Relative Asymmetric Induction in the Intramolecular Reaction between Alkynes and Cyclopropylcarbene−Chromium Complexes: Stereocontrolled Synthesis of Five-Membered Rings Fused to Oxygen Heterocycles

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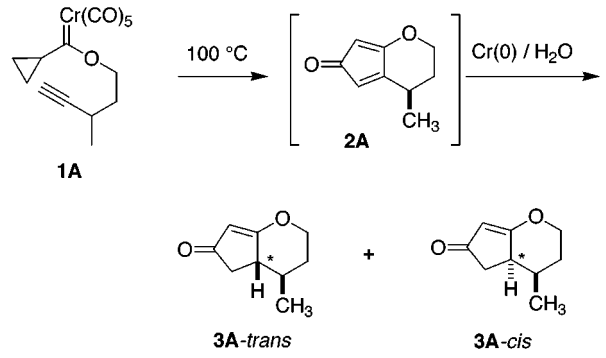
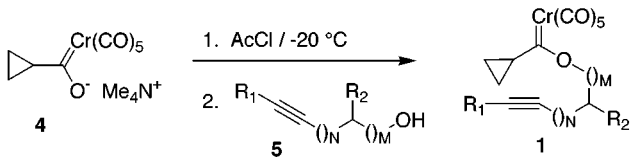
Synthesis of cyclopentenone derivatives fused to oxygen heterocycles by means of the intramolecular coupling of alkynes and cyclopropylcarbene−chromium complexes has been examined for a variety of cases in which the tethering chain features a stereogenic center. In some cases, this process proceeds with a very high degree of stereoselectivity; however, the extent and direction of relative asymmetric induction is very dependent upon the position of the chiral atom within the tethering chain and the length of the tethering chain. In the best case, featuring a two-carbon tether and a stereogenic center at the homopropargylic position (complex **1N**), the heterocyclic ring was produced with 97:3 selectivity for the cis heterocycle (**3N**). In the worst case, featuring a three-carbon tether and a stereogenic center at the homopropargylic position (complexes **1F** and **1I**), no stereoselectivity was observed. Improvement in stereoselectivity was noticed when terminal alkynes were replaced by silylated alkynes and when proton sources were eliminated from the reaction.

The intramolecular coupling of alkynes and cyclopropylcarbene−chromium complexes in aqueous solvents affords cyclopentenone rings fused to oxygen heterocycles in good-to-excellent yield (Scheme 1).[1] Thermolysis of alkyne−carbene complex **1A** initially produces a cyclopentadienone intermediate (**2A**),[2] which is reduced to the cyclopentenone vinylogous ester derivatives **3A** under the reaction conditions. A new stereocenter is created at the asterisked carbon atom during the reduction process. In the example in Scheme 1, the tethering chain of complex **1A** features a stereogenic center, and in this case, the heterocyclic ring of the products was constructed in a 94:6 trans:cis ratio, favoring the diequatorial isomer (heterocyclic ring substituents trans).[3] On the basis of the high degree of diastereoselectivity observed in this system, coupled with the myriad of methods available for manipulation of the vinylogous ester functionality,[4] a wide variety of cyclopentanoid ring structures can potentially be prepared stereoselectively by using cyclopentenones derived from intramolecular alkyne−cyclopropylcarbene complex coupling reactions. In this manuscript, thermolysis of a variety of alkyne-containing cyclopropylcarbene complexes that differ in the length of tether and position of the stereogenic center has been examined. The effect of position and ring size on the degree and direction of relative asymmetric induction will be discussed.

Scheme 1



Scheme 2



See Table I Entry Letters for Definition of R_1, R_2, M, N

Results

Synthesis of Alkyne-Containing Cyclopropylcarbene Complexes. Alkyne-containing cyclopropylcarbene complexes were readily prepared from the corresponding alkynols (**5**) using acylate salt **4** and acetyl chloride (Scheme 2). The yield for this process was usually greater than 70% when a primary alcohol was employed but

(1) Herndon, J. W.; Matasi, J. J. *J. Org. Chem.* **1990**, *55*, 786−788.
(2) In some cases, this intermediate can be isolated. (a) Herndon, J. W.; Patel, P. P. *Tetrahedron Lett.* **1997**, *38*, 59−62. (b) Tumer, S. U.; Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1992**, *114*, 8394−8404.
(3) Yan, J.; Herndon, J. W. *J. Org. Chem.* **1998**, *63*, 2325−2331.
(4) (a) For a review, see: Schick, H.; Eichhorn, I. *Synthesis* **1989**, 477−492. (b) Bhatia, G. S.; Lowe, R. F.; Stoodley, R. J. *J. Chem. Soc., Chem. Commun.* **1997**, 1981−1983. (c) Schinzer, D.; Kalesse, M. *Tetrahedron Lett*: **1991**, *32*, 4691−4694. (d) Ohba, M.; Haneishi, T.; Fujii, T. *Chem. Pharm. Bull.* **1995**, *43*, 26−31. (e) Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453−1473. (f) Smith, A. B., III; Dorsey, B. D.; Ohba, M.; Lupo, A. T., Jr.; Malamas, M. S. *J. Org. Chem.* **1988**, *53*, 4314−4325. (g) Bunnelle, W. H. *Adv. Cycloaddit.* **1993**, *3*, 67−98. (h) Stork, G.; Danheiser, R. L. *J. Org. Chem.* **1973**, *38*, 1775−1777.

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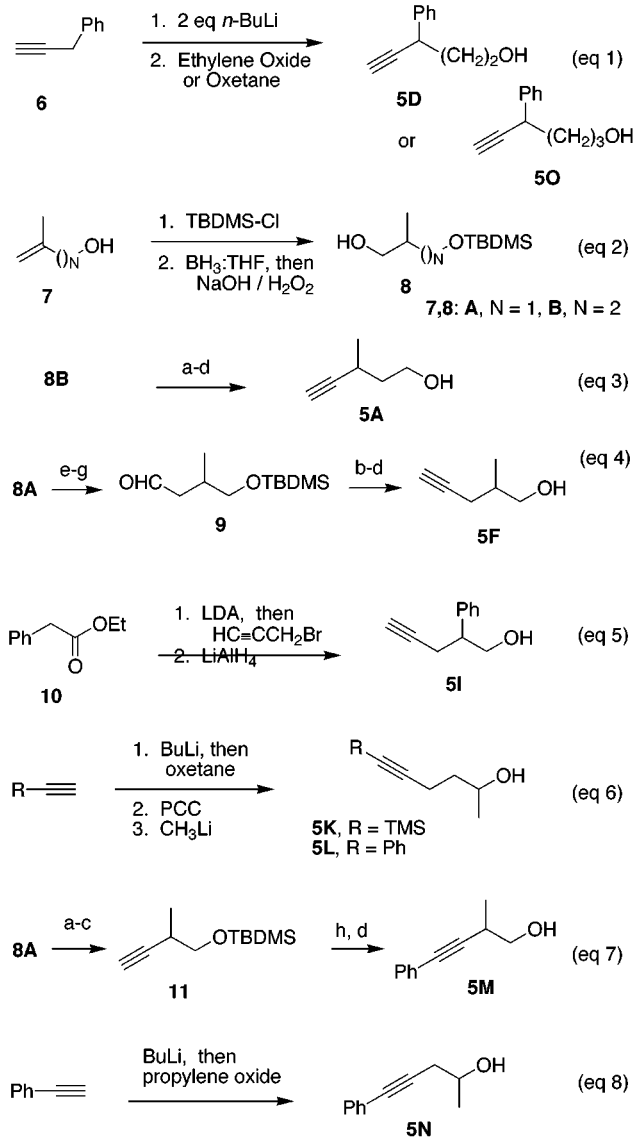
Scheme 3



substantially less with a secondary alcohol, although higher yields were observed when an excess of acylate salt **4** and acetyl chloride was employed.

Alkynol derivatives were prepared according to one of the general synthetic protocols in Scheme 3. Synthesis of 4-methyl-5-pentyn-1-ol derivatives (**5A**−**C**; substituent letters correlate with Table 1 entry letters for compounds **1**−**3**, **5**, and **12**−**17**) has previously been discussed.[3] Alkynols bearing a propargylic phenyl group (**5D**, **E**, and **O**) were prepared by treatment of the dianion[5] of 3-phenyl-1-propyne[6] (**6**) with either ethylene oxide[7] or oxetane (eq 1). Many of the alkynol derivatives were prepared from monoprotected diols (**8**) derived from methallyl alcohol (**7A**) or 3-methyl-3-buten-1-ol (**8A**) (eq 2). Alkynol **5F** was prepared from monoprotected diol **8A** by means of the multistep synthetic route in eq 4. Alkynol **5I**, which features a homopropargylic phenyl group, was prepared via propargylation of ethyl phenylacetate, followed by reduction (eq 5). Alkynols **5K** and **5L** were prepared from terminal alkynes via the synthetic route in eq 6. Alkynol **5M** was prepared from monoprotected diol **8A** (eq 7). Alkynol **5N** was prepared from phenylacetylene and propylene oxide (eq 8).

Solvent Effects on the Stereoselectivity of Heterocyclic Ring Construction. A variety of alkyne−carbene complexes (**1**) have been synthesized and converted to the corresponding heterocycle-fused cyclopentenone derivatives (**3**) upon thermolysis in aqueous solvent; the results are depicted in Table 1. The effect of solvent on the stereoselectivity of cyclopentadienone reduction was examined for two of the table entries (L and N). Thermolysis of alkyne−carbene complex **1N** was tested in both toluene and dioxane at various temperatures. The observed stereoselectivity for formation of the cis heterocyclic ring was considerably higher when the reaction was conducted in 1% aqueous toluene (97:3) than in 1% aqueous dioxane (65:35). A similar study was conducted on complex **1L**, and nearly identical stereoselectivity was observed in toluene (70:30) and dioxane (75:25).[1] Only the results from thermolyses in toluene are presented in the table. A noteworthy advantage of the toluene solvent system is that terminal alkynes are more suitable substrates for the intramolecular cyclopentannulation reaction, even in cases where a six-membered heterocyclic ring is formed as a result of intramolecular carbene−alkyne coupling. As reported in our earlier work and in related studies by others,[1,8] these complexes cyclize inefficiently unless the heterocyclic ring under construction contains at least seven atoms.

Substrate Dependence on the Stereoselectivity of Heterocyclic Ring Construction. Thermolysis of a variety of alkyne-containing complexes is reported in Table 1. Five-, six-, and seven-membered heterocyclic ring-forming reactions were tested. Reduction of the cyclopentadienone intermediate afforded heterocyclic rings with a high degree of stereoselectivity for three substrate classes: entries A−C, which feature a propargylic methyl group and a three-carbon tether; entry N, which features a homopropargylic stereocenter and a two-carbon tether; and entry O, which features a propargylic stereocenter and a four-carbon tether. Alkyne−carbene complexes featuring propargylic stereocenters afforded trans heterocycles as the major product (entries A−E, M, O), whereas alkyne−carbene complexes featuring homopropargyl stereocenters (entries F−J, N) afforded cis heterocycles. In the two cases featuring a more distant stereocenter (entries K and L), predominantly the cis heterocycle was obtained. In all cases involving nonsilylated internal alkynes (entries B−C, L−M), the trans carbocycle was the major product. Carbocyclic ring stereoselectivity appears to be unrelated to heterocyclic ring stereoselectivity, because both terminal and internal alkynes usually afforded nearly identical levels of stereoselectivity in construction of the heterocyclic ring (compare entries B and C with A). Comparison of silylated alkynes, which ultimately afforded desilylated cyclopentenones, and nonsilylated

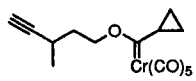
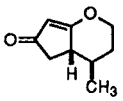
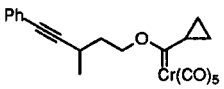
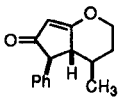
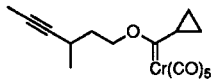
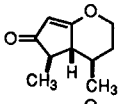
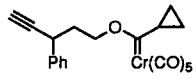
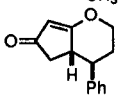
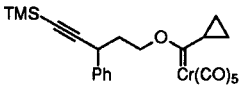
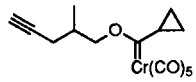
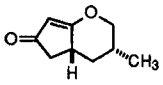
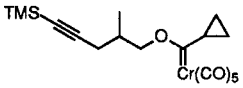
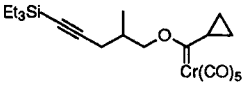
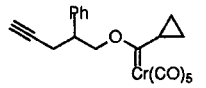
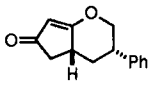
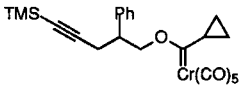
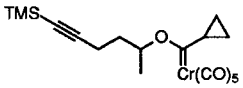
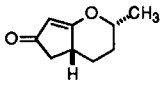
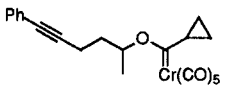
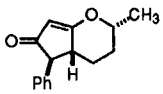
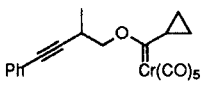
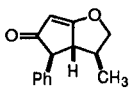
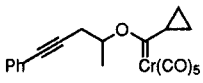
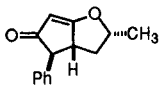
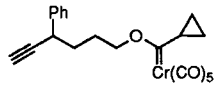
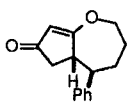
(5) Hommes, H.; Verkruijsse, H. D.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 113−114.

(6) This surprisingly expensive compound was readily prepared by isomerization of 1-phenyl-1-propyne. Mulvaney, J. E.; Folk, T. L.; Newton, D. J. *J. Org. Chem.* **1967**, *32*, 1674−1675.

(7) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5245−5253.

(8) (a) Wulff, W. D.; McCallum, J. S.; Kunng, F.-A. *J. Am. Chem. Soc.* **1988**, *110*, 7419−7434. (b) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Speiss, E. J.; Wulff, W. D.; Zask, A. *Tetrahedron* **1985**, *41*, 5803−5812.

Table 1. Dependence of Structural Variables on the Stereoselectivity of Heterocyclic Ring Construction

Entry	Carbene Complex		Yield 3[a]	Major Product[b]		Isomer Ratio[c]	Heterocycle Stereoselectivity
A[d]		(1A)	62%		(3A-*trans*)	94:6	94:6
B[d]		(1B)	72%		(3B-*trans-trans*)	84:7:9:0	91:9
C[d]		(1C)	70%		(3C-*trans-trans*)	90:5:5:0	95:5
D		(1D)	62%		(3D-*trans*)	50:50	50:50
E[e]		(1E)	65% (30%)	3D-*trans*		75:25 (100:0)	75:25 (100:0)
F[f]		(1F)	67% (81%)		(3F-*cis*)	50:50 (69:31)	50:50 (69:31)
G		(1G)	66%	3F-*cis*		67:33	67:33
H		(1H)	65%	3F-*cis*		67:33	67:33
I		(1I)	56%		(3I-*cis*)	50:50	50:50
J		(1J)	65%	3I-*cis*		67:33	67:33
K		(1K)	66%		(3K-*cis*)	72:28	72:28
L		(1L)	68%		(3L-*cis-trans*)	60:10:26:4	70:30
M		(1M)	60%		(3M-*trans-trans*)	38:25:33:4	63:37
N		(1N)	74%		(3N-*cis-trans*)	63:34:3:0	97:3
O[e]		(1O)	68% (30%)		(3O-*trans*)	86:14 (100:0)	86:14 (100:0)

[a] Combined yield of all stereoisomers.
[b] The first cis-trans designation refers to relative stereochemistry of the heterocyclic ring substituents. The second one refers to the carbocylic ring substituents.
[c] In cases where more than two diastereomers are possible, the first number refers percentage of the major stereoisomer, the second number refers to the other stereoisomer which has the same heterocyclic ring configuration as the major isomer, and the third number refers the stereoisomer which differs from the major isomer in the configuration of the heterocyclic ring but not the carbocyclic ring.
[d] Presented in reference 3.
[e] The numbers in parentheses refer to an experiment conducted in an anhydrous toluene.
[f] The numbers in parentheses refer to an experiment where tris(*o*-tolyl)phosphine was added to the reaction mixture.

alkynes is not consistent with this observation (see below). Alkyne−carbene complexes featuring a propargylic phenyl group (entries D−E) afforded cyclopentapyran derivatives with a lower degree of stereoselectivity than the analogous complexes featuring a propargylic methyl group (entries A−C).

Optimization of Stereoselectivity for Entries F−J. Some attempts to further optimize the stereoselectivity in the least selective system, entries F−J, were undertaken. A variety of additives that might also serve as ligands or cyclopentadienone reductants were added to the reaction mixture. Reducing additives included iron pentacarbonyl, chromium hexacarbonyl, molybdenum hexacarbonyl, and stannous chloride. Only iron pentacarbonyl produced a stereoselectivity enhancement; however, the yield of cyclopentenones was severely reduced. The only noticeable stereoselectivity enhancement occurred when tris(*o*-tolyl)phosphine was present during the reaction; the stereoselectivity increased from 1:1 to 2:1. In the cases involving homopropargylic stereocenters and three-carbon tethers (entries F−J), silylated alkynes afforded heterocyclic rings in greater stereoselectivity than terminal alkynes. A similar effect was noted for entries D and E, which feature a propargylic phenyl group.

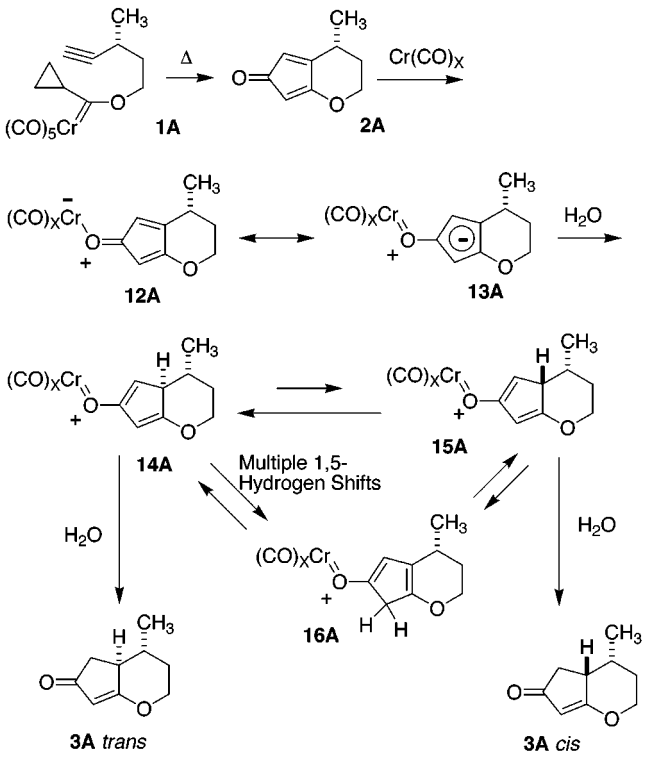
Dependence of Stereoselectivity on Water Concentration. The amount of water added to the system had a dramatic effect on the stereoselectivity of heterocyclic ring formation for entries E, F, and O. In the absence of any proton source,[9] the reaction was completely stereoselective, forming only the trans heterocycle; however, as expected the yield was very low (30%). When only enough water to balance the reaction equation was used (2 equiv), the stereoselectivity was lower and the yield was only marginally improved (36%).

Discussion

Rationalization of the Observed Stereochemistry. As noted in previous papers,[1,2b] the trans stereochemistry is anticipated for the carbocyclic ring, and this seems to be observed in all cases. With the exception of entries K and L, the heterocyclic ring in which the two substituents were either diequatorial or pseudodiequatorial was the major reaction product.

On the basis of previous studies,[2b,3] the mechanistic events in Scheme 4 best account for the observed stereoselectivity. Complexation of chromium at the cyclopentadienone oxygen[10] affords complex **12**. Resonance structure **13**, which features a cyclopentadienyl anion, would afford the corresponding cyclopentadiene (e.g., **14**−**16**)[11] upon monoprotonation. A rapid series of 1,5-hydrogen shifts[12] would afford a net equilibrium between diastereomers **14** and **15**,[13,14] which would afford the observed products **3A**-*trans* and **3A**-*cis* after addition of a second proton. Thus, the more stable stereoisomer (**14** vs **16**) is the major product of the reaction. For a more detailed discussion of this theory, see ref 3.

Scheme 4



The major product of entries K and L is the cis heterocycle,[15] which would not be the more stable isomer on the basis of simple axial vs equatorial arguments. Because there is substantial resonance interaction in the vinylogous ester system, there is substantial double bond character in the sp^2-carbon−oxygen bond of the heterocyclic ring. In a simple system featuring similar resonance interaction, δ-valerolactone, the boat conformation was determined to be slightly more stable than the chairlike form,[16] and substituted derivatives can adopt either form.[17] If the boat conformation is more stable, the trans isomer of compounds featuring the 1,4-stereochemical relationship would be destabilized because one of the substituents would be forced to occupy an axial position at the prow of the boat.

In many cases, silicon-substituted alkynes afforded different stereoisomeric ratios than terminal alkynes. A possible reason for this effect is that, under the reaction conditions, the initially produced α-silyl ketone can

(9) In the absence of an external proton source, the unreacted carbene complex might function as the proton source. (a) H/D deuterium exchange was observed upon thermolysis of a related cyclopropylcarbene−chromium complex in DMF/D_2O. Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 6854−6856. (b) For a more detailed account of carbene complex acidity and exchange reactions, see Bernasconi, C. F. *Chem. Soc. Rev.* **1997**, *26*, 299−308.

(10) Both oxygen- and η^4−diene complexes have been proposed in the reaction of cyclopentadienones with group VI metal carbonyls. These results are more consistent with a simple reduction−protonation sequence, which employs an oxygen-bound complex. (a) Brown, D. A.; Hargaden, J. P.; McMullin, C. M.; Gogan, N.; Sloan, H. *J. Chem. Soc.* **1963**, 4914−4918. (b) Adams, H.; Bailey, N. A.; Hempstead, P. D.; Morris, M. J.; Riley, S.; Beddoes, R. L.; Cook, E. S. *J. Chem. Soc., Dalton Trans.* **1993**, 91−100.

(11) In theory, any of the cyclopentadiene regioisomers could be obtained kinetically upon protonation; however, the reaction temperature is substantially greater than the temperature required for 1,5-hydrogen shifts in cyclopentadienes and thus rapid equilibration of all cyclopentadiene isomers is anticipated.

(12) For a recent example of a 1,5-hydrogen shift of a cyclopentadienol anion in a protic medium, see: Clark, W. N.; Tickner-Eldridge, A. M.; Huang, G. K.; Pridgen, L. N.; Olsen, M. A.; Mills, R. J.; Lantos, I.; Baine, N. H. *J. Am. Chem. Soc.* **1998**, *120*, 4550−4551.

(13) Compounds **14** and **15** would appear to be the major isomers at equilibrium since 3-alkoxy-2-cyclopenten-1-one derivatives (vinylogous esters) are formed almost exclusively and not 4-alkoxy-2-cyclopenten-1-ones or 3-alkoxy-3-cyclopenten-1-ones. Previous studies[2b] have shown that 4-alkoxy-2-cyclopenten-1-ones do not rearrange to vinylogous esters under the conditions for the cyclopentannulation reaction.

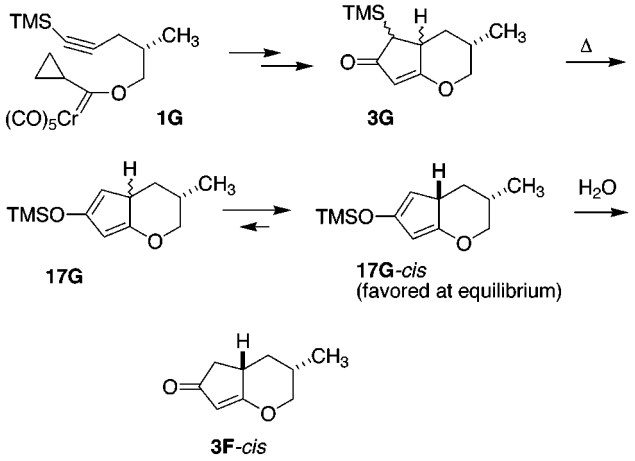
(14) The scrambling of hydrogen atoms was confirmed through deuterium labeling studies; see ref 2b.

(15) The stereochemistry depicted for the major isomer of **3L** is the cis heterocycle−trans carbocyle; the original stereochemical assignment in ref 1 is in error.

(16) Allinger, N. L.; Chang, S. H. M. *Tetrahedron* **1977**, *33*, 1561−1567.

(17) Axiotis, S.; Dreux, J.; Perrin, M.; Royer, H. *Tetrahedron* **1982**, *38*, 499−504.

Scheme 5



undergo thermodynamic equilibration during the desilylation process, which could proceed through either an enolate or a silyl enol ether (e.g., **17G**, Scheme 5)[18] that can further equilibrate through 1,5-hydrogen shifts. Thus, the reactions of nonsilylated alkynes might reflect the thermodynamic preferences of the chromoxycyclopentadiene intermediates **14**−**16**, whereas the silylated alkynes reflect the thermodynamic preferences of the siloxycyclopentadiene intermediates (e.g., **17G**). Alternatively, if the second proton is added prior to complete equilibration of the cyclopentadiene intermediate, the silylated systems have a second chance to equilibrate through the mechanism depicted in Scheme 5.

A correlation between stereoselectivity and amount of water additive was also noted. Five-membered ring-containing products are produced in low yield from the coupling of cyclopropylcarbene−chromium complexes and alkynes in the absence of water.[2b] However, superior relative asymmetric induction was observed under these conditions for substrates containing propargylic phenyl groups (entries D, E, and O). A possible origin of this effect is enhanced equilibration of the cyclopentadiene intermediates (e.g., **14** and **15**). In the absence of an added proton source, the starting carbene complex could serve as the proton source. Because there are now insufficient protons to balance the reaction equation, there is greater opportunity for the reaction intermediates **14** and **15** to equilibrate prior to addition of the second proton. Thermal decomposition of the anionic carbene complex[19] could then account for the low yield of cycloadducts.

Assignment of Stereochemistry. In all of the cases involving nonterminal alkynes, the carbocyclic ring stereochemistry was assigned on the basis of the coupling constant between the protons at the 4- and 5-positions (cyclopentenone numbering) of the cyclopentenone rings. The couplings between cis protons are usually larger (>7 Hz) than couplings between trans protons (<5 Hz). Assignment of heterocyclic ring stereochemistry for compounds featuring a propargylic stereocenter and a three-carbon tether (entries A−E) have previously been discussed.[3]

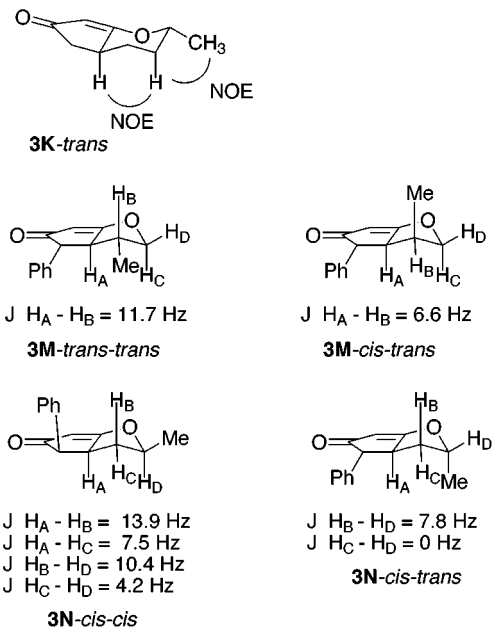


Figure 1.

The stereochemistry of compound **3I**-*cis* was assigned through X-ray analysis; the X-ray structure also showed that **3I**-*cis* exists in the chair conformation in the solid state. Stereochemical assignment of the major isomer for a related compound, **3F**-*cis*, was based on observed similarities in the proton NMR spectra of compounds **3F**-*cis* and **3I**-*cis*. Most notably, both compounds feature a long-range coupling (1.3−1.4 Hz) for the equatorial proton next to oxygen.

The stereochemistry of **3K**-*trans* (the minor isomer) was assigned on the basis of a NOESY experiment (Figure 1); the axial proton β to oxygen (δ 1.65) exhibits a cross-peak with both the bridgehead hydrogen (δ 2.68) and the methyl group (δ 1.40), which implies that the methyl group and the bridgehead hydrogen are cis (i.e., the trans heterocycle). Thus, the other isomer, **3K**-*cis*, was assigned as cis. Assignment of the stereochemistry for the products of entry L was based upon chemical shift similarities to the stereoisomers of **3K**, in which the proton next to oxygen is less shielded in the cis isomer (δ 4.46 in **3K**-*cis* and δ 4.12 in **3K**-*trans*). This same proton in the products from entry L is less shielded in the cis heterocycles (δ 4.40 in **3L**-*cis*−*trans* and d 4.45 in **3L**-*cis*-*cis*) than in the trans heterocycles (δ 4.10 in both **3L**-*trans*-*trans* and **3L**-*trans*-*cis*). For compounds featuring three stereocenters, the first cis-trans designation refers to the stereochemistry in the heterocyclic ring, and the second designation refers to the stereochemistry in the carbocyclic ring.

An additional noteworthy observation concerning six-membered ring heterocycles deserves comment. If both of the six-membered ring substituents can be diequatorial, the coupling constants of the heterocyclic ring protons suggest a chair conformation, whereas the observed couplings are inconsistent with a chair conformation if one of the substituents would be axial in the chair conformation. Thus, in the chair conformation, each proton of the heterocyclic ring is either axial (featuring one large geminal coupling, a similar coupling constant to the axial protons on the adjacent carbon, and a small coupling to the equatorial protons on the adjacent carbon)

(18) (a) Brook, A. G.; MacRae, D. M.; Limburg, W. W. *J. Am. Chem. Soc.* **1967**, *89*, 5493−5495. (b) Larson, G. L.; Berrios, R.; Prieto, J. A. *Tetrahedron Lett.* **1989**, *30*, 283−286.

(19) See: Bernasconi, C. F.; Leyes, A. E.; Ragains, M. L.; Shi, Y.; Wang, H.; Wulff, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 8632−8639, and references therein.

or equatorial (featuring one large geminal coupling and small couplings to all the protons on the adjacent carbons).

The heterocyclic ring stereochemistry for the products of entries L and M was assigned on the basis of their ^{1}H NMR spectra coupled with observed and calculated couplings in a related system, γ-butyrolactone.[20] This compound was chosen as a model because the sp^2-carbon−oxygen bond of **3M** and **3N** is anticipated to have substantial double bond character due to resonance interaction with the carbonyl compound, as is featured in γ-butyrolactone. The observed coupling constant between the bridgehead hydrogen and the proton next to the methyl group in the trans heterocycles (**3M**-*trans-trans* and **3M**-*trans-cis*) is 12.1 and 11.7 Hz. The observed coupling in the corresponding cis heterocycle is 6.6 Hz. The analogous calculated couplings in 2,3-dimethyl-γ-butyrolactone are 10.46 Hz for the trans isomer and 7.44 Hz for the cis isomer. The observed couplings between the bridgehead protons and the adjacent protons of the heterocyclic ring of **3N**-*cis-cis* are 13.9 and 7.5 Hz, which are closer to the values predicted for the cis isomer (12.8 and 8.5 Hz in cis 2,4-dimethyl-γ-butyrolactone and 9.0 and 8.0 Hz in the trans isomer). In compound **3N**-*trans-trans*, coupling of the proton next to oxygen and the adjacent protons is 7.8 and 0 Hz, which is very close to the calculated values of 8.8 and 1.6 Hz in trans 2,4-dimethylbutyolactone.

The stereochemistry of the major isomer in **3O** was assigned as trans on the basis of trends established in the five- and six-membered ring heterocycles. The benzylic proton is coupled to protons on adjacent carbons with coupling constants of 11.2, 11.2, and 3.2 Hz, which is consistent with an axial or (pseudoaxial) proton coupling to two other axial protons and an equatorial proton.[21] The same proton in the minor isomer occurs at δ 3.29, and is coupled to protons on adjacent carbons with coupling constants totaling 3.7 Hz, which is consistent with an equatorial (or pseudoequatorial) proton coupling to three other axial or equatorial protons.

Conclusion

The diastereoselectivity of the intramolecular coupling of alkynes and cyclopropylcarbene−chromium complexes has been evaluated for a diverse array of alkyne−carbene complexes featuring a chiral carbon in the tether. Regardless of ring size, the major product was trans if the stereocenters of the heterocyclic ring were in a 1,2-relationship and cis if the stereocenters were in a 1,3- or 1,4-relationship. Excellent diastereoselectivity was observed as a result of the cyclopentadienone reduction in many but not all cases. The extent of diastereoselectivity was very dependent on the position of the chiral center and the ring size of the heterocyclic ring produced. The low-yielding cycloaddition performed in anhydrous solvent proceeded with a very high degree of stereoselectivity in the systems examined and may hold the key to future development of a high-yielding stereoselective synthesis of cyclopentenones fused to oxygen heterocycles.

Experimental Section

For general experimental procedures, see ref 2b. The experimental procedure for entry C has been presented in a previous full paper.[3]

General Procedure I: Synthesis of Alkyne-Containing Carbene Complexes. To a solution of acylate salt **4**[22] (0.40 g, 1.20 mmol) in dichloromethane (20 mL) at 0 °C under nitrogen was added acetyl chloride (0.08 mL, 1.20 mmol) via syringe, followed by the immediate addition of alkynol (1.20 mmol). The reaction mixture was stirred at 0 °C for about 1 h, warmed to 25 °C, and stirred for 20 min. The solvent was removed on a rotary evaporator. Flash chromatography of the residue after evaporation, with hexane as the eluent, gave the pure carbene complex after solvent removal.

Preparation of Carbene Complex 1A. To a solution of 3-methyl-1-(*tert*-butyldimethylsilyloxy)-4-pentyne (350 mg, 1.81 mmol) in dichloromethane (20 mL) at room temperature was added boron trifluoride etherate (741 mg, 5.21 mmol). The reaction was stirred at room temperature for 2 h. The reaction solution was poured into water (20 mL) and extracted with ethyl ether (3 × 20 mL). The organic layers were combined and dried over anhydrous magnesium sulfate. The solvent was partially removed by distillation until about 20 mL of the solution remained (because of volatility of the product), and then General Procedure I was followed using this solution, acylate salt **4** (643 mg, 1.81 mmol), and acetyl chloride (0. 13 mL, 1.81 mmol) in dichloromethane (20 mL). After chromatographic purification, a yellow oil (245 mg, 40%) identified as carbene complex **1A** was obtained. ^{1}H NMR ($CDC1_3$): d 5.03 (t, 2 H, J = 6.1 Hz), 3.45 (m, 1 H), 2.62 (m, 1 H), 2. 1 0 (d, 1 H, J = 2.6 Hz), 2.02 (m, 2 H), 1.33 (m, 2 H), 1.26 (d, 3 H, J = 7.0 Hz), 1.23 (m, 2 H). ^{13}C NMR ($CDC1_3$): δ 352.0, 223.6, 216.8, 86.5, 78.4, 70.0, 41.4, 36.0, 22.9, 21.0, 17.8. IR ($CC1_4$): 3303 (m) 2061 (vs), 1952 (vs) cm^{-1}. MS (CI): *m/e* 343 (M + 1, 8), 342 (M, 29), 52 (100). HRMS: calcd for $C_{15}H_{14}CrO_6$ 342.0196, found 342.0174.

Preparation of Carbene Complex 1B. General Procedure I was followed using a solution of 3-methyl-5-phenyl-4-pentynl-ol (311 mg, 1.79 mmol) in dichloromethane (10 mL), acylate salt **4** (634 mg, 1.79 mmol), and acetyl chloride (0.13 mL, 1.7 mmol) in dichloromethane (20 mL). After chromatographic purification, a yellow oil (516 mg, 69%) identified as carbene complex **1B** was obtained. ^{1}H NMR ($CDC1_3$): δ 7.24 (m, 5 H), 5.02 (dd, 2 H, J = 11.8, 6.2 Hz), 3.40 (m, 1 H), 2.78 (m, 1 H), 2.05 (m, 2 H), 1.47 (m, 2 H), 1.30 (d, 3 H, J = 6.9 Hz), 1.14 (m, 2 H). ^{13}C NMR ($CDC1_3$): δ 351.9, 223.5, 216.8, 131.6, 128.2, 127.8, 123.3, 91.8, 82.2, 41.4, 36.2, 23.8, 21.2, 17.8. IR ($CC1_4$): 2054 (s), 1936 (vs) cm^{-1}. MS (CI): *m/e* 419 (M + 1, 1), 418 (M, 2), 226 (100). HRMS: calcd for $C_{21}H_{18}CrO_6$ 418.0509, found 418.0549.

Preparation of Carbene Complex 1D. General Procedure I was followed using a solution of 3-phenyl-4-pentyn-1-ol (240 mg, 1.50 mmol) in dichloromethane (10 mL), acylate salt **4** (506 mg, 1.50 mmol), and acetyl chloride (0.106 mL, 1.50 mmol) in dichloromethane (20 mL). After chromatographic purification, a yellow oil (383 mg, 63%) identified as carbene complex **1D** was obtained. ^{1}H NMR ($CDCl_3$): δ 7.4 (m, 5 H), 5.02 (m, 2 H), 3.89 (t, 1 H, J = 7.5 Hz), 3.50 (m, 1 H), 2.29 (m, 2 H), 1.1−1.5 (m, 4 H), −0.21 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 224.1, 217.3, 140.8, 129.5, 129.0, 106.0, 89.7, 79.3, 41.9, 39.0, 36.1, 19.2, 0.1.

(20) (a) Experimental studies: Hussain, S. A. M. T.; Ollis, W. D.; Smith, C.; Stoddart, J. F. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1480−1492. (b) Theoretical studies: Jaime, C.; Ortuño, R. M.; Font, J. *J. Org. Chem.* **1986**, *51*, 3946−3951.

(21) (a) Conformational studies of cycloheptane derivatives suggest that cycloheptane exists largely in a chairlike conformation. Elliel, E. L.; Wilen, S. H. In *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; pp 762−765. (b) The chair conformation is more pronounced in cycloheptene, which might be a better model due to the double bond character in the sp^2 C−O bond. Ermolaeva, L. I.; Mastryukov, V. S.; Allinger, N. L. Almenningen, A. *J. Mol. Struct.* **1989**, *196*, 151-156. c. Menard, D.; St.-Jacques, M. *Tetrahedron* **1983**, *39*, 1041−1060.

(22) For a procedure for synthesis of this compound, see: Herndon, J. W.; Tumer, S. U.; McMullen, L. A.; Matasi, J. J.; Schnatter, W. F. K. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1994; Vol. III, pp 51−95.

IR (neat): 2061, 1982, 1929 cm^{-1}. An acceptable mass spectrum or elemental analysis could not be obtained for this molecule.[23]

Preparation of Carbene Complex 1E. . General Procedure I was followed using a solution of 3-phenyl-5-trimethylsilyl-4-pentyn-1-ol (230 mg, 0.99 mmol) in dichloromethane (10 mL), acylate salt **4** (338 mg, 1.00 mmol), and acetyl chloride (0.071 mL, 1.00 mmol) in dichloromethane (20 mL). After chromatographic purification, a yellow oil (293 mg, 62%) identified as carbene complex **1E** was obtained. ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 5.04 (m, 2 H), 3.90 (t, 1 H, J = 7.1 Hz), 3.50 (m, 1 H), 2.32 (m, 2 H), 1.45−1.15 (m, 4 H), 0.21 (s, 9 H). ^{13}C NMR: δ 223.6, 216.6, 140.1, 128.8, 128.4, 127.2, 105.5, 89.0, 78.0, 59.9, 41.4, 37.5, 35.7, 17.8, −0.1. IR (neat): 2178 (w), 2061 (m), 1982 (m), 1929 (vs) cm^{-1}. An acceptable mass spectrum or elemental analysis could not be obtained for this molecule.[23]

Preparation of Carbene Complex IF. To a solution of 4-methyl-5-(*tert*-butyldimethylsilyloxy)-1-pentyne (683 mg, 3.53 mmol) in dichloromethane (20 mL) at room temperature was added boron trifluoride etherate (741 mg, 5.21 mmol). The reaction was stirred at room temperature for 2 h. The reaction solution was poured into water (20 mL) and extracted with ethyl ether (3 × 20 mL). The organic layers were combined and dried over anhydrous magnesium sulfate. The solvent was partially removed by distillation until about 20 mL of the solution remained (because of volatility of the product), and then General Procedure I was followed using acylate salt **4** (1.18 g, 3.53 mmol) and acetyl chloride (0.21 mL, 3.53 mmol) in dichloromethane (20 mL). After chromatographic purification, a yellow oil (785 mg, 65%) identified as carbene complex **1F** was obtained. ^{1}H NMR ($CDCl_3$): δ 4.82 (d, 2 H, J = 5.6 Hz), 3.48 (m, 1 H), 2.29 (m, 3 H), 2.02 (t, 1 H, J = 3.9 Hz), 1.38 (m, 2 H), 1.19 (m, 2 H), 1.13 (d, 3 H, J = 6.8). ^{13}C NMR ($CDC1_3$): δ 352.2, 223.5, 216.7, 83.2, 80.7, 70.6, 41.5, 32.2, 22.5, 17.6, 16.2. IR ($CC1_4$): 2060 (s), 1936 (vs) cm^{-1}. MS (CI): *m/e* 342 (M, 6), 150 (100). HRMS: calcd for $C_{15}H_{14}CrO_6$ 342.0196, found 342.0211.

Preparation of Carbene Complex 1G. General Procedure I was followed using a solution of 2-methyl-5-trimethylsilyl-4-pentyn-1-ol (296 mg, 1.74 mmol) in dichloromethane (10 mL), acylate salt **4** (528 mg, 1.74 mmol), and acetyl chloride (0.12 mL, 1.74 mmol) in dichloromethane (20 mL). After chromatographic purification, a yellow oil (533 mg, 74%) identified as carbene complex **1G** was obtained. ^{1}H NMR ($CDC1_3$): δ 4.81 (dd, 2 H, J = 5.7, 2.0 Hz), 3.47 (m, 1 H), 2.30 (m, 3 H), 1.37 (m, 2 H), 1.19 (m, 2 H), 1.11 (d, 3 H, J = 6.6 Hz), 0.12 (s, 9 H). ^{13}C NMR ($CDC1_3$): δ 352.0, 223.5, 216.8, 103.2, 83.4, 41.6, 33.0, 24.0, 17.7, 16.4, −0.03. IR (CCl_4): 2061 (s), 1928 (vs) cm^{-1}. MS (CI): *m/e* 414 (M, 3), 272 (100). HRMS: calcd for $C_{18}H_{22}CrO_6Si$ 414.0591, found 414.0604.

Preparation of Carbene Complex 1H. General Procedure I was followed using a solution of 2-phenyl-4-pentyn-1-ol (310 mg, 1.94 mmol) in dichloromethane (20 mL), acylate salt **4** (649 mg, 1.94 mmol), and acetyl chloride (0.14 mL, 1.94 mmol) in dichloromethane (20 mL). After chromatographic purification, a yellow oil (557 mg, 71%) identified as carbene complex **1H** was obtained. ^{1}H NMR ($CDCl_3$): δ 7.27 (m, 5 H), 5.20 (dd, 1 H, J = 10.4, 6.0 Hz), 5.06 (dd, 1 H, J = 10.2, 7.6 Hz), 3.35 (m, 2 H), 2.62 (dd, 2 H, J = 7.1, 2.6 Hz), 2.01 (t, 1 H, J = 2.6 Hz), 1.07 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 352.5, 223.4, 216.6, 139.6, 128.8, 127.6, 127.3, 81.9, 80.5, 71.2, 44.0, 41.7, 22.3, 17.9. IR (CCl_4): 2060 (s), 1935 (vs) cm^{-1}. MS (CI): *m/e* 404 (M, 1), 212 (79), 104 (83). HRMS: calcd for $C_{20}H_{16}CrO_6$ 404.0352, found 404.0385.

Preparation of Carbene Complex 1I. General Procedure I was followed using a solution of 2-phenyl-5-trimethylsilyl-4-pentyn-l-ol (425 mg, 1.84 mmol) in dichloromethane (20 mL), acylate salt **4** (614 mg, 1.84 mmol), and acetyl chloride (0.13 mL, 1.84 mmol) in dichloromethane (20 mL). After chromatographic purification, a yellow oil (596 mg, 68%) identified as carbene complex **1I** was obtained. ^{1}H NMR ($CDCl_3$): δ 7.26 (m, 5 H), 5.26 (dd, 1 H, J = 10.4, 5.9 Hz), 5.08 (dd, 1 H,10.3, 8.1 Hz), 3.35 (m, 2 H), 2.65 (d, 2 H, J = 6.2 Hz), 1.04 (m, 4 H), 0.11 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 352.3, 223.4, 216.6, 139.9, 128.7, 127.4, 102.8, 87.9, 81.8, 44.0, 41.6, 23.9, 17.9, 17.8, −0.24. IR (CCl_4): 2060 (s), 1923 (vs) cm^{-1}. MS (CI): *m/e* 477 (M + 1, 2), 476 (M, 4), 104 (100). HRMS: calcd for $C_{23}H_{24}CrO_6Si$ 476.0747, found 476.0744.

Preparation of Carbene Complex 1J. General Procedure I was followed using a solution of 2-methyl-5-triethylsilyl-4-pentyn-1-ol (285 mg, 1.34 mmol) in dichloromethane (20 mL), acylate salt **4** (450 mg, 1.34 mmol), and acetyl chloride (0.10 mL, 1.34 mmol) in dichloromethane (20 mL). After chromatographic purification, a yellow oil (428 mg, 70%) identified as carbene complex **1J** was obtained. ^{1}H NMR ($CDCl_3$): δ 4.82 (d, 2 H, J = 5.8 Hz), 3.46 (m, 1 H), 2.37 (d, 2 H, J = 5.6 Hz), 2.27 (m, 1 H), 1.34 (m, 2 H), 1.21 (m, 2 H), 1.15 (d, 3 H, J = 6.6 Hz), 0.96 (t, 9 H, J = 7.6 Hz), 0.54 (q, 6 H, J = 7.8). ^{13}C NMR ($CDCl_3$): δ 351.9, 223.5, 216.7, 104.2, 84.4, 83.2, 41.5, 33.0, 24.0, 17.6, 16.2, 7.3, 4.4. IR (CCl_4): 2060 (s), 1941 (vs), 1981 (s) cm^{-1}. MS (CI): *m/e* 456 (M, 3), 235 (100). HRMS: calcd for $C_{2l}H_{28}CrO_6Si$ 456.1016, found 456.1021.

Preparation of Carbene Complex 1K. General Procedure I was followed using a solution of 6-trimethylsilyl-5-hexyn-2-ol (321 mg, 1.89 mmol) in dichloromethane (20 mL), acylate salt **4** (1.27 g, 3.78 mmol), and acetyl chloride (0.27 mL, 3.78 mmol) in dichloromethane (20 mL). After chromatographic purification, a yellow oil (297 mg, 38%) identified as carbene complex **1K** was obtained. ^{1}H NMR ($CDCl_3$): δ 5.66 (m, 1 H), 3.38 (m, 1 H), 2.33 (m, 2 H), 2.00 (m, 2 H), 1.42 (d, 3 H, J = 6.2 Hz), 1.29 (m, 4 H), 0.13 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 347.8, 223.8, 216.6, 104.8, 87.5, 85.7, 41.3, 34.6, 19.9, 17.5, 17.3, 15.8, −0.7. IR (CCl_4): 2060 (s), 1920 (vs) cm^{-1}. MS (CI): *m/e* 414 (M, 4), 272 (100). HRMS: calcd for $C_{18}H_{22}CrOSi$ 414.0591, found 414.0562.

Preparation of Carbene Complex 1L. General Procedure I was followed using 6-phenyl-5-hexyn-2-ol (0.196 g, 1.10 mmol), acylate salt **4** (0.767 g, 2.30 mmol), and acetyl chloride (0.160 mL, 2.20 mmol) in dichloromethane (40 mL). After purification by flash chromatography on silica gel using pure hexane as the eluent, a yellow oil (0.267 g, 56%) identified as carbene complex **1L** was obtained. ^{1}H NMR ($CDCl_3$): δ 7.38−7.24 (m, 5 H), 5.68 (quintet, 1 H, J = 6.2 Hz), 3.40 (m, 1 H), 2.50 (m, 2 H), 3.40 (m, 1 H), 2.50 (m, 2 H), 2.08 (m, 2 H), 1.44 (d, 3 H, J = 6.2 Hz), 1.39−1.08 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 347.9, 223.5, 216.7, 131.5, 128.2, 127.5, 123.5, 88.0, 87.6, 81.5, 41.4, 35.0, 20.2, 17.7, 17.4, 15.4. IR (CH_2Cl_2): 2061 (s), 1979 (sh), 1938 (vs) cm^{-1}. MS (EI): 418 (M, 2), 226 (100). HRMS: calcd for $C_{21}H_{18}CrO_6$ 418.0508, found 418.0522.

Preparation of Carbene Complex 1M. General Procedure I was followed using a solution of 2-methyl-4-phenyl-3-butyn-1-ol (298 mg, 1.86 mmol) in dichloromethane (10 mL), acylate salt **4** (620 mg, 1.86 mmol), and acetyl chloride (146 mg, 1.86 mmol) in dichloromethane (20 mL). After chromatographic purification, a yellow oil (511 mg, 68%) identified as carbene complex **1M** was obtained. ^{1}H NMR ($CDCl_3$): δ 7.28 (m, 5 H), 4.85 (m, 2 H), 3.42 (m, 1 H), 3.15 (m, 1 H), 1.47 (m, 2 H), 1.34 (d, 3 H, J = 7.0 Hz), 1.15 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 352.2, 223.4, 216.7, 131.6, 128.3, 128.1, 123.0, 89.2, 82.6, 41.8, 27.6, 18.1, 17.6. IR (CCl_4): 2062 (s), 1936 (vs) cm^{-1}. MS (CI): *m/e* 404 (M, 8), 212 (99), 129 (100). HRMS: calcd for $C_{20}H_{16}CrO_6$ 404.0352, found 404.0376.

Preparation of Carbene Complex 1N. General Procedure I was followed using 5-phenyl-4-pentyn-2-ol (0.197 g, 1.25 mmol), acylate salt **4** (0.836 g, 2.50 mmol), and acetyl chloride (0.180 mL, 2.50 mmol) in dichloromethane (40 mL). After purification by flash chromatography on silica gel using pure hexane as the eluent, a yellow oil identified as carbene complex **IN** (0.177 g, 36%) was obtained. ^{1}H NMR ($CDCl_3$): δ 7.32−7.15 (m, 5 H), 5.22 (qt, 1 H, J = 6.2, 5.4 Hz), 3.27 (m, 1 H), 2.30 (d, 2 H, J = 5.4 Hz), 1.52 (d, 3 H, J = 6.2 Hz), 1.48−1.30 (m, 2 H), 1.20−1.05 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 348.6, 223.5,

(23) The stability of this complex was not noticeably different from that of the other carbene complexes. We attribute the failure to acquire these data to decomposition during shipment. Successful acquisition of mass spectral data for alkyne−carbene complexes was possible at the University of Maryland as a result of the presence of in-house high-resolution mass spectrometry facilities.

216.7, 131.6, 128.3, 128.1, 123.1, 85.4, 83.7, 41.6, 27.3, 19.9, 18.2, 17.5. IR ($CDCl_3$): 2161 (vs), 1982 (sh), 1926 (vs), cm^{-1}; MS (EI): 404 (M, 3), 212 (100), 141 (100). HRMS: calcd for $C_{20}H_{16}CrO_6$ 404.0354, found 404.0352.

Preparation of Carbene Complex 1O. General Procedure I was followed using a solution of 4-phenyl-5-hexyn-1-ol (250 mg, 1.02 mmol) in dichloromethane (20 mL), acylate salt **4** (355 mg, 1.05 mmol), and acetyl chloride (0.075 mL, 1.05 mmol) in dichloromethane (20 mL). After chromatographic purification, a yellow oil (262 mg, 72%) identified as carbene complex **1O** was obtained. ^{1}H NMR ($CDCl_3$): δ 7.4 (m, 5 H), 4.97 (t, 2 H, J = 5.9 Hz), 3.80 (m, 1 H), 3.51 (m, 1 H), 2.40 (d, 1 H, J = 2.4 Hz), 2.0 (m, 4 H), 1.1−1.5 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 224.1, 217.3, 141.0, 129.2, 127.7, 85.3, 80.5, 72.3, 41.9, 37.6, 34.9, 27.4, 18.2. IR (neat): 2060, 1982, 1941 cm^{-1}. An acceptable mass spectrum or elemental analysis could not be obtained for this molecule.[23]

General Procedure II: Intramolecular Reactions of Carbene Complexes with Alkynes. To a three-neck round-bottom flask equipped with a reflux condenser and rubber septum, under nitrogen, was added toluene (100 mL) and water (1 mL), and the solution was heated to reflux. To this refluxing solution was added a solution of carbene complex in toluene (30 mL) via syringe pump over a period of 4 h. After the addition was complete, the mixture was heated at reflux for an additional 20 h and then cooled to room temperature. The resulting green mixture was filtered through Celite, and the solvent was removed on a rotary evaporator. Final purification was achieved by a flash chromatography on silica gel using 4:1 hexane/ethyl acetate as eluent unless otherwise noted. In all cases, a separate experiment was performed in which the individual isomers of **3** were not separated (i.e., isolated as a single fraction); the yields and the ratios (obtained via relative integration of the alkene protons at δ 5.2−5.5) quoted in Table 1 were obtained from this experiment.

Thermolysis of Carbene Complex 1A. General Procedure II was followed using carbene complex **1A** (225 mg, 0.66 mmol); two fractions were isolated.

The compound in the first fraction (53.2 mg, 53%) was identified as compound **3A-***trans*. ^{1}H NMR ($CDCl_3$): δ 5.27 (d, 1 H, J = 1.6 Hz), 4.34 (m, 1 H), 4.10 (m, 1 H), 2.55 (dd, 1 H, J = 17.5, 6.7 Hz), 2.44 (m, 1 H), 2.06 (dd, 1 H, J = 17.5, 3.4 Hz), 1.98 (m, 1 H), 1.56 (m, 1 H), 1.03 (d, 3 H, J = 6.3). ^{13}C NMR ($CDCl_3$): δ 203.9, 190.9, 107.6, 68.7, 43.1, 40.2, 32.4, 31.5, 20.6. IR (CCl_4): 1699 (s), 1601 (s) cm^{-1}. MS (EI): *m/e* 152 (M, 24), 91 (100). HRMS: calcd for $C_9H_{12}0_2$ 152.0837, found 152.0842. The trans relative configuration of the substituents on the six-membered ring was assigned to this compound. This assignment was based on the large coupling constant (13.4 Hz) between the allylic hydrogen and the hydrogen next to methyl group, which is consistent with the coupling of two axial protons, as exists in the trans heterocyclic ring.

The compound in the second fraction (9.03 mg, 9%) was identified as compound **3A-***cis*. ^{1}H NMR ($CDCl_3$): δ 5.33 (d, 1 H, J = 1.4 Hz), 4.28 (t, 2 H, J = 6.4 Hz), 3.13 (dddd, 1 H, J = 7.0, 6.5, 3.7, 1.5 Hz), 2.42 (dd, 1 *H*, J = 18.0, 6.5 Hz), 2.28 (dd, 1 H, J = 18.0, 3.7 Hz), 2.24 (m, 1 H), 1.65 (m, 2 H), 0.93 (d, 3 H, J = 7.0). ^{13}C NMR ($CDCl_3$): δ 204.7, 190.3, 108.1, 66.2, 39.3, 37.1, 31.1, 25.7, 14.5.

Thermolysis of Carbene Complex 1B. General Procedure II was followed using carbene complex **1B** (355 mg, 0.85 mmol); three fractions were isolated.

The first fraction was identified as a mixture of compound **3B**-*trans-trans* and compound **3B**-*cis-trans*. The further purification was accomplished by preparative thin-layer chromatography (2% methanol in dichloromethane) to give 9.7 mg (5%) of compound **3B**-*cis-trans*. ^{1}H NMR ($CDCl_3$): δ 7.20 (m, 5 H), 5.44 (d, 1 H, J = 1.6 Hz), 4.31 (dd, 1 H, J = 6.8, 5.6 Hz), 3.50 (d, 1 H, J = 4.0 Hz), 3.10 (ddd, 1 H, J = 7.8, 4.0, 1.6 Hz), 2.39−2.21 (m, 2 H), 1.10 (d, 3 H, J = 7.2). The relative configuration on the cyclopentenone ring was assigned as trans on the basis of the small coupling constant (4.0 Hz) between the hydrogen at the benzylic and allylic positions. The relative configuration of substituents on the six-membered heterocycle was established as cis on the basis of the smaller (relative to **3B**-*trans-trans*, see below) coupling constant (7.8 Hz) between the allylic proton and the proton next to the methyl group. The compound in the other fraction (110 mg, 57%) was identified as **3B**-*trans-trans*. ^{1}H NMR ($CDCl_3$): δ 7.21 (m, 5 H), 5.36 (d, 1 H, J = 1.5 Hz), 4.36 (ddd, 1 H, J = 4.8, 6.1, 11.3 Hz), 4.13 (ddd, 1 H J = 11.3, 8.1, 4.5 Hz), 3.28 (d, 1 H, J = 3.2 Hz), 2.56 (ddd, 1 H, J = 11.0, 3.2, 1.5 Hz), 2.00 (dddd, J = 13.0, 10.6, 6.1, 4.5 Hz), 2.05−1.6 (m, 2 H), 1.54 (dddd, 1 H, J = 13.0, 13.0, 8.1, 4.8 Hz), 0.93 (d, 3 H, J = 6.5). ^{13}C NMR ($CDCl_3$): δ 203.5, 189.8, 139.5, 128.7, 128.1, 126.9, 106.3, 68.7, 58.7, 52.1, 31.7, 20.6. IR (CCl_4): 1679 (s), 1598 (s) cm^{-1}. MS (EI): *m/e* 228 (M, 100). HRMS: calcd for $C_{15}H_{16}O_2$ 228.1150, found 228.1144. The relative configuration on the cyclopentenone ring was assigned as trans on the basis of the small coupling constant (3.2 Hz) between the hydrogen at the benzylic and allylic positions. The relative configuration of substituents on the six-membered heterocycle was established as trans on the basis of the large coupling constant (11.0 Hz) between the allylic proton and the proton next to the methyl group (see the text), which is consistent with the coupling of two axial protons.

The second fraction was identified as a mixture of compound **3B**-*trans-cis* and compound **3B**-*cis-cis* (trace). The further purification was accomplished by preparative thin-layer chromatography (2% methanol in dichloromethane) to give 11.6 mg (6%) of compound **3B**-*trans-cis*. ^{1}H NMR ($CDCl_3$): δ 7.18 (m, 5 H), 5.50 (d, 1 H, J = 1.9 Hz), 4.38 (ddd, 1 H, J = 11.1, 4.4, 4.4 Hz), 4.07 (ddd, 1 H, J = 11.1, 11.1, 5.3 Hz), 3.78 (d, 1 H. J = 7.0 Hz), 2.74 (ddd, 1 H, J = 10.8, 7.0, 1.9 Hz), 1.80 (m, 1 H), 1.52 (m, 2 H), 0.65 (d, 3 H, J = 6.0). ^{13}C NMR ($CDCl_3$): δ 204.4, 190.6, 137.1, 129.7, 129.3, 128.5, 108.6, 69.1, 55.8, 48.5, 31.9, 26.6, 20.2. The relative configuration on the cyclopentenone ring was assigned as cis on the basis of the large coupling constant (7.0 Hz) between the hydrogen at the benzylic and allylic positions. The relative configuration of substituents on the six-membered heterocycle was established as trans on the basis of the large coupling constant (10.8 Hz) between the allylic proton and the proton next to the methyl group (see the text), which is consistent with the coupling of two axial protons.

Thermolysis of Carbene Complex 1D. General Procedure II was followed using carbene complex **1D** (290 mg, 0.655 mmol); two fractions were isolated.

The compound in the first fraction (44 mg, 31%) was identified as **3D**-*trans*. ^{1} H NMR ($CDCl_3$): δ 7.4−7.2 (m, 10 H), 5.44 (d, 1 H, J = 1.5 Hz), 4.60 (ddd, 1 H, J = 11.3, 5.6, 5.6 Hz), 4.30 (ddd, 1 H, J = 11.3, 8.2, 4.8 Hz), 3.11 (dddd, 1 H, J = 12.1, 6.6, 3.6, 1.5 Hz), 2.76 (ddd, 1 H, J = 12.1, 9.1, 6.2 Hz), 2.40 (dd, 1 H, J = 18.0, 6.6 Hz), 2.20 (m, 2 H), 2.13 (dd, 1 H, J = 18.0, 3.6 Hz). ^{13}C NMR ($CDCl_3$): δ 203.6, 189.8, 142.6, 128.9, 127.3, 126.6, 108.3, 69.0, 43.7, 42.1, 40.0, 31.8. IR (neat): 1686, 1596 cm^{-1}. Combustion Analysis: calcd for $C_{14}H_{14}O_2$ C 78.48%, H 6.59%; found C 78.29%, H 6.59%. The compound was assigned as the trans isomer on the basis of the large coupling constant between the bridgehead and benzylic hydrogens (12.1 Hz), which is consistent with an axial−axial coupling as exists in the trans isomer.

The compound in the second fraction (43 mg, 31%) was identified as **3D**-*cis*. ^{1}H NMR ($CDCl_3$): δ 7.4−7.0 (m, 10H), 5.40 (br s, 1 H), 4.42 (m, 2 H), 3.46 (m, 2 H), 2.49 (m, 1 H), 2.31 (dd, 1 H, J = 18.0, 7.1 Hz), 2.21 (m, 1 H), 1.84 (dd, 1 H, J = 18.0, 2.2 Hz). ^{13}C NMR ($CDCl_3$): δ 203.9, 190.2, 141.1, 128.7, 128.0, 127.1, 107.5, 65.8, 37.6, 37.3, 31.0. The compound was assigned as the cis isomer on the basis of similarity to the NMR spectra of compound **3A**-*cis*, most notably the protons on the same carbon as oxygen have the same chemical shift in **3D**-*cis* (δ 4.42 Hz); this was also observed for **3A**-*cis* and **3B**-*cis-trans*.

Thermolysis of Carbene Complex 1E. General Procedure II was followed using carbene complex **1E** (286 mg, 0.600 mmol); two fractions were isolated and identified as **3D**-*trans* (62 mg, 49%) and **3D**-*cis* (21 mg, 16%). The spectral data were identical to those previously listed for these compounds, which was also obtained via thermolysis of carbene complex **1D**.

Thermolysis of Carbene Complex 1F. General Procedure II was followed using carbene complex **1F** (226 mg, 0.66 mmol); two fractions were isolated.

The compound in the first fraction (34.4 mg, 34%) was identified as **3F**-*cis*. ^{1}H NMR ($CDCl_3$): δ 5.31 (t, 1 H, J = 1.4 Hz), 4.35 (ddd, 1 H, J = 11.1, 4.6, 1.4 Hz), 3.66 (dd, 1 H, J = 11.1, 8.4 Hz), 2.81 (m, 1 H), 2.60 (dd, 1 H, J = 17.6, 6.8 Hz), 2.22 (m, 2 H), 2.12 (dd, 1 H, J = 17.6, 3.7 Hz), 1.06 (ddd, 1 H, J = 12.5, 11.1, 11.1 Hz), 0.95 (d, 3 H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$): δ 204.3, 190.9, 107.9, 75.1, 41.4, 36.2, 34.5, 29.0, 18.0. IR (CCl_4): 1672 (s), 1600 (vs) cm^{-1}. MS (EI): *m/e* 152 (M, 100). HRMS: calcd for $C_9H_{12}O_2$ 152.0837, found 152.0850. The compound was assigned as cis on the basis of the long-range coupling observed for the proton at δ 4.35, which is also present in a structurally related compound, **3I**-*cis*, whose structure was confirmed by X-ray.

The compound in the second fraction (32.9 mg, 33%) was identified as the other isomer, **3F**-*trans*. ^{1}H NMR ($CDCl_3$): δ 5.29 (d, 1 H, J = 1.6 Hz), 4.17 (dd, 1 H, J = 11.1, 5.2 Hz), 3.89 (t, 1 H, J = 11.1 Hz), 3.05 (m, 1 H), 2.64 (dd, 1 H, J = 17.8, 6.8 Hz), 2.20 (m, 1 H), 2.05 (dd, 1 H, J = 17.8, 2.9 Hz), 1.65 (m, 2 H), 0.99 (d, 3 H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$): δ 204.7, 190.3, 108.1, 66.2, 39.3, 37.1, 31.1, 25.7, 14.5. IR (CCl_4): 1678 (s), 1600 (vs) cm^{-1}. MS (EI): *m/e* 153 (M + 1, 17), 152 (M, 100). HRMS: calcd for $C_9H_{12}O_2$ 152.0837, found 152.0847. This isomer was assigned as trans on the basis of spectral similarity to **3I**-*trans*, most notably the absence of the long-range coupling observed in **3F**-*cis* and **3I**-*cis*.

Thermolysis of Carbene Complex 1G. General Procedure II was followed using carbene complex **1G** (230 mg, 0.56 mmol). Purification by flash chromatography on silica gel using hexane/ethyl acetate (3:2) as the eluent provided two fractions. The compound in the first fraction (37.6 mg, 44%) was identified as **3F**-*cis*. The compound in the second fraction (18.1 mg, 22%) was identified as the other isomer, **3F**-*trans*. The ratio of **3F**-*cis* to **3F**-*trans* (67:33) was determined by integration of alkene protons at 5.3 ppm. The spectral data were identical to those previously listed for these compounds, which was also obtained via thermolysis of carbene complex **1F**.

Thermolysis of Carbene Complex 1H. General Procedure II was followed using carbene complex **1H** (230 mg, 0.56 mmol). Purification by flash chromatography on silica gel using hexane/ethyl acetate (3:2) as the eluent provided two fractions. The compound in the first fraction (37.6 mg, 44%) was identified as **3F**-*cis*. The compound in the second fraction (18. 1 mg, 22%) was identified as the other isomer, **3F**-*trans*. The spectral data were identical to those previously listed for these compounds, which was also obtained via thermolysis of carbene complex **1F**.

Thermolysis of Carbene Complex 1I. General Procedure II was followed using carbene complex **1I** (284 mg, 0.70 mmol). Purification by flash chromatography on silica gel using 2% methanol in dichloromethane as the eluent provided two fractions.

The compound in the first fraction (45.1 mg, 30%) was identified as **3I**-*cis*. ^{1}H NMR ($CDCl_3$): δ 7.45 (m, 5 H), 5.33 (d, 1 H, J = 1.5 Hz), 4.45 (ddd, 1 H, J = 11.2, 5.2, 1.3 Hz), 3.95 (dd, 1 H, J = 11.2, 9.4 Hz), 3.24 (m, 1 H), 2.95 (m, 1 H), 2.61 (dd, 1 H, J = 17.6, 6.6 Hz), 2.35 (ddd, 1 H J = 12.7, 5.2, 5.2 Hz), 2.14 (dd, 1 H, J = 17.6, 3.9 Hz), 1.65 (ddd, 1 H, J = 12.7, 12.7, 11.0 Hz). ^{13}C NMR ($CDCl_3$): δ 204.1, 190.2, 140.4, 128.9, 127.5, 108.8, 74.5, 41.4, 40.9, 36.8, 33.4. IR (CCl_4): 1698 (s), 1613 (s) cm^{-1}. MS (EI): *m/e* 214 (M, 100). HRMS: calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.1011. This compound is a solid with a melting point of 122.5−123.5 °C. Recrystalization was performed in a two-solvent system of dichloromethane and methanol. The compound was assigned as having the cis relative configuration of the substituents on the six-membered heterocyclic ring on the basis of an X-ray structure determination.

The compound in the second fraction (39.1 mg, 26%) was identified as the other isomer, **3I**-*trans*. ^{1}H NMR ($CDCl_3$): δ 7.25 (m, 5 H), 5.3 0 (d, 1 H, J = 1. 5), 4.25 (t, 1 H, J = 11.1 Hz), 4.23 (dd, 1 H, J = 11.1, 6.2 Hz), 3.24 (m, 2 H), 2.63 (dd, 1 H, J = 17.9, 6.8 Hz), 2.32 (ddd, 1 H, J = 14.0, 8.5, 6.5 Hz), 2.05 (dd, 1 H, J = 17.9, 2.8 Hz), 1.86 (ddd, 1 H, J = 14.0, 11.5, 9.8 Hz). ^{13}C NMR ($CDCl_3$): δ 204.0, 191.0, 140.8, 129.1, 127.5, 127.3, 106.2, 71.5, 42.2, 39.2, 33.2, 33.0. IR (CCl_4): 1698 (s), 1600 (vs) cm^{-1}. MS (EI): *m/e* 214 (M, 83), 116 (100). HRMS: calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0981.

Thermolysis of Carbene Complex 1J. General Procedure II was followed using carbene complex **1J** (273 mg, 0.57 mmol). Purification by flash chromatography on silica gel using hexane/ethyl acetate (3:2) as the eluent provided two fractions. The compound in the first fraction (49.3 mg, 40%) was identified as the **3I**-*cis*. The compound in the second fraction (24.3 mg, 20%) was identified as the other isomer, **3I**-*trans*. The spectral data were identical to those previously listed for these compounds, which was also obtained via thermolysis of carbene complex **1I**.

Thermolysis of Carbene Complex IK. General Procedure II was followed using carbene complex **IK** (188 mg, 0.45 mmol). Purification by flash chromatography on silica gel using 2% methanol in dichloromethane as the eluent provided two fractions.

The compound in the first fraction (27.4 mg, 40%) was identified as **3K**-*cis*. ^{1}H NMR ($CDCl_3$): δ 5.25 (d, 1 H, J = 1.4 Hz), 4.47 (m, 1 H), 3.01 (ddddd, 1 H, J = 11.5, 8.4, 6.8, 2.8, 1.4 Hz), 2.61 (dd, 1 H, J = 17.8, 6.8 Hz), 2.22 (dddd, 1 H, J = 13.3, 10.6, 8.4, 6.2 Hz), 2.03 (dd, 1 H, J = 17.8, 2.8 Hz), 1.94 (dddd, 1 H, J = 14.5, 10.6, 4.5, 3.3 Hz), 1.69 (dddd, 1 H J = 14.5, 10.6, 10.6, 6.2 Hz), 1.42 (dddd, 1 H, J = 13.3, 11.5, 10.6, 4.5 Hz), 1.35 (d, 3 H, J = 6.2 Hz); Irradiate δ 1.35: δ 4.47 (dd, J = 10.6, 3.3 Hz). ^{13}C NMR ($CDCl_3$): δ 204.3, 192.4, 105.3, 74.0, 42.0, 33.4, 28.9, 24.0, 20.7. IR (CCl_4): 1667 (s), 1593 (vs) cm^{-1}. MS (EI): *m/e* 152 (M, 100). HRMS: calcd for $C_9H_{12}O_2$ 152.0837, found 152.0831. This isomer is believed to have a cis relationship between the methyl group and the carbocyclic ring as a result of the coupling constants within the heterocyclic ring; the coupling constants for these hydrogens (δ 4.47, 3.01, 2.22, 1.94, 1.69, and 1.42) are less suggestive of a chair conformation than those of the other isomer (see discussion for other isomer). Because this isomer would have an axial substituent in a perfect chair, this is the isomer which is most likely to deviate from the chair conformation.

The compound in the second fraction (18.2 mg, 26%) was identified as other isomer, **3K**-*trans*. ^{1}H NMR ($CDCl_3$): δ 5.30 (d, 1 H, J = 1.6 Hz), 4.12 (m, 1 H), 2.68 (ddddd, 1 H, J = 12.8, 6.7, 5.0, 4.1, 1.6 Hz), 2.56 (dd, 1 H, J = 17.4, 6.7 Hz), 2.11 (dd, 1 H, J = 17.4, 4.1 Hz), 2.04 (dddd, 1 H, J = 12.8, 5.0, 3.2, 3.2 Hz), 1.93 (dddd, 1 H, J = 13.1, 3.2, 3.2, 3.2 Hz), 1.65 (dddd, 1 H, J = 13.1, 12.8, 10.4, 3.2 Hz), 1.48 (dddd, 1 H, J = 12.8, 12.8, 12.8, 3.2 Hz), 1.40 (d, 3 H, J = 6.4 Hz). Irradiate at δ 4.12: δ 1.93 (ddd, J = 13.1, 3.2, 3.2 Hz), 1.65 (dddd, 1 H, J = 12.8, 12.8, 10.4, 3.2 Hz), 1.40 (s). Irradiate at δ 1.40: δ 4.12 (dd, J = 10.4, 3.2 Hz). ^{13}C NMR ($CDCl_3$): δ 204.7, 191.3, 109.2, 78.8, 41.2, 37.0, 32.1, 27.1, 21.8. IR (CCl_4): 1661 (s), 1590 (vs) cm^{-1}. MS (EI): *m/e* 152 (M, 100). HRMS: calcd for $C_9H_{12}O_2$ 152.0837, found 152.0830. The compound was assigned as having the trans relative configuration of the substituents on the six-membered heterocyclic ring. The ^{1}H NMR data are suggestive of a chair conformation in which the methyl group is equatorial. Every proton in a CH_2 group of the ring appears as a quartet of doublets if axial (one geminal, two axial−axial, and one equatorial axial couplings) or a doublet of quartets (one geminal and three gauche-type couplings). This assignment was further supported by NOESY experiment, which showed cross-peaks between the proton at δ 1.65 (axial proton β to oxygen) and both δ 2.68 (bridgehead H) and δ 1.40 (the methyl group), implying that the bridgehead hydrogen and the methyl group are on the same face of the ring.

Thermolysis of Carbene Complex 1L. General Procedure II was followed using carbene complex **1L** (300 mg, 0.700 mmol); two fractions were isolated after chromatographic separation.

The compound in the first fraction was an inseparable mixture of three compounds (64 mg, 40%). The major component (58% of the mixture) was assigned as **3L**-*cis*-*trans*. ^{1}H NMR ($CDCl_3$): δ 7.30−7.00 (m, 5 H), 5.34 (d, 1 H, J = 1.4 Hz), 4.40 (m, 1 H), 3.20 (d, 1 H, J = 3.2 Hz), 2.99 (dddd, 1 H,

J = 8.5, 8.5, 3.2, 1.4 Hz), 2.27 (dddd, 1 H, J = 13.9, 10.4, 8.5, 6.0 Hz), 1.88 (dddd, 1 H, J = 14.3, 10.4, 8.2, 4.3 Hz), 1.60−1.70 (m, 2 H), 1.34 (d, 3 H, J = 6.2). Irradiate at δ 1.34: δ 4.40 (dd, J = 10.0, 3.6 Hz). The carbocyclic ring stereochemistry was assigned as trans on the basis of the smaller coupling constant (3.2 Hz) between the benzylic and allylic protons. The heterocyclic ring stereochemistry was assigned as cis on the basis of chemical shift similarity to **3K**-*cis*; the proton next to oxygen features a chemical shift of δ 4.40, which is closer to the value for the same proton in **3K**-*cis* (δ 4.47) than that for the same proton in the **3K**-*trans* (δ 4.12). The second most abundant component (34% of the mixture) was assigned as **3L**-*trans-trans*. ^{1}H NMR ($CDCl_3$): δ 7.30−7.00 (m, 5 H), 5.38 (d, 1 H, J = 1.2 Hz), 4.10 (m, 1 H), 3.27 (d, 1 H, J = 4.7 Hz), 2.66 (m, 1 H), 2.09 (m, 1 H), 1.38 (d, 3 H, J = 6. 1) (the remaining protons cannot be reliably assigned because of overlap with peaks for the other isomers in this fraction). Irradiate at δ 1.38: δ 4. 10 (dd, J = 10.7, 3.2 Hz). The carbocyclic ring stereochemistry was assigned as trans on the basis of the small coupling constant (4.7 Hz) between the benzylic and allylic protons. The heterocyclic ring stereochemistry was assigned as trans on the basis of chemical shift similarity to **3K**-*trans*; the proton next to oxygen features a chemical shift of δ 4.10, which is closer to the value for the same proton in **3K**-*trans* (δ 4.12) than that for the same proton in the **3K**-*cis* (δ 4. 47). The minor component (8% of the mixture) was assigned as **3L**-*trans-cis*. ^{1}H NMR ($CDCl_3$): δ 7.30−7.00 (m, 5 H), 5.56 (d, 1 H, J = 1. 9), 4.10 (m, 1 H), 3.78 (d, 1 H, J = 7.3 Hz), 2.78 (m, 1 H) 2.06 (m, 1 H), 1.35 (d, 3 H, J = 6.1 Hz), 0.97 (dddd, 1 H, J = 13.7, 13.7, 13.7. 3.3) (the remaining protons cannot be reliably assigned because of overlap with peaks for the other isomers in this fraction). Irradiate at δ 1.35: δ 4.10 (dd, J = 10.7, 3.2 Hz). The carbocyclic ring stereochemistry was assigned as cis on the basis of the large coupling constant (7.3 Hz) between the benzylic and allylic protons. The heterocyclic ring stereochemistry was assigned as trans on the basis of chemical shift similarity to **3K**-*trans*; the proton next to oxygen features a chemical shift of δ 4.10, which is closer to the value for the same proton in **3K**-*trans* (δ 4.12) than that for the same proton in the **3K**-*cis* (δ 4. 47).

The compound in the second fraction was a identified as compound **1L**-*cis-cis* (34 mg, 21%). ^{1}H NMR ($CDCl_3$): δ 7.30−6.95 (m, 5 H), 5.47 (d, 1 H, J = 1.5 Hz), 4.45 (m, 1 H), 3.85 (d, 1 H, J = 7.3 Hz), 3.33 (dddd, 1 H, J = 11.9, 7.3, 7.3, 1.5 Hz), 1.83 (m, 1 H), 1. 35 (d, 3 H, J = 6.1 Hz), 1.65−0.85 (m, 3 H). Irradiate at δ 1.35: δ 4.45 (dd, J = 9.3, 3.7 Hz). ^{13}C NMR ($CDCl_3$): δ 205.1, 192.2, 137.5, 129.4, 128.5, 127.0, 106.4, 74.5, 55.3, 38.3, 29.0, 20.8, 19.5. IR ($CDCl_3$): 1679 (s), 1598 (vs) cm^{-1}. MS (EI): 228 (M, 20), 86 (100). HRMS: calcd for $C_{l5}H_{16}O_2$ 228.1158, found: 228.1150. The carbocyclic ring stereochemistry was assigned as cis on the basis of the large coupling constant (7.3 Hz) between the benzylic and allylic protons. The heterocyclic ring stereochemistry was assigned as cis on the basis of chemical shift similarity to **3K**-*cis*; the proton next to oxygen features a chemical shift of δ 4.45, which is closer to the value for the same proton in **3K**-*cis* (δ 4.47) than the same proton in the **3K**-*trans* (δ 4. 12).

Thermolysis of Carbene Complex 1M. General Procedure II was followed using carbene complex **1M** (235 mg, 0.58 mmol); three fractions were obtained.

The first fraction was identified as a mixture (8:1) of compound **3M**-*cis-trans* and compound **3M**-*cis-cis*. Further purification was accomplished by preparative thin-layer chromatography (hexane/ethyl acetate, 3:2) to give 22.3 mg (18%) of compound **3M**-*cis-trans*. ^{1}H NMR ($CDCl_3$): δ 7.23 (m, 5 H), 5.26 (d, 1 H, J = 1.7 Hz), 4.64 (dd, 1 *H*, J = 9.1, 4.5 Hz), 4.35 (d, 1 H, J = 9.1 Hz), 3.50 (d, 1 H, J = 5.2 Hz), 3.38 (ddd, 1 H, J = 6.6, 5.2, 1.7 Hz), 2.58 (m, 1 H), 1.02 (d, 3 H, J = 7.2 Hz). Irradiate at δ 3.50: δ 3.38 (dd, 1 H, J = 6.6, 1.7 Hz). ^{13}C NMR ($CDCl_3$): δ 206.4, 192.8, 138.2, 128.8, 128.4, 127.2, 99.5, 85.1, 55.1, 54.4, 32.4, 13. 1. The relative configuration on the cyclopentenone ring was assigned as trans on the basis of the small coupling constant (5.2 Hz) between the hydrogen at the benzylic and allylic positions. The relative configuration of substituents on the five-membered heterocycle was established as cis due to the smaller coupling (relative to **3M**-*trans-trans*, see below) of 6.6 Hz between the allylic hydrogen and the hydrogen on the same carbon as the methyl group.

The compound in the second fraction (32.3 mg, 26%) was identified as **3M**-*trans-trans*. ^{1}H NMR ($CDCl_3$): δ 7.32 (m, 5 H), 5.23 (d, 1 H, J = 1.0 Hz), 4.67 (dd, 1 H, J = 18.1, 8.8 Hz), 4.09 (dd, 1 H, J = 18.1, 9.1 Hz), 3.40 (d, 1 H, J = 4.9 Hz), 2.81 (ddd, 1 H, J = 11.7, 4.9, 1.0 Hz), 2.30 (m, 1 H), 1.03 (d, 3 H, J = 6.6 Hz); Irradiate δ 3.40: δ 2.81 (dd, 1 H, J = 11.7, 1.0 Hz). Irradiate δ 1.03: δ 2.30 (ddd, J = 11.7, 9.1, 8.8 Hz). ^{13}C NMR ($CDCl_3$): δ 205.6, 194.3, 138.0, 128.8, 128.3, 127.1, 99.5, 83.6, 59.2, 57.4, 38.8, 14.0. IR (CCl_4): 1699 (m), 1625 (s) cm^{-1}; MS (EI): *m/e* 214 (M, 100). HRMS: calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0976. The relative configuration of substituents on the cyclopentenone ring was assigned as trans due to the small coupling constant (4.9 Hz) between the hydrogen at the benzylic and allylic positions. The relative configuration of substituents on the five-membered heterocycle was established as trans due to the extremely large coupling constant between the allylic hydrogen and the hydrogen on the same carbon as the methyl group (11.7 Hz), which is consistent only with coupling of two pseudoaxial protons, as exists in the trans heterocyclic ring.

The compound in third fraction (19.9 mg, 16%) was identified as **3M**-*trans-cis*. ^{1}H NMR ($CDCl_3$): δ 7.13 (m, 5 H), 5.35 (d, 1 H, J = 1.9 Hz), 4.54 (dd, 1 H, J = 8.8, 7.4 Hz), 4.04 (dd, 1 H, J = 10.6, 8.8 Hz), 3.91(d, 1 H, J = 7.5 Hz), 3.00 (ddd, 1 H, J = 12.1, 7.5, 1.9 Hz), 1.75 (m, 1 H), 0.81 (d, 3 H, J = 6.4 Hz). Irradiate at δ 3.91: δ 3.00 (dd, 1 H, J = 12.1, 1.9 Hz). ^{13}C NMR ($CDCl_3$): δ 206.5, 196.6, 136.6, 128.6, 127.3, 101.1, 83.7, 55.5, 54.0, 33.6, 29.7, 13.8. IR (CCl_4): 1699 (m), 1623 (s) cm^{-1}. MS (EI): *m/e* 214 (M, 100). HRMS: calcd for $C_{l4}H_{14}O_2$ 214.0994, found 214.1000. The relative configuration on the cyclopentenone ring was assigned as cis on the basis of the large coupling constant (7.5 Hz) between the hydrogen at the benzylic and allylic positions. The relative configuration of substituents on the five-membered heterocycle was established as trans on the basis of the extremely large coupling constant between the allylic hydrogen and the hydrogen on the same carbon as the methyl group (12.1 Hz), which is consistent only with coupling of two pseudoaxial protons, as exists in the trans heterocyclic ring.

Thermolysis of Carbene Complex IN in Toluene. General Procedure II was followed using carbene complex **1N** (112 mg, 0.300 mmol); two fractions were isolated after chromatographic purification.

The compound in the first fraction was identified as **3N**-*cis-trans* (27 mg, 48%). ^{1}H NMR ($CDCl_3$): δ 7.38−7.10 (m, 5 H), 5.26 (d, 1 H, J = 1.1 Hz), 4.92 (m, 1 H), 3.45 (d, 1 H, J = 5. 1 Hz), 3.33 (m, 1 H), 2.46 (ddd, 1 H, J = 11.7, 8.1, 4.0 Hz), 1.52 (d, 3 H, J = 6.3 Hz) overlapping with 1.52 (m, 1 H). Irradiate at δ 1.52: δ 4.65 (d, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 205.6, 193.4, 138.0, 128.8, 127.2, 98.8, 88.5, 59.4, 52.3, 37.7, 20.2. IR (CH_2Cl_2): 1694 (s), 1623 (s) cm^{-1}. MS (EI): 214 (M, 100). HRMS: calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0989. The relative configuration of substituents on the cyclopentenone ring was assigned as trans on the basis of the small coupling constant (5.1 Hz) between the hydrogen at the benzylic and allylic positions. The relative configuration of the substituents on the heterocyclic ring was established as cis on the basis of similarity of the ^{1}H NMR spectrum to that of **3N**-*cis-cis*; most notably the chemical shift of the proton on the same carbon as oxygen (δ 4.92 in **3N**-*cis-trans*) more closely resembles the value for the same proton in **3N**-*cis-cis* (δ 4.94) than that of **3N**-*trans-trans* (δ 5.14).

The compound in the second fraction was identified as **3N**-*cis-cis* (15 mg, 26%). ^{1}H NMR ($CDCl_3$): δ 7.28−6.95 (m, 5 H), 5.35 (d, 1 H, J = 2.0 Hz), 4.94 (m, 1 H), 3.90 (d, 1 H, J = 7.5 Hz), 3.57 (dddd, 1 H, J = 12.8, 7.5, 7.5, 1.1 Hz), 1.89 (ddd, 1 H, J = 12.8, 7.5, 4.2 Hz), 1.36 (d, 3 H, J = 6.7 Hz), 1.00 (ddd, 1 H, J = 12.8, 12.7, 10.4 Hz). Irradiate at δ 1.36: δ 4.94 (dd, 1 H, J = 10.4, 4.2 Hz). The relative configuration on the cyclopentenone ring was assigned as cis on the basis of the large coupling constant (7.5 Hz) between the hydrogen at the

benzylic and allylic positions. The relative configuration of substituents in the heterocyclic ring was established as cis on the basis of the agreement of all of the coupling constants involving protons in the heteocyclic ring with predicted values (see text). Most notably a large pseudoaxial−pseudoaxial coupling exists for both the bridgehead proton at δ 3.57 (12.8 Hz) and the proton on the same carbon as oxygen at δ 4.94 (10.4 Hz).

Thermolysis of Carbene Complex 1N in Dioxane. General Procedure II was followed using carbene complex **1N** (112 mg, 0.300 mmol) and dioxane as the solvent. Final purification was achieved using flash chromatography on silica gel using 4:1 hexane/ethyl acetate as the eluent.

An additional compound over the previous experiment could never be isolated in pure form but exhibits the following spectral characteristics. ^{1}H NMR ($CDCl_3$): δ 7.40−7.10 (m, 5 H), 5.23 (d, 1 H, J = 1.5 Hz), 5.14 (dq, 1 H, J = 7.8, 6.7 Hz, appears as a quintet), 3.39 (d, 1 H, J = 5.5 Hz), 3.35 (m, 1 H), 2.05 (m, 1 H), 1.36 (d, 3 H, J = 6.7 Hz), 1.15 (m, 1 H). Irradiate at δ 1.36: δ 5.14 (d, J = 7.8 Hz). The carbocyclic ring was assigned as trans because the coupling of the vicinal protons on the carbocyclic ring was 5.5 Hz, which was identical to that for **3N**-*cis*-*trans* from the previous experiment. The heterocyclic ring was assigned as trans on the basis of the coupling pattern for the proton next to oxygen (δ 5.14). Decoupling the methyl group afforded a doublet with a coupling constant of 7.8 Hz. Because this proton is vicinal to two protons, the coupling to one of them is zero; only the trans heterocyclic ring isomer features a 90° dihedral angle involving the proton at δ 5.14 in the energy-minimized conformation.

Thermolysis of Carbene Complex 1O. General Procedure II was followed using carbene complex **1O** (240 mg, 0.560 mmol); two fractions were isolated after chromatographic purification.

The product in the first fraction (76 mg, 58%) was identified as **3O**-*trans*. ^{1}H NMR ($CDCl_3$): δ 7.4−7.1 (m, 5 H); 5.44 (s, 1 H), 4.48 (dddd, 1 H, J = 12.4, 5.2, 2.0, 2.0 Hz), 4.33 (dd, 1 H, J = 12.4, 10.4 Hz), 3.44 (ddd, 1 H, J = 11.2, 6.8, 2.4 Hz), 2.68 (ddd, 1 H, J = 11.2, 11.2, 3.2 Hz), 2.38 (dd, 1 H, J = 18.4, 6.8 Hz), 2.10 (m, 2 H), 1.96 (dd, 1 H, J = 18.4, 2.4 Hz), (1.85, m, 2 H). ^{13}C NMR ($CDCl_3$): δ 203.8, 192.7, 144.5, 128.4, 126.4, 109.3, 71.7, 50.2, 44.3, 42.4, 38.6, 29.5. IR (neat): 1675, 1588 cm^{-1} ; Combustion Analysis: calcd for $C_{15}H_{16}O_2$ C 78.91%, H 7.06%; found C 79.15%, H 6.85%. The heterocyclic ring was assigned as trans on the basis of the coupling for the benzylic proton (δ 2.68), which features two large pseudoaxial−pseudoaxial couplings (11.2 Hz).

The product in the second fraction (13 mg, 10%) was identified as **3O**-*cis*. ^{1}H NMR ($CDCl_3$): δ 7.2 (m, 5 H), 5.40 (d, 1 H, J = 1.0 Hz), 4.54 (br d, 1 H, J = 12.6 Hz), 4.34 (t, 1 H, J = 12.6 Hz), 3.50 (dddd, 1 H, J = 7.3, 3.7, 3.3, 1.0 Hz), 3.29 (q, 1 H, J = 3.7 Hz), 2.63 (dd, 1 H, J = 18.2, 7.2 Hz), 2.08 (dd, 1 H, J = 18.2, 3.3 Hz) overlapping with 1.75−2.22 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 203.7, 192.5, 138.9, 129.4, 128.3, 127.1, 111.4, 72.3, 47.0, 43.1, 40.8, 35.8, 26.1. The heterocyclic ring was assigned as cis on the basis of the coupling for the benzylic proton (δ 3.29), which features only small pseudoequatorial−pseudoequatorial or pseudoequatorial−pseudoaxial couplings (3.7 Hz).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all significant compounds in Table 1, X-ray parameters for compound **3I**-*cis*, and experimental procedures for the synthesis of alkynols used to synthesize carbene complexes **1A**−**O**. This material is available free of charge via the Internet at http://pubs.acs.org.

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