209 (100), 187 (85), 172 (100), 157 (27), 144 (98), 128 (30), 115 (38), 103 (46), 91 (28), 77 (48).

Anal calcd for $C_{17}H_{13}NO_6Cr$: C, 53.83; H, 3.46; N, 3.69. Found: C, 53.89; H, 3.19; N, 3.61.

Chelate Carbene Complexes 59a and 59b

A solution of BuLi (0.43 mL of a 2.5 M solution in hexanes, 1.08 mmol) was added to a solution of (4*R*,5*S*)-1,5-dimethyl-4-phenyl-2-imidazolidinone (203 mg, 1.08 mmol) in THF (10 mL) cooled to –78 °C. The light yellow anion solution was stirred 15 min and a solution of the carbene complex **57** (337 mg, 0.89 mmol) in THF (3 mL) THF was added. The reaction was allowed to warm to r.t. and stirred for 18 h. The reaction can be monitored by TLC (50:50 hexane/EtOAc). The mixture was then concentrated and purified by column chromatography (70:30 hexane/EtOAc) to give a combined yield of 217 mg (48%) of two atropomeric chelate carbene complexes. The ratio of the two rotamers is 1:1.2 (89 mg of **59a**, 108 mg of **59b**, and 20 mg of a mixture of the two). Additional experiments gave yields varying from 16% to 48% with rotamer ratios of 1.9:1 to 1:1.2.

59a

Lustrous black crystals; mp 152 °C (dec.); R_f 0.43 (50:50 hexane/EtOAc).

^{1}H NMR ($CDCl_3$): δ = 0.91 (d, 3 H, *J* = 6.7 Hz), 2.38 (s, 3 H), 3.04 (s, 3 H), 3.23 (s, 3 H), 4.51 (pentet, 1 H, *J* = 7.6 Hz), 5.28 (d, 1 H, *J* = 8.5 Hz), 6.78 (br s, 1 H), 7.05-7.25 (m, 7 H), 7.59 (d, 1 H, *J* = 7.9 Hz).

^{13}C NMR ($CDCl_3$): δ = 9.6, 13.9, 27.9, 30.7, 59.4, 64.0, 100.4, 108.9, 119.2, 119.8, 122.5, 127.6, 128.0, 128.3, 135.3, 139.2, 144.3, 163.3, 215.4, 218.2, 230.6, 234.9, 302.8.

IR (neat): ν = 2006s, 1897s, 1836s, 1700s, 1457w, 1399w, 1319br m, 1283w, 1259w, 1214w, 1199w, 743w, 731w, 718w, 700w, 667w, 619w cm^{-1}.

MS (EI): *m/z* (%) = M^+ not detected, 220 (8), 108 (5), 86 (4), 78 (100), 63 (4), 52 (82).

Anal. calcd for $C_{26}H_{23}N_3O_5Cr$ as a 1:1 crystalline complex with benzene: C, 65.41; H, 4.97; N, 7.15; Cr, 8.85. Found: C, 64.34; H, 5.10; N, 7.13; Cr, 8.80.

59b

Lustrous black crystals; mp 162 °C; R_f 0.31 (50:50 hexane/EtOAc).

^{1}H NMR (CD_2Cl_2): δ = 0.85 (d, 3 H, *J* = 6.7 Hz), 1.92 (s, 3 H), 3.01 (s, 3 H), 3.63 (s, 3 H), 4.43–4.48 (m, 1 H), 5.00 (d, 1 H, *J* = 8.6 Hz), 7.04 (t of d, 1 H, *J* = 6.9, 1.2 Hz), 7.15 (t, 1 H, *J* = 7.3 Hz), 7.25–7.36 (m, 7 H).

^{13}C NMR (CD_2Cl_2): δ = 8.8, 14.1, 28.1, 31.3, 59.7, 64.1, 109.4, 116.9, 118.9, 119.2, 123.6, 126.4, 128.0, 128.4, 129.1, 133.9, 138.4, 140.5, 163.4, 216.9, 217.8, 230.5, 235.2, 304.9.

IR (neat): ν = 2006s, 1900br s, 1838br s, 1703s, 1457w, 1438w, 1394w, 1348w, 1334w, 1307w, 1282w, 1260w, 1199w, 907w, 741w, 718w, 699w, 668w, 630w, 618w cm^{-1}.

MS (EI): *m/z* (%) = M^+ not detected, 220 (3), 108 (4), 88 (6), 86 (9), 78 (100), 63 (10), 52 (60), 51 (61).

Anal. calcd for $C_{26}H_{23}N_3O_5Cr$ as a 1:1 crystallization complex with benzene: C, 65.41; H, 4.97; N, 7.15; Cr, 8.85. Found: C, 63.24; H, 4.39; N, 6.91; Cr, 9.46.

Reaction of Carbene Complex 59a with Pent-1-yne

A Kontes flask was charged with carbene complex **59a** (314 mg, 0.62 mmol) under argon and dissolved in MeCN (120 mL). Pent-1-yne (90 μL, 0.91 mmol) was added and the flask was freeze pump thawed (3 cycles) and placed in a 48 °C oil bath for 21 h. The reaction was opened to the air, diluted with Et_2O and stirred vigorously for 1 h. The turbid solution was filtered through a pad of Celite, concentrated, and purified via column chromatography (50:50 hexane/EtOAc) to give 145 mg (54%) of **63**. Careful ^{1}H NMR analysis established that the stereoselectivity of the reaction is ≥39:1. Large, X-Ray quality crystals were obtained by layering pentane on an Et_2O solution of the carbazole at r. t. In separate experiments yields of 58% and 70% were realized.

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Deep orange crystals; mp 188–190 °C; R_f 0.22 (50:50 hexane/EtOAc).

^{1}H NMR (This compound is ~1:1 mixture of atropomers at r.t., $CDCl_3$): δ = 0.58 (t, *J* = 7.3 Hz), 0.86 (t, *J* = 7.3 Hz), 0.94 (m, *J* = 5.3 Hz), 1.02 (sextet, *J* = 7.4 Hz), 1.60 (s), 1.87 (m), 2.08 (m), 2.22 (m), 2.86 (s), 2.92 (s), 3.50 (s), 3.69 (s), 3.90-3.98 (m), 4.40 (d, *J* = 8.3 Hz), 5.06 (d, *J* = 8.0 Hz), 6.20 (s), 6.69 (s), 6.75 (d, *J* = 8.0 Hz), 6.81 (d, *J* = 7.9 Hz), 6.93 (t, *J* = 7.5 Hz), 7.19–7.30 (m), 7.87 (t, *J* = 7.6 Hz).

^{13}C NMR ($CDCl_3$): δ = 13.2, 13.5, 13.6, 14.4, 21.5, 22.0, 28.5, 29.0, 29.8, 30.4, 30.5, 31.4, 35.6, 55.7, 59.8, 59.9, 64.6, 66.8, 101.7, 101.9, 107.3, 107.5, 118.3, 118.4, 120.6, 120.8, 124.0, 124.3, 127.4, 127.5, 127.7, 127.9, 128.0, 128.1, 128.2, 128.26, 128.33, 128.8, 131.9, 132.3, 135.3, 136.5, 141.7, 144.7, 145.6, 145.7, 160.8, 161.1, 161.2, 163.8, 200.4, 200.6.

IR (neat): ν = 3034m, 2957br s, 2925br s, 2868br m, 2856br m, 1707s, 1661s, 1630s, 1607s, 1537s, 1462br s, 1426br s, 1399s, 1366m, 1259m, 1125br m, 1022m, 806m, 752br m, 702m, 680m cm^{-1}.

MS (EI): *m/z* (%) = 441 (M^+, 100), 426 (14), 412 (12), 399 (68), 384 (8), 370 (9), 341 (5), 313 (5), 295 (4), 280 (5), 267 (10), 252 (65), 237 (17), 223 (39), 211 (30), 194 923), 181 (20), 167 (14), 144(12), 131 (8), 117 (25), 105 (10), 91 (17), 77 (8).

HRMS: *m/z* calcd for $C_{28}H_{31}N_3O_2$: 441.2416, found 441.2410.

Anal. calcd for $C_{28}H_{31}N_3O_2$: C, 76.16; H, 7.08; N, 9.52. Found: C, 76.29; H, 7.19; N, 9.39.

Reaction of Carbene Complex 59b with Pent-1-yne

A Kontes flask was charged with carbene complex **59b** (170 mg, 0.33 mmol) under argon and dissolved in MeCN (67 mL). Pent-1-yne (50 μL, 0.51 mmol) was added and the flask was freeze pump thawed (3 cycles) and placed in a 55 °C oil bath for 21 h. The reaction was opened to the air, diluted with Et_2O and stirred vigorously for 1 h. The turbid solution was filtered through a pad of Celite, concentrated, and purified via column chromatography (50:50 hexane/EtOAc) to give 38 mg (26%) of **64**. Careful ^{1}H NMR analysis established that the stereoselectivity of the reaction is ≥ 38:1 (95% de). In separate experiments yields of 48% and 26% were realized.

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Deep red crystals; mp 194–197 °C; R_f 0.22 (50:50 hexane/EtOAc).

^{1}H NMR (This compound exists as ~1:4.2 mixture of atropomers at r.t., $CDCl_3$): δ (major atropomer) = 0.71 (t, 3 H, *J* = 7.4 Hz), 1.03 (d, 3 H, *J* = 6.6 Hz), 1.17 (s, 3 H), 1.25–1.31 (m, 2 H), 1.86–1.92 (m, 1 H, *J* = 7.3 Hz), 2.17-2.23 (m, 1 H, *J* = 7.0 Hz), 2.87 (s, 3 H), 3.50 (s, 3 H), 3.99 (pent, 1 H, *J* = 7.2 Hz), 4.66 (d, 1 H, *J* = 8.4 Hz), 6.52 (s, 1 H), 7.75 (d, 1 H, *J* = 8.0 Hz), 6.93 (t, 1 H, *J* = 7.3 Hz),

7.15–7.31 (m, 8 H), 7.83 (d, 1 H, J = 7.4 Hz); δ (minor atropomer) = 0.64 (t, 3 H, J = 7.3 Hz), 0.79 (d, 3 H, J = 6.5 Hz), 1.25–1.31 (m, 2 H), 1.66 (s, 3 H), 2.06–2.11 (m, 2 H), 2.94 (s, 3 H), 3.60 (s, 3 H), 3.88–3.91 (m, 1 H), 5.21 (d, 1 H, J = 8.2 Hz), 6.69 (s, 1 H), 6.93 (t, 1 H, J = 7.3 Hz), 7.15–7.31 (m, 8 H), 7.75 (d, 1 H, J = 8.0 Hz), 7.89 (d, 1 H, J = 7.3 Hz).

^{13}C NMR ($CDCl_3$): δ = 13.3, 13.5, 14.0, 14.8, 21.7, 22.1, 28.9, 29.2, 29.9, 30.5, 31.4, 31.9, 35.8, 36.7, 55.5, 56.2, 59.7, 60.7, 62.9, 67.4, 102.2, 102.4, 107.4, 107.7, 120.7, 121.2, 121.7, 122.1, 124.4, 124.5, 127.7, 127.8, 128.1, 128.3, 128.6, 128.7, 129.1, 132.2, 132.5, 135.0, 136.1, 139.2, 145.7, 145.9, 160.2, 160.7, 160.9, 162.2, 200.3.

IR (neat): ν = 1700s, 1659w, 1627m, 1607w, 1534s, 1463m, 1426s, 1399s, 1366m, 1121br m, 754s cm^{-1}.

MS (EI): m/z (%) = 441 (M^+, 100), 426 (15), 412 (13), 399 (97), 304 (10), 368 (15), 341 (11), 313 (8), 295 (9), 279 (10), 267 (12), 252 (58), 237 (16), 224 (33), 211 (37), 194 (27), 175 (43), 149 (33), 132 918), 117 (35), 105 (20), 91 (33), 78 (46), 69 (33).

Anal. calcd for $C_{28}H_{31}N_3O_2$: C, 76.16; H, 7.08; N, 9.52. Found: C, 66.02; H, 7.52; N, 7.28.

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