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Reaction of cyclopropylcarbene–metal complexes with nucleophiles, halogens and HX

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Abstract

The reaction of halogens, pseudohalogens, and HX with cyclopropyl(phenylthio)carbene-chromium complexes leads to the formation of 1,4-dihalo-1-thiophenyl-1-butene systems with a moderate-high degree of stereocontrol in the formation of the alkene. A mechanism involving electrophilic activation of the carbene complex followed by nucleophilic attack at the cyclopropane carbon has been proposed.

Keywords: Fischer carbene; Halogens; Nucleophilic addition; Cyclopropane ring opening

1. Introduction

Cyclopropane ring opening reactions have proven to be very valuable tool in synthetic organic chemistry [1]. Electron-deficient cyclopropanes are susceptible to ring opening by nucleophiles (i.e., the homo-Michael reaction, Scheme 1) [2] and by electrophilic activation followed by reaction with a nucleophile [3]. The existence of numerous routes for the preparation of stereochemically pure cyclopropanes, coupled with the often stereoselective processes by which they undergo ring opening, provides a potentially powerful method for asymmetric organic synthesis. Unfortunately, the nucleophilic ring opening of cyclopropylketones/esters is often restricted to systems that have two electron groups on one of the cyclopropane ring carbons. The presence of the second electron withdrawing group can present an unwanted complication in a synthetic scheme. As part of a goal to make the homo-Michael addition reactions more general, an investigation into the ring opening of cyclopropylcarbene-chromium complexes was initiated [4]. In theory, since carbene complexes stabilize adjacent carbanions better than two ester groups [5], the cyclopropylcarbene complex will be as activated as a cyclopropane 1,1-dioic ester derivative. Successful realization of this reaction can eliminate the steps often required to remove the extra electron-withdrawing group, and can provide additional reaction possibilities due to the wide variety of reactions unique to Fischer carbene complexes [6]. These studies will emphasize the ring opening reactions of cyclopropyl thiocarbene complexes. The greater acidity of this class of compounds compared to alkoxycarbene complexes [7] coupled with the greater synthetic utility of vinyl sulfides compared to enol ethers [8] offers potentially powerful improvements for the homo-Michael reaction.

This manuscript expands upon a previous communication [9]. Herein is a full experimental plus complete

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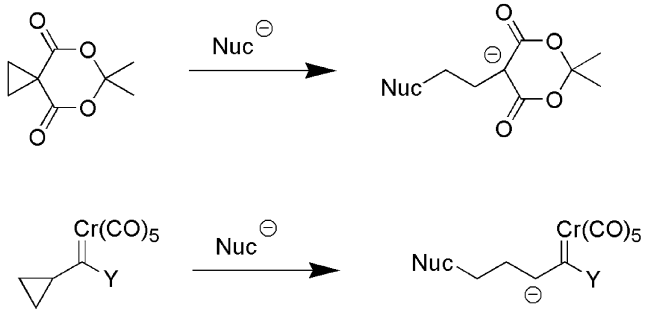


Scheme 1.

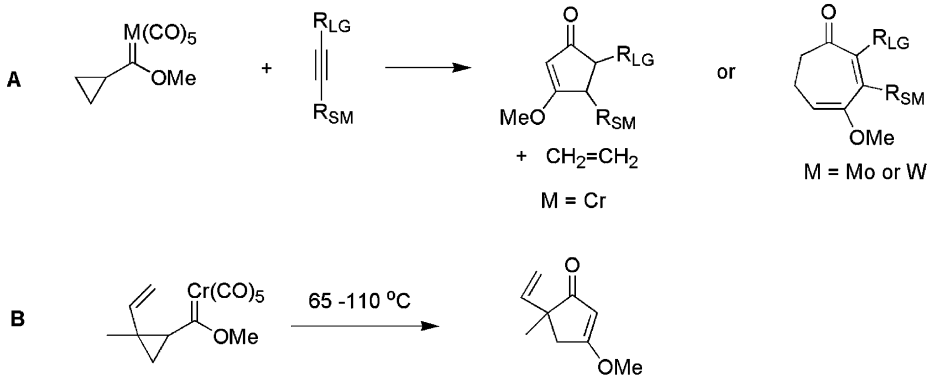
details (successes and failures) on our investigation of ring opening reactions of cyclopropylcarbene complexes, primarily using iodine to effect the ring opening process. Since the appearance of the preliminary communication, several investigators have reported iodine oxidation of Fischer carbene complexes. Examples include: (1) the iodine oxidation chemistry of diheteroatom-stabilized carbene complexes [10], (2) a procedure for the conversion of hydrazinocarbene complexes to the corresponding amides using iodine generated in situ from sodium perborate [11], and (3) the oxidation of carbene complex derived anions with iodine in methanol, which afforded CO inserted products [12].

2. Original investigational objectives and preliminary experiments

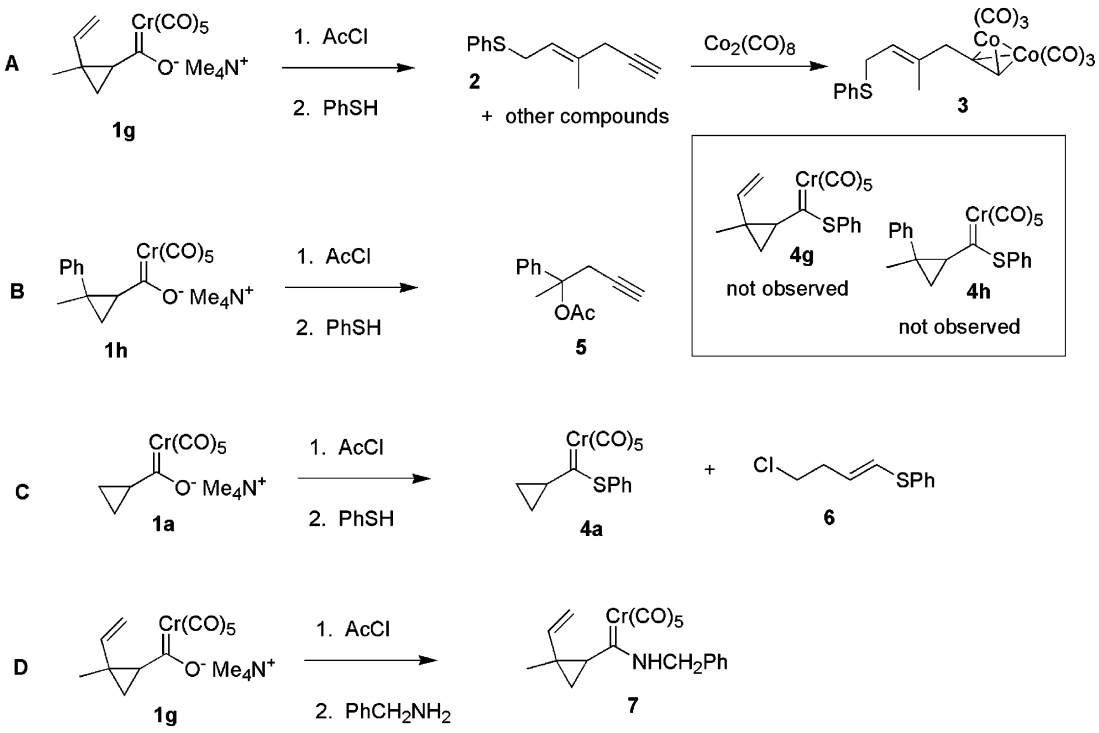
In all honesty our investigation of ring opening reactions of cyclopropyl thiocarbene complexes should be regarded as an accidental discovery. The original objective was to study two new processes developed in our laboratory: (1) coupling of cyclopropylcarbene-Group VI metal carbene complexes with alkynes to produce either cyclopentenones or cycloheptadienones (Scheme 2, Reaction A) and (2) thermal ring expansion of alkenylcyclopropylcarbene complexes (Scheme 2, Reaction B). An important variable to test is replacement of oxygen with either nitrogen or sulfur. Aminocarbene complexes are generally more stable than alkoxycarbene complexes and less likely to provide CO-insertion products [13]. Thiocarbene complexes are generally equal or slightly more reactive than alkoxycarbene complexes [14], and ultimately will afford alkenyl sulfides, a useful group for organic synthesis [8]. Since thiocarbene complexes offer a more favorable reactivity profile, synthesis of cyclopropyl(thiocarbene) complexes and subsequent examination of their reaction with alkynes were the initial research objectives.

Attempts to prepare thiophenylcarbene complex **4g** (Scheme 3) proved challenging. Use of the acetoxycarbene complex method [15] for the preparation of this thiocarbene complex was not successful. This reaction produced numerous products, however prominent peaks suggestive of a terminal alkyne could be observed in the crude proton NMR and IR spectra. The crude reaction mixture was treated with dicobalt octacarbonyl to retrieve the terminal alkyne, which was assigned the structure **3**. Attempted synthesis of phenylcyclopropylcarbene complex **4h** resulted in the alkyne ester **5**. The reaction was successful for the formation of simple cyclopropylcarbene complex **4a**, however extended reaction times led to the formation of minor amounts of chloro-vinyl sulfide derivative **6**. The mechanism depicted in Scheme 4 can account for the formation of compounds **2** and **5**, and was unique to complexes that feature carbocation stabilizing groups on the cyclopropane ring. It cannot be ascertained whether the X group of intermediates **8**–**10** are acetoxy or thiophenyl groups. In the absence of these groups simple carbene complex substitution was observed. The reaction was similarly successful for the formation of aminocarbene complex **7**. Use of the more nucleophilic amine species resulted in formation of the desired product, likely because capture of the intermediate acetoxycarbene complex **8g**,**h** was more efficient.

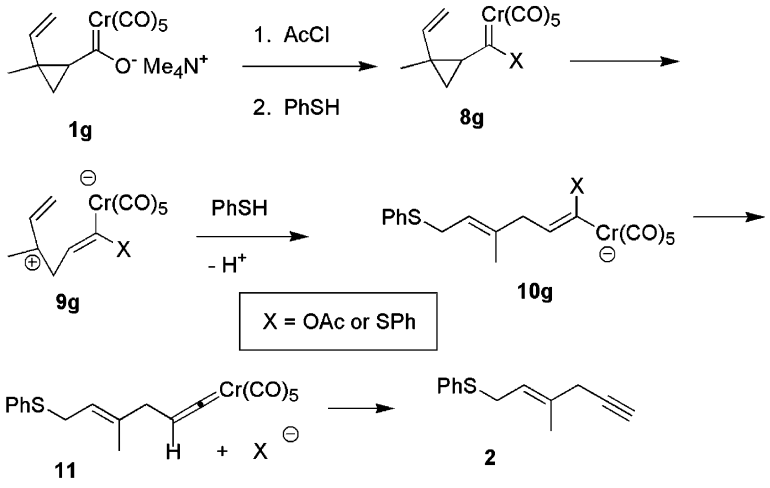
The results in Scheme 3 suggest that either cyclopropyl thiocarbene complexes or cyclopropyl acetoxycarbene



Scheme 2.



Scheme 3.

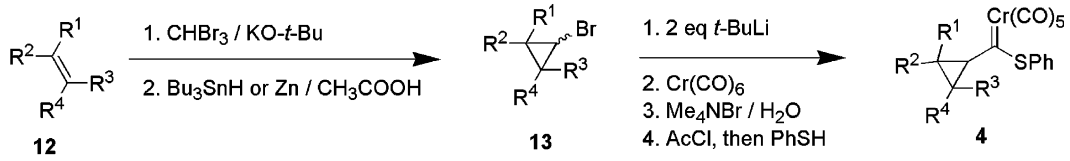


Scheme 4.

complexes are susceptible to ring opening. Based on the unexpected results in Scheme 3, a program to examine nucleophilic ring opening of cyclopropyl thiocarbene complexes was thus initiated.

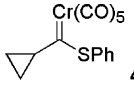
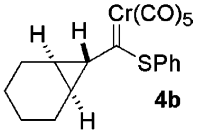
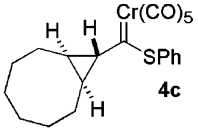
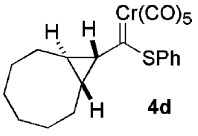
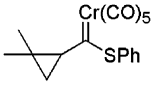
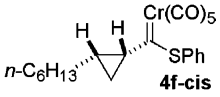
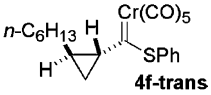
3. Synthesis of cyclopropyl thiocarbene complexes

A variety of cyclopropyl thiocarbene complexes were prepared according to the general synthetic route depicted in Scheme 5 [16]. Although superior yields have been reported for the tributyltin hydride reduction of dibromocyclopropanes [17], the separation processes were far simpler if zinc and acetic acid were used in the reduction step. In most cases, the eventual carbene complexes were obtained as a single isomer. The chemical shift of the carbene carbon was very stereochemistry dependent. As noted in Table 1, if there is an alkyl substituent *cis* to the carbene carbon, the chemical shift was typically greater than δ 370. In all of the cases lacking this feature, the chemical shift was less than δ 360.



Scheme 5.

Table 1
Chemical shifts of various carbene complexes

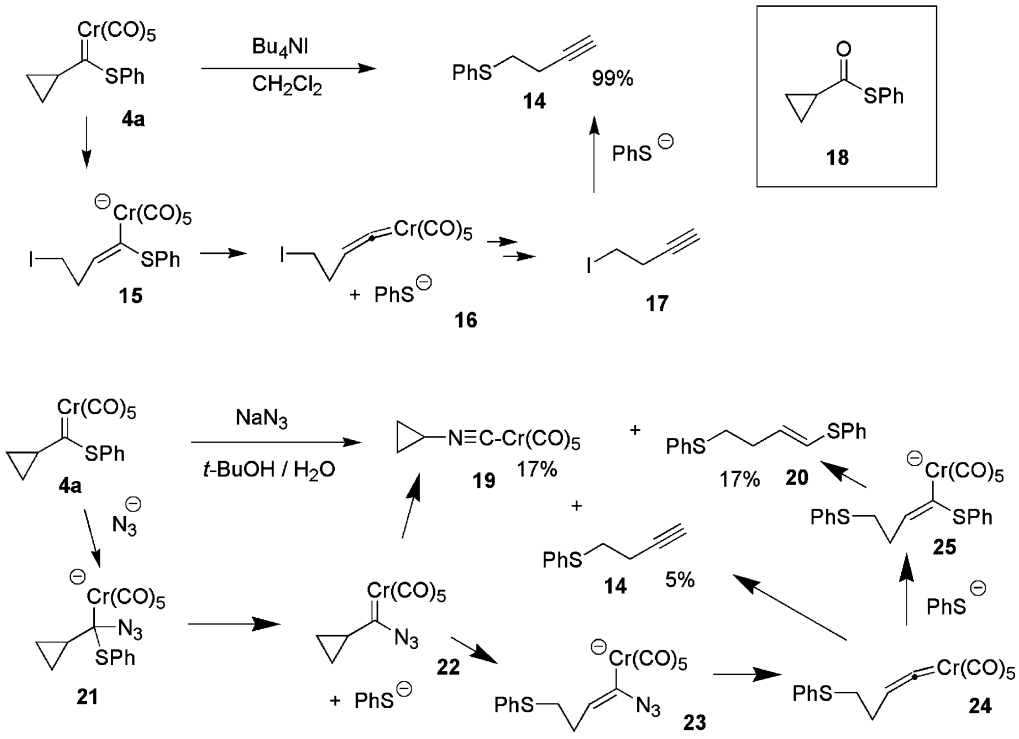
Carbene complex	δ carbene C
 **4a**	360.0
 **4b**	354.1
 **4c**	353.8
 **4d**	372.2
 **4e**	373.1
 **4f-cis**	372.6
 **4f-trans**	356.3

4. Reaction of cyclopropylcarbene complexes with nucleophiles and pseudohalogens

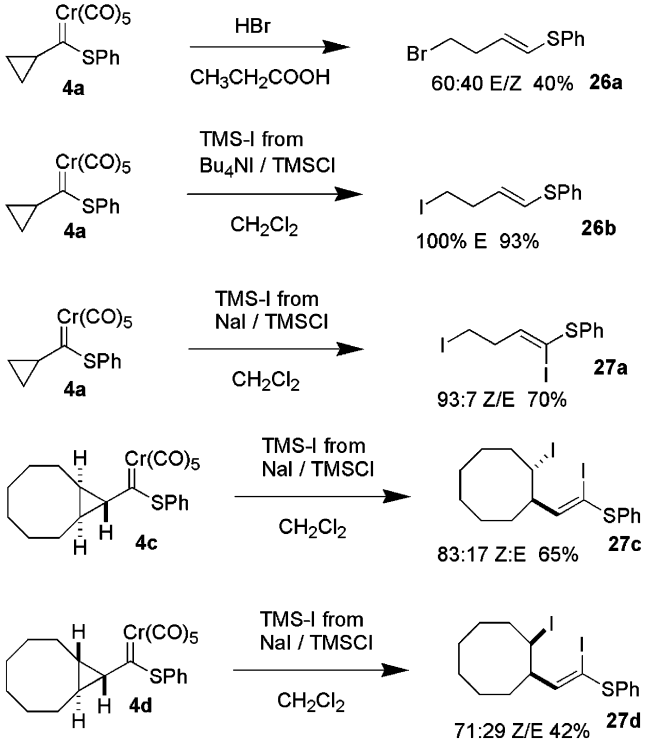
In the first phase of these studies, cyclopropyl thiocarbene complex **4a** was subjected to reaction with a variety of nucleophiles (Scheme 6). In two cases, cyclopropane ring opening products were observed. Coupling of cyclopropylcarbene complex **4a** with tetrabutylammonium iodide led to alkyne sulfide **14** in nearly quantitative yield. Reaction with sodium azide led to a mixture of the isocyanide complex **19**, bis(thiophenyl)derivative **20** and alkyne **14**. No other nucleophile afforded a cyclopropane ring opening product. Nucleophiles tested include bromide, cyanide, thiophenol anion, the potassium salt of ethyl acetoacetate, and trimethyl phosphite. All of these reactants induced decomposition of the carbene complex and afforded no identifiable products other than low yields of the carbene oxidation product **18**. Iodide ion was reactive only to the unsubstituted carbene complex **4a**. No reaction was observed with any of the cyclopropane-substituted analogs **4b**–**f**. No reaction was observed upon treatment of complex **4a** with tetrabutylammonium bromide.

Next the coupling of the carbene complex **4a** with strong acids and Lewis acids that have nucleophilic counterions was tested (Scheme 7). Reaction with HBr in propionic acid afforded the ring opened product **26a** as a mixture of stereoisomers. The reaction with iodotrimethylsilane equivalents proved to be quite intriguing [18], and provided different products depending upon the source of iodide ion. Coupling with chlorotrimethylsilane and tetrabutylammonium iodide afforded compound **26b** [19], while use of sodium iodide led to diiodo derivative **27a** [3b]. The reaction leading to **27a** appears to be a general process. Treatment of either of the substrates **4c** or **4d** with sodium iodide/chlorotrimethylsilane led to the analogous products **27c/d** in comparable yield. In each case the reaction provided a single diastereomer with respect to the ring substituents but an E/Z mixture of trisubstituted alkenes; major stereoisomer is the one pictured. The method of stereochemical assignment will be discussed in a subsequent session.

The mechanism depicted in Scheme 8 can account for the formation of compounds **26a** and **26b**. Although bromide ion was ineffective at promoting cyclopropane ring opening, HBr was quite effective. This suggests that the presence of acid is somehow activating the ring opening process. A plausible mechanism involves protonation of the carbene complex followed by attack of bromide on the activated complex **28**. The reaction products are the net result of adding H and X to chromium and the carbon–X of the cyclopropane ring respectively. Apparently the combination of tetrabutylammonium iodide/chlorotrimethylsilane generates a sufficient quantity of HI to afford the products of HI



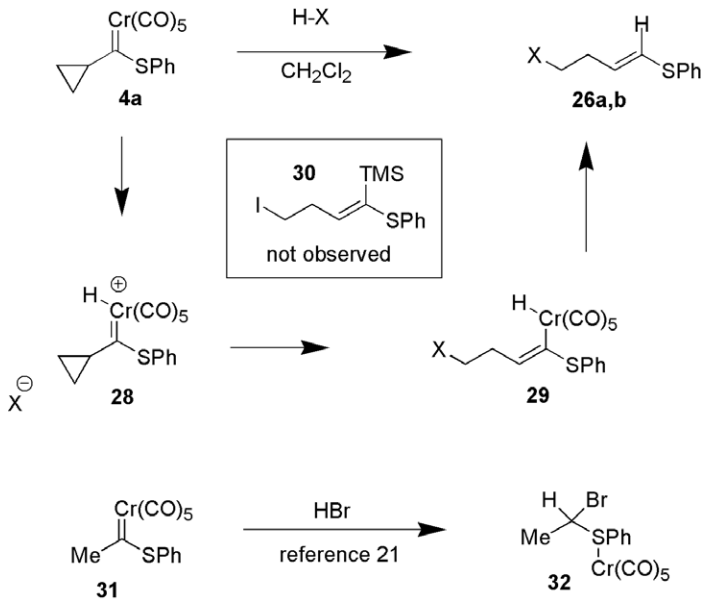
Scheme 6.



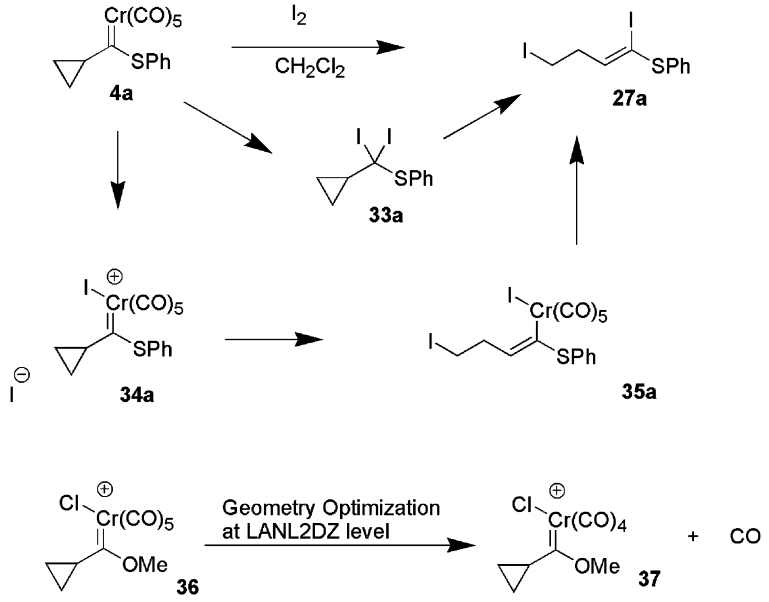
Scheme 7.

addition. Under no conditions could the expected vinylsilane product **30** be isolated. The addition of HBr to methylcarbene complex **31** had already been reported [20], however no mechanism was proposed.

The mechanism leading to the diiodo compounds **27** is difficult to explain. Although the combination of sodium iodide and chlorotrimethylsilane in acetonitrile is a well-documented alternative to iodotrimethylsilane [19], there is some debate as to whether this combination of reagents actually generates iodotrimethylsilane [21]. The mixing of sodium iodide and chlorotrimethylsilane in dichloromethane generates dark colors suggestive of the presence of iodine. The optimal yields of **27a** were obtained using a threefold excess of sodium iodide/chlorotrimethylsilane. Use of only one equivalent of this reagent resulted in diiodo derivative **27a** in low yield. Based on this observation, the coupling of cyclopropylcarbene complex **4a** with iodine itself was examined. This reaction afforded a 97:3 *E*/*Z* mixture of **27a** in excellent yield using only a slight excess of iodine. The major isomer (*Z*) is the one depicted. The mechanism for the formation of **27a** is depicted in Scheme 9. Activation of the carbene complex by iodine followed by CO dissociation and attack of the resulting iodide at the cyclopropane carbon followed by reductive elimination has been proposed. The CO dissociation step is an essential mechanistic feature revealed during attempted geometry optimization of intermediate carbene complex **36**. This is also consistent with other studies where a pentacarbonyl analog of intermediate **34a** afforded only CO-inserted products [12]. An alternative mechanism that cannot be ruled out is formation of diiodide derivative **33a** followed by rearrangement [22]. Further support for the mechanism employing intermediate



Scheme 8.

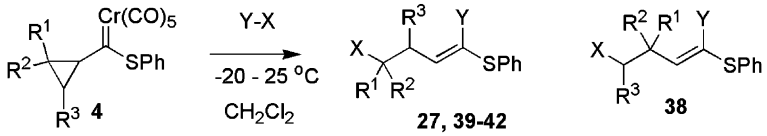


Scheme 9.

34a is the recently reported formation of stable seven-coordinate Group VI metal carbene complexes in the +2 oxidation state through treatment of Fischer carbene complexes with halogens or tin(IV) halides [23].

The reaction of complex **4a** with other halogens and pseudohalogens was tested (Table 2). A similar reaction was observed using bromine (Entry B). Phenylselenenyl chloride afforded a mixture of the selenide **40** (X = Cl, Y = SePh) and the dichloride compound **41** (X, Y = Cl) (Entry C). Attempted reaction with iodine azide afforded only the diiodo derivative **27a** in low yield. A variety of more highly substituted cyclopropylcarbene complexes were tested in their reaction with iodine and the reaction was found to be general (Entries D–J). Reaction with unsymmetrical cyclopropylcarbene complexes led preferentially to compounds where iodide attacks the more substituted carbon of the cyclopropane ring (Entries G–J). In nearly all cases, the reaction afforded mostly the *Z* isomer. The double bond stereochemistry appears to be established under conditions of kinetic control. The same compound (**27f**) produced from two different substrates affords different ratios of double bond isomers (Entries I and J). Since the more substituted iodide was preferentially obtained in unsym-

Table 2
Reaction of cyclopropylcarbene complexes with halogens and pseudohalogens



Entry	R^1	R^2	R^3	Y–X	Yield **27**, **39**–**42**	*Z*/*E* **27**	Yield **38**
A	H	H	H	I_2	88% (**27a**)	97:3	
B	H	H	H	Br_2	61% (**39**)	93:7	
C	H	H	H	PhSe–Cl	46% (**40**) 30% (X, Y = Cl) (**41**)	50:50	
D[a]	H	R^2, R^3 = –$(CH_2)_4$		I_2	85% (**27b**)	72:28	
E[a]	H	R^2, R^3 = –$(CH_2)_6$ *cis* ring fusion		I_2	82% (**27c**)	93:7	
F	H	R^2, R^3 = –$(CH_2)_4$ *trans* ring fusion		I_2	71% (**27d**)	75:25	
G[b]	Me	Me	H	I_2		19:81	
H	Me	Me	H	Br_2	22% (**42**)	20:80	
I	H	*n*-C_6H_{13} *cis* isomer	H	I_2	68% (**27f**)	17:83	3% (**38f**)
J	H	*n*-C_6H_{13} *trans* isomer	H	I_2	54% (**27f**)	84:16	22% (**38f**)

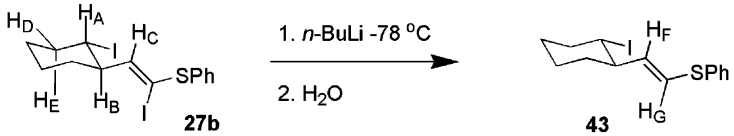
[a] The starting carbene complex was exclusively the exo isomer.
[b] The product was unstable and rearranged to the allylic iodide.

metrical substrates (Entries G–J), this implies that there is substantial positive charge character at the cyclopropane carbons in intermediates **34**.

5. Assignment and rationalization of stereochemistry

The stereochemistry of the ring opening process was established by analysis of the coupling constants for the iodine-bearing carbon atom in compound **27b** (Scheme 10). In the cyclohexyl case this proton (H_A) appears as a td with *J* values of ~11 Hz (t) and ~4 Hz (d), suggesting that this proton is axial and coupled to two other axial protons (H_B and H_E) and an equatorial proton (H_D). A similar pattern was noted in the proton NMR spectrum of the product **27c** derived from *cis*-cyclooctyl-fused carbene complex **4c**. The alkene stereochemistry was determined through halogen metal exchange and protonation on compound **27b**. This substrate was chosen for this study since there is a significant amount of the minor isomer. In this case, a mixture of alkenes (**43**) was obtained which could easily be assigned through their coupling constants (the major isomer is structure **43** depicted in Scheme 10); the major isomer from halogen replacement is *trans*, thus suggesting that the major isomer in the starting compound **27b** is *Z* [24]. In diiodide **27b**, the chemical shift of H_C differs by 0.55 ppm, and the higher chemical shift is observed in the minor stereoisomer. This chemical shift difference is consistent throughout all of the products in Table 2, and has been used to assign the double bond configuration of all of the diiodide products (i.e., the isomer where the alkene proton has the higher chemical shift has been assigned as the *E* isomer).

An attempt to improve the stereochemistry in one of the less stereoselective systems was initiated through adjustment of the steric bulk of the sulfur substituent. Reaction of a variety of cyclohexyl fused cyclopropyl-



MAJOR ISOMER

Proton (δ)	Pattern
H_A 4.00	td, J = 11.4, 4.0
H_C 6.00	d, J = 9.1
H_F 5.68	dd, J = 14.8, 8.7
H_G 6.08	d, J = 14.8

MINOR ISOMER

Proton (δ)	Pattern
H_A 3.90	td, J = 11.2, 4.1
H_C 6.55	d, J = 9.6
H_F 5.52	t, J = 8.7
H_G 6.14	d, J = 8.7

Scheme 10.

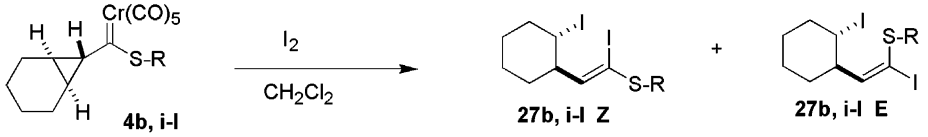
carbene complexes with iodine was examined. As noted in the Table 3, as the steric bulk of the sulfur substituent increases, the reaction becomes more *Z* selective. The highest stereoselectivity was observed in the reaction employing the 2-methylphenylthiocarbene complex derivative. For the alkylthiocarbene complexes, slightly higher stereoselectivity was noted for the isopropylthiocarbene complex vs. the ethylthiocarbene complex. Attempts to prepare the *t*-butylthiocarbene complex and the mesitylphenylthiocarbene complex were not successful.

Based on these results, the model depicted in Scheme 11 has been proposed to rationalize the stereoselectivity. The essential features of the model are: (1) the s-*cis* conformation is predominant at equilibrium and (2) overlap of the C–C bond that is broken and the p-orbital at the carbene carbon is essential for the bond breaking step. The methylcarbene analog of **4a** (complex **47** in Scheme 12) exists as the s-*cis* conformation in the solid state [25] and cyclopropylcarbene complex **4a** also minimizes in this conformation. The observed stereochemistry suggests that in intermediate **34a** the thiophenyl group exerts a more powerful steric influence versus the $Cr(CO)_4I$ group, thus favoring properly aligned structure **34a**-*Z* over alternative properly aligned structure **34a**-*E*. Structure **34a**-*Z* eventually leads to the observed product of the reaction. These preferences are apparently reversed for cases where there is a *cis* substituent at the carbon undergoing attack by halide ion (Entries G–I of Table 2); the *E* isomer is the major product in these cases.

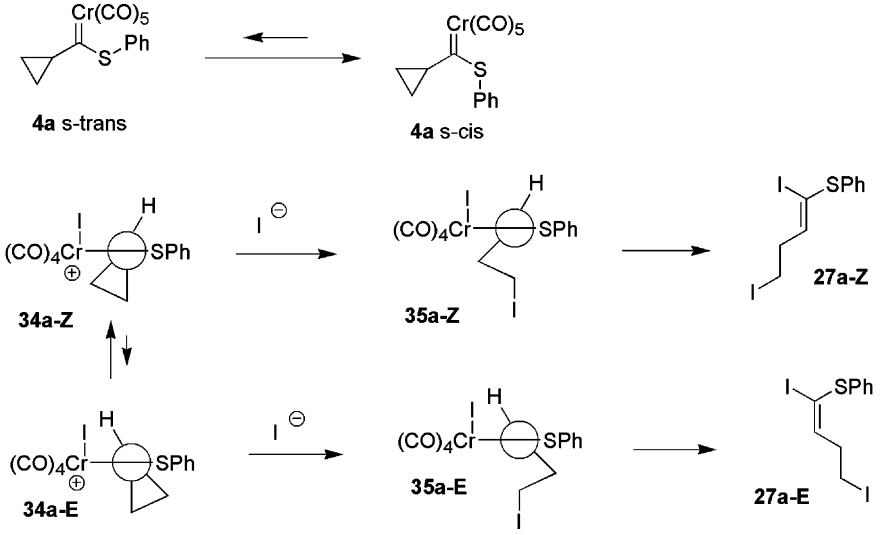
6. Iodine oxidation of other carbene complexes

The iodine oxidation reaction was also attempted on related carbene complexes. The alkoxycarbene complex analog **44** (Scheme 12) was not reactive to iodide ion, however, iodoester derivative **46** was obtained upon treatment with iodine. This reaction likely proceeds through enol ether derivative **45**, which should be highly susceptible to hydrolysis [26]. The methylcarbene com-

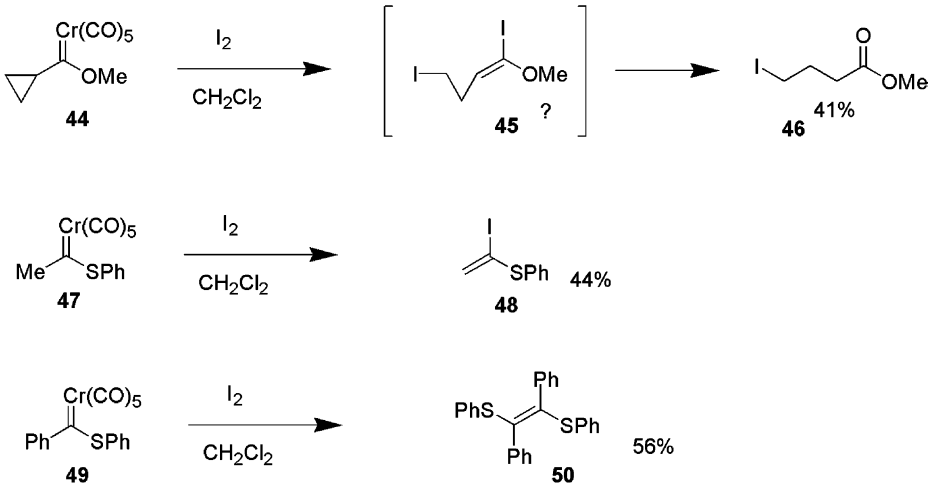
Table 3
Stereoselectivity of various cyclopropyl thiocarbene complexes reacting with iodine



R	*Z*/*E*
Ph (b series)	72:28
2-Methylphenyl (i series)	91:9
3-Methylphenyl (j series)	69:31
Ethyl (k series)	51:49
Isopropyl (l series)	58:42



Scheme 11.



Scheme 12.

plex **47** led to the iodo-alkene **48** in moderate yield. The carbene dimer **50** was observed upon treatment of the phenylcarbene complex **49** with iodine [27].

7. Palladium-catalyzed coupling reactions

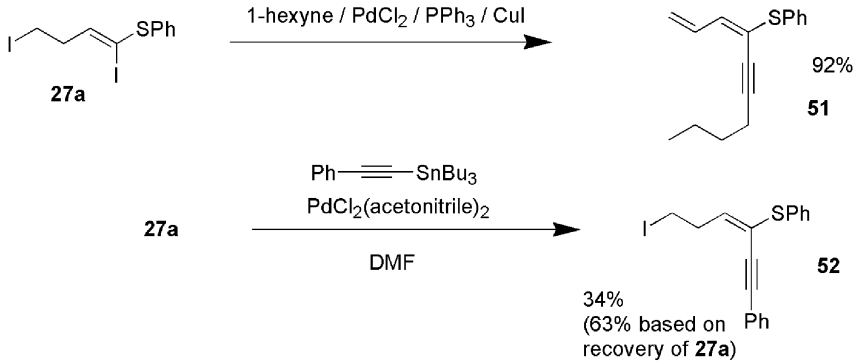
Palladium-catalyzed alkynylation reactions were examined for diiodide **27a** (Scheme 13). Under the standard conditions for the Sonogashira coupling [28], the dienyne derivative **51** was obtained in high yield. In the highly basic solvent system employed elimination accompanies the Sonogashira coupling. The Stille alkynylation [29], which employs a less basic solvent system, led exclusively to the conjugated enyne-iodide **52** in moderate yield.

8. Summary

In summary, cyclopropyl thiocarbene complexes undergo a variety of ring opening reactions resulting in the efficient preparation of highly functionalized organic molecules. In most cases, the reaction proceeds with a high degree of stereoselectivity. A mechanism has been proposed that involves initial electrophilic activation at chromium followed by nucleophilic ring opening of the activated cyclopropane derivative. The diiodide products undergo selective palladium-catalyzed coupling reactions at the alkenyl iodide functionality.

9. Experimental [30]

Starting materials. Cyclopropyl bromide, chromium hexacarbonyl, and all of the thiol derivatives employed in this investigation are commercially available. All of the monobromocyclopropane derivatives were prepared through a sequence involving addition of dibromocarbene to an alkene followed by monodehalogenation using zinc in acetic acid [16]. Dibromocarbene addition to cyclohexene afforded 7,7-dibromobicyclo[4.1.0]heptane [31]. Dibromocarbene addition to *cis* cyclooctene afforded *cis*-9,9-dibromobicyclo[6.1.0]nonane [32]. Dibromocarbene addition to *trans*-cyclooctene afforded *trans*-9,9-dibromobicyclo[6.1.0]nonane [33]. Dibromo-



Scheme 13.

carbene addition to isobutylene afforded 1,1-dibromo-2,2-dimethylcyclopropane [34]. Dibromocarbene addition to 1-octene afforded 1-(2,2-dibromocyclopropyl)hexane [35].

General procedure 1 – Conversion of monobromocyclopropanes to the corresponding acylate salts. To a solution of monobromocyclopropane (10 mmol) in anhydrous ether (25 mL) at −78 °C under nitrogen was added *t*-butyllithium (20 mmol of a 1.7 M hexane solution) dropwise over a 10 min period. This solution was stirred for 20 min at −78 °C, and then transferred via cannula to a suspension of chromium hexacarbonyl (10 mmol) in ether (50 mL) at 0 °C. The reaction was warmed to 25 °C and stirred for 1 h. The solvent was removed on a rotary evaporator and the residue dissolved in a minimum amount of water, then filtered through Celite. To the filtrate a saturated aqueous solution of tetramethylammonium bromide (20 mL) was added. The resulting precipitate was collected by suction filtration, then dissolved in dichloromethane and dried over sodium sulfate. The solvent was removed on a rotary evaporator to afford the acylate salt, which was used without further purification. In some cases, the NMR spectrum could not be acquired, likely due to the presence of paramagnetic impurities.

General procedure 2 – Conversion of cyclopropylcarbene acylates to the corresponding thiocarbene complexes. To a solution of the crude acylate salt (1.0 mmol) in dichloromethane (25 mL) at 0 °C under nitrogen was added via syringe a solution of acetyl chloride (1.0 mmol) in dichloromethane (2 mL), followed immediately by addition of a solution of thiophenol (1.0 mmol) in dichloromethane. The reaction mixture was stirred at 0 °C for a 30 min period. Evaporation of the solvent followed by flash chromatography on silica gel using pure hexane as the eluent afforded the pure thiocarbene complex.

*Preparation of cyclopropylcarbene complex **4a***. General procedure 1 was followed using cyclopropyl bromide (1.200 g, 10.0 mmol), *t*-butyllithium (11.8 mL, 20.0 mmol of a 1.7 M hexane solution), and chromium hexacarbonyl (2.200 g, 10.0 mmol). A yellow solid (2.010 g, 60% yield) identified as acylate salt **1a** was obtained. Acylate salt **1a**. ^{1}H NMR (acetone-d_6): δ 3.44 (s, 12H), 2.76 (m, 1H), 0.65 (m, 2H), 0.27 (m, 2H). The spectral data are consistent with that previously reported for this compound [36]. General procedure 2 was followed using thiophenol (0.150 mL, 1.49 mmol), acylate salt **1a** (0.500 g, 1.49 mmol), and acetyl chloride (0.110 mL, 1.49 mmol). A red oil identified as carbene complex **4a** (0.433 g, 82% yield) was obtained. A minor product (<10% yield) tentatively identified as 4-chloro-1-thiophenyl-1-butene (**6**) was observed when the reaction was allowed to proceed for a long time. Carbene complex **4a**: ^{1}H NMR ($CDCl_3$): δ 7.41 (m, 5H), 2.78 (tt, 1H, $J = 7.8$, 4.3 Hz), 1.96 (m, 2 H), 1.58 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 360.0, 226.0, 216.6, 136.4, 132.1, 130.5, 129.8, 42.5, 22.7; IR (CH_2Cl_2): 2053 (s), 1948 (vs) cm^{-1}; Mass Spec (EI): 354 (M^+, 1), 326 (59), 270 (66), 218 (30), 186 (10), 162 (60), 110 (100); HRMS; calcd for $C_{15}H_{10}CrO_5S$ 353.9654, found 353.9652. 4-chloro-1-thiophenyl-1-butene (**6**): ^{1}H NMR ($CDCl_3$): major isomer: δ 6.19 (d, 1H, $J = 14.9$ Hz); minor isomer: δ 6.25 (d, 1H, $J = 13.0$ Hz); the following peaks are overlapping in both isomers: δ 7.21 (m, 5H), 3.55 (m, 2H), 2.64 (m, 2H). Integration of the alkene protons reveals that this compound is a 60:40 *E*:*Z* mixture.

*Preparation of the cyclohexyl fused carbene complex **4b***. General procedure 1 was followed using 7-bromobicyclo[4.1.0]heptane (1.000 g, 5.70 mmol), *t*-butyllithium (6.72 mL, 11.4 mmol of a 1.7 M hexane solution), and chromium hexacarbonyl (1.257 g, 5.70 mmol). A yellow solid (1.394 g, 54% yield) identified as acylate salt **1b** was obtained. Acylate salt **1b**: IR (CH_2Cl_2): 2030 (sh), 1981 (sh), 1896 (vs) cm^{-1}. General procedure 2 was followed using thiophenol (0.110 mL, 1.03 mmol), acylate salt **1b** (0.400 g, 1.03 mmol), and acetyl chloride (0.070 mL, 1.03 mmol). A red-orange solid identified as carbene complex **4b** (0.156 g, 35% yield) was obtained. Carbene complex **4b**: ^{1}H NMR ($CDCl_3$): δ 7.45–7.32 (m, 5H), 2.69 (br s, 3H), 1.98–1.93 (m, 2H), 1.48 (m, 2H), 1.23–1.15 (m, 2H), 0.83–0.80 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 354.1, 225.5, 216.9, 136.3, 132.6, 130.4, 129.5, 58.7, 39.9, 23.5, 20.6; IR (CH_2Cl_2): 2056 (s), 1975 (s), 1938 (vs) cm^{-1}; Mass Spec (EI): 408 (M^+, 1), 380 (31), 324 (34), 242 (9), 216 (48), 186 (23), 134 (24), 123 (35), 110 (100); HRMS: calcd for $C_{19}H_{16}CrO_5S$ 408.0124, found 408.0148.

*Preparation of the cis-cyclooctyl-fused carbene complex **4c***. General procedure 1 was followed using *cis*-9-bromobicyclo[6.1.0]nonane (1.179 g, 5.80 mmol), *t*-butyllithium (6.8 mL, 11.6 mmol of a 1.7 M hexane solution), and chromium hexacarbonyl (1.278 g, 5.80 mmol). A yellow oil (1.518 g, 63% yield) identified as acylate salt **1c** was obtained. Acylate salt **1c**. ^{1}H NMR (acetone-d_6): δ 3.40 (s, 12H), 2.95 (t, 1H, $J = 5.0$ Hz), 1.90 (m, 2H), 1.33 (m, 12H); IR (CH_2Cl_2): 2055 (s), 1980 (vs) cm^{-1}. General procedure 2 was followed using thiophenol (0.050 mL, 0.51 mmol), acylate salt **1c** (0.213 g, 0.51 mmol), and acetyl chloride (0.040 mL, 0.50 mmol). A red solid identified as carbene complex **4c** (0.134 g, 60% yield) was obtained. Carbene complex **4c**. ^{1}H NMR ($CDCl_3$): δ 7.45–7.20 (m, 5H), 2.42–2.40 (m, 2H), 2.32 (t, 1H, $J = 3.9$ Hz), 1.96–1.87 (d of m, 2H, $J = 13.9$ Hz), 1.57–1.18 (m, 8H), 0.93–0.81 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 353.8, 225.7, 217.0, 136.3, 132.6, 130.4, 129.5, 59.4, 44.4, 29.1, 26.3; IR (CH_2Cl_2): 2054 (s), 1976 (vs), 1904 (s) cm^{-1}; Mass Spec (EI): 408 ($M^+ - CO$, 31), 352 (46), 324 (5), 296 (15), 270 (32), 244 (95), 218 (100), 186 (27), 151 (90), 135 (74); HRMS: calcd for $C_{20}H_{20}CrO_4S$ 408.0487, found 408.0493.

*Preparation of the trans-cyclooctyl fused carbene complex **4d***. General procedure 1 was followed using

trans-9-bromobicyclo[6.1.0]nonane (1.304 g, 6.43 mmol), *t*-butyllithium (7.6 mL, 12.9 mmol of a 1.7 M hexane solution), and chromium hexacarbonyl (1.414 g, 6.43 mmol). A green oil (1.142 g, 43% yield) identified as acylate salt **1d** was obtained. Acylate salt **1d**: IR (CH_2Cl_2): 2055 (s), 1975 (vs), 1902 (s) cm^{-1}. General procedure 2 was followed using thiophenol (0.280 mL, 2.73 mmol), acylate salt **1d** (1.140 g, 2.73 mmol), and acetyl chloride (0.200 mL, 2.73 mmol). A red solid identified as carbene complex **4d** (0.650 g, 55% yield) was obtained. Carbene complex **4d**: ^1H NMR ($CDCl_3$): δ 7.45–7.20 (m, 5H), 2.70 (br s, 1H), 2.19 (d of m, 1H, $J = 16$ Hz), 2.05–1.62 (m, 6H), 1.55–0.95 (m, 6H), 0.79 (qd, 1H, $J = 10.5$, 5.0 Hz); ^{13}C NMR ($CDCl_3$): δ 372.2, 222.7, 216.5, 134.5, 131.8, 130.3, 129.6, 53.5, 43.2, 39.0, 33.5, 31.9, 31.4, 29.7, 28.6, 28.1; IR (CH_2Cl_2): 2055 (s), 1941 (vs) cm^{-1}; Mass Spec (EI): 408 ($M^+ - CO$, 6), 352 (14), 270 (29), 244 (65), 220 (56), 151 (100), 135 (39), 117 (34); HRMS: calcd for $C_{20}H_{20}CrO_4S$ 408.0487, found 408.0471.

*Preparation of the 2,2-dimethylcyclopropylcarbene complex **4e***. General procedure 1 was followed using 2-bromo-1,1-dimethylcyclopropane (1.000 g, 4.88 mmol), *t*-butyllithium (5.74 mL, 13.4 mmol of a 1.7 M hexane solution), and chromium hexacarbonyl (1.477 g, 6.70 mmol). A greenish-yellow oil (1.606 g, 66% yield) identified as acylate salt **1e** was obtained. IR (CH_2Cl_2): 2056 (s), 1974 (vs), 1906 (s) cm^{-1}. General procedure 2 was followed using thiophenol (0.140 mL, 1.38 mmol), acylate salt **1e** (0.500 g, 1.38 mmol), and acetyl chloride (0.100 mL, 1.38 mmol). A red solid identified as carbene complex **4e** (0.266 g, 51% yield) was obtained. Carbene complex **4e**: ^1H NMR ($CDCl_3$): δ 7.45–7.20 (m, 5H); 2.69 (br s, 1H); 1.94 (br t, 1H, $J = 5.9$ Hz); 1.51 (br t, 1H, $J = 5.8$ Hz), 1.01 (s, 3H), 0.61 (br s, 3H); ^{13}C NMR ($CDCl_3$): δ 373.1, 227.7, 216.4, 138.0, 132.1, 130.4, 129.6, 56.3, 34.0, 32.2, 27.5, 20.5; IR (CH_2Cl_2): 2056 (s), 1944 (vs) cm^{-1}; Mass Spec (EI): 382 (M^+, 1), 354 (27), 298 (28), 270 (7), 240 (20), 216 (21), 186 (32), 151 (26), 134 (19), 110 (100); HRMS: calcd for $C_{17}H_{14}CrO_5S$ 381.9967, found 382.0001.

*Preparation of the 2-hexylcyclopropylcarbene complex **4f***. General procedure 1 was followed using 2-bromo-1-hexylcyclopropane (1.000 g, 4.88 mmol), *t*-butyllithium (5.74 mL, 9.76 mmol of a 1.7 M hexane solution), and chromium hexacarbonyl (1.073 g, 4.88 mmol). A green oil (0.644 g, 32% yield) identified as acylate salt **1f** was obtained. General procedure 2 was followed using thiophenol (0.070 mL, 0.67 mmol), acylate salt **1f** (0.250 g, 0.67 mmol), and acetyl chloride (0.050 mL, 0.67 mmol). Chromatography yielded two fractions, both red solids. The product in the first fraction was identified as the *cis*-carbene complex **4f** (0.077 g, 27% yield). The product in the second fraction was identified as the *trans*-carbene complex **4f** (0.029 g, 10% yield). Carbene complex **4f**-*cis*: ^1H NMR ($CDCl_3$): δ 7.48–7.20 (m, 5H), 3.00 (br s, 1H), 1.85 (m, 1H), 1.70–1.45 (m, 4H), 1.42–1.08 (m, 8H), 0.85 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 372.6, 227.6, 216.4, 134.5, 132.1, 130.4, 129.6, 48.7, 38.7, 31.7, 29.7, 29.5, 28.8, 22.6, 14.0; IR (CH_2Cl_2): 2056 (s), 1938 (vs) cm^{-1}; Mass Spec (EI): 410 ($M - CO$, 1); 354 (5), 247 (70), 218 (41), 207 (27), 175 (33), 147 (28), 134 (47), 108 (100); HRMS: calcd for $C_{20}H_{22}CrO_4S$ 410.0644, found 410.0648. Carbene complex **4f**-*trans*: ^1H NMR ($CDCl_3$): δ 7.47–7.24 (m, 5H), 2.63 (dt, 1H, $J = 8.0$, 4.0 Hz), 2.33 (m, 1H), 2.29 (td, 1H, $J = 8.0$, 4.0 Hz); 1.59–1.51 (m, 2H), 1.25–1.21 (m, 9H), 0.83 (t, 3H, $J = 7.0$ Hz); Irradiate at 2.30: patterns altered at δ 2.63 and 1.59–1.51; ^{13}C NMR ($CDCl_3$): δ 356.3, 225.5, 216.8, 134.5, 132.4, 130.5, 129.7, 51.9, 39.6, 33.4, 31.7, 31.6, 28.8, 28.4, 22.5, 14.0; IR (CH_2Cl_2): 2068 (s), 2056 (s), 1987 (s) 1938 (vs) cm^{-1}; Mass Spec (CI): 410 ($M - CO$, 7); 354 (20), 274 (25); HRMS: calcd for $C_{20}H_{22}CrO_4S$ 410.0644, found 410.0649.

*Preparation of the 2-methyl-2-vinylcyclopropylcarbene acylate (**1g**)*. General procedure 1 was followed using 1-bromo-2-methyl-2-ethenylcyclopropane (1.000 g, 6.20 mmol), *t*-butyllithium (7.40 mL, 12.4 mmol of a 1.7 M hexane solution), and chromium hexacarbonyl (1.368 g, 6.20 mmol). A yellow solid (1.628 g, 70% yield) identified as acylate salt **1g** was obtained. Acylate salt **1g**. ^1H NMR (acetone-d_6): major isomer δ 5.75 (dd, 1H, $J = 17.6$, 10.8 Hz), 1.26 (s, 3H),; minor isomer: δ 5.54 (dd, 1H, $J = 17.2$, 10.5 Hz); the following peaks are overlapping in both isomers: δ 4.81 (m, 2 H), 3.45 (s, 12H), 3.00 (m, 1H), 1.31 (m, 1H), 0.42 (m, 1H); IR (CH_2Cl_2): 2030 (sh), 1981 (sh), 1895 (vs) cm^{-1}.

*Coupling of acylate salt **1g** with acetyl chloride and thiophenol*. General procedure 2 was followed using thiophenol (0.140 mL, 1.38 mmol), acylate salt **1g** (0.500 g, 1.38 mmol), and acetyl chloride (0.100 mL, 1.38 mmol). A yellowish oil identified as enyne **2** (0.067 g, 25% yield) was obtained. Even after chromatography this compound is highly impure. In subsequent experiments, the crude mixture was treated with dicobalt octacarbonyl as outlined below. Alkyne **2**. ^1H NMR ($CDCl_3$): δ 7.21 (m, 5H). 5.33 (tq, 1H, $J = 7.8$, 1.0 Hz), 3.48 (d, 2H, $J = 7.8$ Hz), 2.77 (d, 2H, $J = 2.7$ Hz), 1.90 (t, 1H, $J = 2.7$ Hz), 1.76 (d, 3H, $J = 1.0$ Hz); IR (CH_2Cl_2): 3305 (s) cm^{-1}.

*Conversion of alkyne **2** to the corresponding cobalt complex **3***. The crude product (before chromatography) from the previous reaction was dissolved in pentane (20 mL) and cooled to 0 °C. To this solution was added solid dicobalt octacarbonyl (0.340 g, 1.20 mmol). The reaction was stirred for 10 min at 0°C and then for 12 h at 25 °C. The solvent was removed on a rotary evaporator and the residue was purified by flash chromatography on silica gel using pure hexane as the eluent. A red oil identified as alkyne-cobalt complex **3** (0.174 g, 30% yield) was obtained. Alkyne-cobalt complex **3**. ^1H NMR ($CDCl_3$): δ 7.23 (m, 5H), 5.96 (s, 1H), 5.34 (tq,

1H, $J = 7.8$, 0.7), 3.54 (d, 2H, $J = 7.8$), 3.42 (s, 2H), 1.77 (d, 3H, $J = 0.7$); ^{13}C NMR ($CDCl_3$): δ 199.8, 137.1, 136.2, 130.3, 128.8, 126.4, 122.4, 93.5, 73.5, 36.5, 32.4, 23.5; IR (CH_2Cl_2): δ 2093 (sh), 2053 (s), 2025 (vs) cm^{-1}; MS (CI): 432 ($M^+ - 2CO$, 44.8), 404 (40.1), 376 (9.2), 320 (32.1), 202 (100), 186 (100).

*Preparation of the 2-methyl-2-phenylcyclopropylcarbene acylate (**1h**)*. General procedure 1 was followed using 1-bromo-2-methyl-2-phenylcyclopropane (1.000 g, 4.70 mmol), *t*-butyllithium (5.6 mL, 9.4 mmol of a 1.7 M hexane solution), and chromium hexacarbonyl (1.043 g, 4.70 mmol). A yellow oil (1.088 g, 54% yield) identified as acylate salt **1h** was obtained. Acylate salt **1h**: ^{1}H NMR (acetone-d_6): δ 7.40 (m, 5H), 3.35 (s, 13H), 1.7–0.6 (m, 5H); IR (CH_2Cl_2): 2030 (sh), 1981 (sh), 1896 (vs) cm^{-1}.

*Coupling of acylate salt **1h** with acetyl chloride and thiophenol*. General procedure 2 was followed using thiophenol (0.048 mL, 0.47 mmol), acylate salt **1h** (0.200 g, 0.47 mmol), and acetyl chloride (0.030 mL, 0.47 mmol). In the chromatography 19:1 hexane: ethyl acetate was used as the eluent. A colorless oil identified as alkyne-ester **5** (0.065 g, 68% yield) was obtained. Alkyne-ester **5**: ^{1}H NMR ($CDCl_3$): δ 7.24 (m, 5H), 3.01 (dd, 1H, $J = 16.6$, 2.7 Hz), 2.85 (dd, 1H, $J = 16.6$, 2.7 Hz), 2.10 (s, 3H), 1.93 (t, 1H, $J = 2.7$ Hz), 1.84 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 169.5, 143.4, 128.2, 127.4, 124.5, 81.6, 79.5, 71.0, 32.1, 25.2, 22.0; IR (CH_2Cl_2): 3300 (m), 1737 (s), 1685 (m) cm^{-1}. The spectral data are consistent with those previously reported for this compound [37].

*Coupling of carbene complex **4a** with tetrabutylammonium iodide*. To a solution of carbene complex **4a** (0.100 g, 0.280 mmol) in dichloromethane (10 mL) at 25 °C under nitrogen was added a solution of tetrabutylammonium iodide (0.313 g, 0.86 mmol) in dichloromethane (2 mL). This mixture was stirred at 25 °C for 12 h, and then the solvent was removed on a rotary evaporator. Flash chromatography of the residue using pure hexane as the eluent afforded a colorless oil (0.045 g, 99% yield) identified as 4-phenylthio-1-butyne (**14**). 4-phenylthio-1-butyne (**14**): ^{1}H NMR ($CDCl_3$): δ 7.24 (m, 5H), 3.00 (t, 2H, $J = 7.5$ Hz), 2.41 (td, 2H, $J = 7.5$, 2.6 Hz), 1.97 (t, 1H, $J = 2.6$ Hz); IR (CH_2Cl_2): 3305 (s) cm^{-1}. The spectral data were consistent with those previously reported for this compound [38].

*Coupling of carbene complex **4a** with sodium azide*. To a solution of carbene complex **4a** (0.178 g, 0.480 mmol) in 5:1 *t*-butyl alcohol: water (6 mL) at 25 °C under nitrogen was added a solution of sodium azide (0.037 g, 0.580 mmol) in water (1 mL). The deep red color of the carbene complex immediately turned yellow and eventually colorless after 1 h. Extraction of the crude mixture with dichloromethane followed by flash chromatography using hexane as the eluent afforded three fractions. The product in the first fraction was identified as isocyanide complex **19** (0,020 g, 17% yield). The product in the second fraction was identified as 4-phenylthio-1-buyne (**14**) (0.004 g, 5% yield). The product in the third fraction was identified as 1,4-bis(phenylthio)-1-butene (**20**) (0.022 g, 17%). Isocyanide complex **19**: ^{1}H NMR ($CDCl_3$): δ 3.20 (m, 1H), 1.10 (m, 4H); IR (CH_2Cl_2): 2175 (m), 2063 (m), 1950 (vs) cm^{-1}. The spectral data were consistent with those previously reported for this compound [39]. 1,4-bis(phenylthio)-1-butene (**20**). ^{1}H NMR ($CDCl_3$): major (*trans*) isomer: δ 6.27 (d, 1H, $J = 14.9$ Hz), 2.58 (q, 2H, $J = 7.2$ Hz); minor (*cis*) isomer: δ 6.29 (d, 1H, $J = 8.2$ Hz), 2.58 (q, 2H, $J = 7.2$ Hz); the following peaks are overlapping in both isomers: δ 7.38–7.16 (m, 10H), 5.83 (m, 1H), 3.00 (t, 2H, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$): δ 133.4, 133.0, 130.1, 129.6, 129.5, 129.1, 129.0, 128.9, 128.8, 128.7, 126.4, 126.2, 126.1, 125.2, 123.8, 33.2, 33.0, 32.7, 28.8; Mass Spec (EI): 272 (M^+, 16), 271 (56), 179 (22), 164 (37), 153 (8), 149 (71), 123 (100), 109 (99); HRMS: calcd for $C_{16}H_{16}S_2$ 272.0693, found 272.0683. Integration of the alkene protons reveals that this compound is a 60:40 *E*:*Z* mixture.

General procedure 3 – Reaction of carbene complexes with electrophiles. The electrophile (1.05 eq) was placed in a round bottom flask under nitrogen and cooled to −20 °C. To this solution was added an 0.02M solution of the carbene complex (1.0 eq) in dichloromethane. The solution was allowed to slowly warm to 25 °C and allowed to stir at 25 °C for a specified period of time depending upon the electrophile (iodine – 4 h, pyridinium bromide perbromide – 12 h, phenylselenenyl chloride – 24 h). The mixture was filtered through Celite and the solvent was removed on a rotary evaporator. The residue was purified by flash chromatography on silica gel. The eluent was pure hexane unless otherwise specified.

*Reaction of carbene complex **4a** with HBr*. General procedure 3 was followed using carbene complex **4a** (0.197 g, 0.590 mmol) and hydrogen bromide (0.12 mL of a 30% propionic acid solution, 0.590 mmol). Purification by flash chromatography afforded two fractions. The product in the first fraction was identified as starting carbene complex **4a** (0.040 g, 11% recovery). The product in the second fraction was identified as 4-bromo-1-thiophenyl-1-butene (**26a**) (0.087 g, 40% yield). 4-bromo-1-thiophenyl-1-butene (**26a**): ^{1}H NMR ($CDCl_3$): major isomer (*trans*): δ 6.22 (dt, 1H, $J = 15.0$, 1.4 Hz), 3.35 (t, 2H, $J = 6.9$ Hz), 2.58 (qd, 2H, $J = 6.9$, 1.4 Hz); minor isomer (*cis*): δ 6.30 (dt, 1H, $J = 9.3$, 1.2 Hz), 3.38 (t, 2H, $J = 6.9$ Hz), 2.68 (qd, 2H, $J = 6.9$, 1.2 Hz); the following peaks are overlapping in both isomers: δ 7.30–7.15 (m, 5H), 5.82–5.67 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 130.9, 129.4, 129.2, 129.1, 128.7, 126.6, 126.6, 126.4, 125.5, 36.2, 32.2, 31.6; Mass Spec (EI): 244 (M+2, 50), 242 (M, 50), 163 (44), 149 (100), 135 (36), 116 (64), 109 (73); HRMS:

calcd for $C_{10}H_{11}BrS$ 241.9764, found 241.9803. Integration of the alkene protons reveals that this compound is a 60:40 *E*:*Z* mixture.

*Reaction of carbene complex **4a** with tetrabutylammonium iodide/chlorotrimethylsilane*. To a solution of carbene complex **4a** (0.092 g, 0.26 mmol) in dichloromethane (10 mL) at 0 °C under nitrogen was added a solution of tetrabutylammonium iodide (0.134 g, 0.31 mmol) and chlorotrimethylsilane (0.115 g, 0.39 mmol) in dichloromethane (5 mL). The reaction mixture was stirred at 0 °C for 12 h. After removal of the solvent on a rotary evaporator, the reside was purified by flash chromatography on silica gel using pure hexane as the eluent. A slightly yellow oil identified as *trans*-4-iodo-1-thiophenyl-1-butene (**26b**) was obtained (0.071 g, 93% yield). *trans*-4-Iodo-1-thiophenyl-1-butene (**26b**): ^{1}H NMR ($CDCl_3$): δ 7.38–7.20 (m, 5H), 6.25 (dt, 1H, $J = 15.0$, 1.2 Hz), 5.80 (dt, 1H, $J = 15.0$, 7.1 Hz), 3.18 (t, 2H, $J = 7.1$ Hz), 2.70 (qd, 2H, $J = 7.1$, 1.2 Hz); ^{13}C NMR ($CDCl_3$): δ 135.3, 132.5, 129.4, 129.0, 126.6, 126.2, 36.9, 4.3; Mass Spec (EI): 290 (M^+, 41), 289 (74), 163 (100), 128 (30), 109 (50), 85 (34); HRMS: calcd for $C_{10}H_{11}IS$ 289.9626, found 289.9606.

General procedure 4 – Reaction of carbene complexes with sodium iodide/chlorotrimethylsilane. To a solution of the carbene complex (0.07–0.17 mmol, 1 eq) in dichloromethane (10 mL) at 0 °C under nitrogen was added a suspension of sodium iodide (3 eq) and chlorotrimethylsilane (3 eq) in dichloromethane (5 mL). The reaction mixture was stirred at 0 °C for 12 h. Final purification was achieved by flash chromatography on silica gel using pure hexane as the eluent.

*Reaction of carbene complex **4a** with sodium iodide/chlorotrimethylsilane*. General procedure 4 was followed using carbene complex **4a** (0.025 g, 0.07 mmol), chlorotrimethylsilane (0.023 g, 0.21 mmol) and sodium iodide (0.032 g, 0.21 mmol). Chromatographic purification afforded a colorless compound identified as diiodide **27a** (0.020 g, 70% yield). Diiodide **27a**: ^{1}H NMR ($CDCl_3$): major (*Z*) isomer δ 6.24 (t, 1H, $J = 6.7$), 2.79 (td, 2H, $J = 7.0$, 6.7); minor (*E*) isomer δ 6.80 (t, 1H, $J = 7.2$), 2.93 (m, 2H); the following peaks overlap in both isomers 7.9–7.29 (m, 5H), 3.20 (t, 2H, $J = 7.0$) ; ^{13}C NMR ($CDCl_3$): δ 143.7, 134.5, 131.1, 129.2, 127.9, 95.5, 41.0, 1.7 (peaks for the minor isomer did not appear); Mass Spec (EI): 416 (M, 18), 326 (21), 289 (100), 254 (49), 217 (33), 184 (17), 161 (30), 147 (13), 127 (48), 109 (35); HRMS: calcd for $C_{10}H_{10}I_2S$ 415.8593, found 415.8588. Integration of the alkene peaks revealed that this is a 93:7 *Z*:*E* mixture.

*Reaction of carbene complex **4c** with sodium iodide/chlorotrimethylsilane*. General procedure 4 was followed using carbene complex **4c** (0.025 g, 0.05 mmol), chlorotrimethylsilane (0.019 g, 0.17 mmol) and sodium iodide (0.025 g, 0.17 mmol). Chromatographic purification afforded a colorless compound identified as diiodide **27c** (0.019 g, 65% yield). Diiodide **27c**: ^{1}H NMR ($CDCl_3$): major (*Z*) isomer: δ 6.15 (d, 1H, $J = 9.3$ Hz), 3.15 (m, 1H); minor (*E*) isomer: δ 6.65 (d, 1H, $J = 9.8$ Hz), 3.55 (m, 1H); the following peaks are overlapping in both isomers: δ 7.38–7.19 (m, 5H), 4.37 (dt, 1H, $J = 11.2$, 4.2 Hz); 2.22–2.10 (m, 2H), 1.71–1.43 (m, 10H); Irradiate at δ 3.15: δ 6.15 (s), 4.38 (t), ^{13}C NMR ($CDCl_3$) δ 153.1, 135.4, 130.5, 129.1, 127.4, 91.3, 55.2, 41.6, 35.3, 31.8, 27.7, 26.6, 26.2, 25.7; Mass Spec (CI): 498 (M, 27), 371 (100), 275 (92), 244 (38), 147 (86), 127 (43), 110 (27); HRMS: calcd for $C_{16}H_{20}I_2S$ 497.9375, found 497.9386. Integration of the alkene peaks revealed that this is a 83:17 *Z*:*E* mixture.

*Reaction of carbene complex **4d** with sodium iodide/chlorotrimethylsilane*. General procedure 4 was followed using carbene complex **4d** (0.069 g, 0.16 mmol), chlorotrimethylsilane (0.051 g, 0.47 mmol) and sodium iodide (0.071 g, 0.47 mmol). Chromatographic purification afforded a colorless compound identified as diiodide **27d** (0.033 g, 42% yield). Diiodide **27d**: ^{1}H NMR ($CDCl_3$): major (*Z*) isomer: δ 6.09 (d, 1H, $J = 8.8$ Hz), 2.47 (m, 1H); minor (*E*) isomer: δ 6.69 (d, 1H, $J = 8.0$ Hz), 2.85 (m, 1H); the following peaks are overlapping in both isomers: δ 7.34–7.15 (m, 5H), 4.48 (m, 1H), 2.32–2.23 (m, 2H), 1.86–1.69 (m, 4H), 1.46–1.21 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 158.5, 152.2, 136.8, 136.0, 31.2, 29.8, 29.7, 26.9, 25.7, 25.5; Mass Spec (EI): 498 (M^+, 9), 371 (100), 243 (39), 218 (65), 147 (53), 133 (65), 123 (46); HRMS: calcd for $C_{16}H_{20}I_2S$ 497.9375, found 497.9384. Integration of the alkene peaks revealed that this is a 71:29 *Z*:*E* mixture.

*Reaction of carbene complex **4a** with iodine*. General procedure 3 was followed using carbene **4a** (0.128 g, 0.36 mmol) and iodine (0.096 g, 0.38 mmol). Chromatographic purification afforded a colorless compound identified as diiodide **27c** (0.118 g, 78% yield). The spectral data were identical to that from the product of reaction of carbene complex **4a** and sodium iodide/chlorotrimethylsilane. Integration of the alkene peaks revealed that this is a 97:3 *Z*:*E* mixture.

*Reaction of carbene complex **4a** with pyridinium bromide perbromide*. General procedure 3 was followed using carbene **4a** (0.022 g, 0.06 mmol) and pyridinium bromide perbromide (0.024 g, 0.07 mmol). Chromatographic purification afforded a colorless compound identified as dibromide **39** (0.012 g, 61% yield). Dibromide **39**. ^{1}H NMR ($CDCl_3$): major (*Z*) isomer δ 6.46 (t, 1H, $J = 6.8$ Hz), 2.83 (q, 2H, $J = 6.8$ Hz); minor (*E*) isomer δ 6.55 (t, 1H, $J = 7.2$ Hz), 2.93 (dt, 2H, $J = 7.2$, 6.8 Hz); the following peaks are overlapping in both isomers δ 7.45–7.20 (m, 5H), 3.44 (t, 2H, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$): δ 141.1, 137.4, 133.4, 130.6, 127.9, 119.9, 35.9, 30.0; Mass Spec (EI): 324 (M $^{81}Br_2$, 4), 322 (M $^{81}Br^{79}Br$, 15), 320 (M $^{79}Br_2$, 7), 243 (23), 232 (17), 178 (20), 161 (61), 147 (100), 128 (92), 109 (86); HRMS: calcd for $C_{10}H_{10}{}^{79}Br_2S$ 319.8870,

found 319.9949. Integration of the alkene peaks revealed that this is a 93:7 *Z*:*E* mixture.

*Reaction of carbene complex **4a** with phenyl selenenyl chloride*. General procedure 3 was followed using carbene **4a** (0.180 g, 0.51 mmol) and phenyl selenenyl chloride (0.117 g, 0.61 mmol). Chromatographic purification afforded two fractions. The product in the first fraction was identified as dichloride **41** (0.046 g, 39% yield). The product in the second fraction was identified as selenide **40** (0.083 g, 46% yield). 1,4-dichloro-1-thiophenyl-1-butene (**41**): ^{1}H NMR ($CDCl_3$): major (*Z*) isomer δ 6.23 (t, 1H, $J = 6.9$ Hz), 2.70 (dt, 2H, $J = 6.9$, 6.6 Hz); minor (*E*) isomer δ 6.24 (t, 1H, $J = 7.4$ Hz), 2.80 (dt, 2H, $J = 7.4$, 6.6 Hz); the following peaks are overlapping in both isomers δ 7.40–7.19 (m, 5 H), 3.53 (t, 2H, $J = 6.6$ Hz); ^{13}C NMR ($CDCl_3$): δ 135.5, 133.2, 132.7, 130.7, 129.2, 127.8, 42.4, 33.2; Mass Spec (EI): 236 (M $^{37}Cl_2$, 11), 234 (M $^{37}Cl^{35}Cl$, 54), 232 (M $^{35}Cl_2$, 78), 197 (28), 183 (66), 147 (100), 125 (16), 109 (25); HRMS: calcd for $C_{10}H_{10}{}^{35}Cl_2S$ 231.9880, found 231.9888. Integration of the alkene peaks revealed that this is a 97:3 *Z*:*E* mixture. 4-Chloro-1-phenylseleno-1-phenylthio-1-butene (**40**). ^{1}H NMR ($CDCl_3$): δ 7.50–7.15 (m, 10H), 6.25 and 6.16 (two t's, total of 1H, $J = 7.1$), 3.46 and 3.45 (two t's, total of 2H, $J = 6.7$), 2.74 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ 139.0, 136.5, 134.4, 133.0, 131.8, 130.1, 129.1, 128.9, 128.8, 128.1, 127.6, 127.5, 126.9, 43.2, 35.8, 34.4; Mass Spec (EI): 354 (M, 59), 197 (91), 161 (72), 147 (20), 128 (100), 121 (59), 107 (28); HRMS: calcd for $C_{16}H_{15}ClS^{80}Se$ 353.9748, found 353.9738. Integration of the alkene peaks revealed that this is a 50:50 *Z*:*E* mixture.

*Reaction of carbene complex **4b** with iodine*. General procedure 3 was followed using carbene complex **4b** (0.030 g, 0.07 mmol) and iodine (0.022 g, 0.09 mmol). Chromatographic purification afforded a colorless compound identified as Diiodide **27b** (0.028 g, 85% yield). Diiodide **27b**: ^{1}H NMR ($CDCl_3$): major (*Z*) isomer: δ 6.00 (d, 1H, $J = 9.1$ Hz), 4.00 (td, 1H, $J = 11.4$, 4.0 Hz), 2.72 (m, 1H); minor (*E*) isomer: δ 6.55 (d, 1H, $J = 9.6$ Hz), 3.90 (td, 1H, $J = 11.2$, 4.1 Hz), 3.15 (m, 1H); the following peaks are overlapping in both isomers: δ 7.48–7.19 (m, 5H), 2.45 (m, 1H), 2.00 (m, 1H), 1.92–1.77 (m, 2H), 1.59–1.03 (m, 4H); Irradiate at δ 2.72: δ 6.00 (s), 4.00 (dd, 1H, $J = 11.4$, 4.0); ^{13}C NMR ($CDCl_3$): δ 156.6, 150.4, 135.2, 130.5, 130.4, 129.1, 127.5, 91.9, 86.1, 56.2, 52.1, 40.0, 35.3, 34.6, 33.6, 32.3, 28.2, 24.7; Mass Spec (EI): 470 (M, 44), 344 (49), 275 (54), 354 (36), 218 (46), 162 (48), 147 (70), 123 (100), 107 (86); HRMS: calcd for $C_{14}H_{16}I_2S$ 469.9062, found 469.9073. Integration of the alkene peaks revealed that this is a 72:28 *Z*:*E* mixture.

*Reaction of carbene complex **4c** with iodine*. General procedure 3 was followed using carbene **4c** (0.021 g, 0.05 mmol) and iodine (0.015 g, 0.06 mmol). Chromatographic purification afforded a colorless compound identified as diiodide **27c** (0.020 g, 82% yield). The spectral data were identical to that from the product of reaction of carbene complex **4c** and sodium iodide/chlorotrimethylsilane. Integration of the alkene peaks revealed that this is a 93:7 *Z*:*E* mixture.

*Reaction of carbene complex **4d** with iodine*. General procedure 3 was followed using carbene **4d** (0.018 g, 0.04 mmol) and iodine (0.011 g, 0.04 mmol). Chromatographic purification afforded a colorless compound identified as diiodide **27d** (0.015 g, 74% yield). The spectral data were identical to that from the product of reaction of carbene complex **4d** and sodium iodide/chlorotrimethylsilane. Integration of the alkene peaks revealed that this is a 75:25 *Z*:*E* mixture.

*Reaction of carbene complex **4e** with iodine*. General procedure 3 was followed using carbene **4e** (0.021 g, 0.05 mmol) and iodine (0.015 g, 0.06 mmol). Chromatographic purification afforded a colorless compound identified as diiodide **27e** (0.020 g, 82% yield). Diiodide **27e**: ^{1}H NMR ($CDCl_3$): δ major (*E*) isomer: 6.95 (t, 1H, $J = 7.2$ Hz), 2.71 (d, 2H, $J = 7.2$ Hz); minor (*Z*) isomer: δ 6.40 (t, 1H, $J = 6.8$ Hz), 2.57 (d, 2H, $J = 6.8$ Hz); the following peaks are overlapping in both isomers: δ 7.66–7.26 (m, 5H), 1.92 (s, 6H), This compound was very unstable and could not be further characterized. Integration of the alkene peaks revealed that this is a 19:81 *Z*:*E* mixture.

*Reaction of carbene complex **4e** with pyridinium bromide perbromide*. General procedure 3 was followed using carbene **4e** (0.176 g, 0.46 mmol) and pyridinium bromide perbromide (0.155 g, 0.48 mmol). Chromatographic purification afforded a colorless compound identified as dibromide **42** (0.035 g, 22% yield). 1,4-dibromo-4-methyl-1-thiophenyl-1pentene (**42**): ^{1}H NMR ($CDCl_3$): δ major (*E*) isomer: 6.67 (t, 1H, $J = 7.4$ Hz), 2.81 (d, 2H, $J = 7.4$ Hz); minor (*Z*) isomer: δ 6.58 (t, 1H, $J = 6.8$ Hz), 2.72 (d, 2H, $J = 6.8$ Hz); the following peaks are overlapping in both isomers: δ 7.35–7.26 (m, 5H), 1.73 (s, 6H), ^{13}C NMR ($CDCl_3$): δ 141.0, 138.0, 133.2, 130.0, 129.1, 127.5, 116.7, 64.3, 50.1, 48.9, 34.1; Mass Spec (EI): 352 (M+4, 34), 250 (M+2, 66), 348 (M^+, 32), 294 (19), 271 (58), 227 (70), 190 (41), 147 (100), 134 (40), 109 (14); HRMS: calcd for $C_{12}H_{14}{}^{81}Br^{79}BrS$ 349.9162, found 349.9156. Integration of the alkene peaks revealed that this is a 20:80 *Z*:*E* mixture.

*Reaction of carbene complex **4f**-cis with iodine*. General procedure 3 was followed using carbene **4f**-*cis* (0.031 g, 0.07 mmol) and iodine (0.019 g, 0.07 mmol). Chromatographic purification afforded a colorless compound identified as diiodide **27f** (0.025 g, 71% yield). Diiodide **27f**. ^{1}H NMR ($CDCl_3$): major (*E*) isomer: δ 6.92 (t, 1H, $J = 7.1$ Hz), 2.93 (t, 2H, $J = 7.1$ Hz), 1.50 (m, 1 H); minor (*Z*) isomer: 6.35 (t, 1H, $J = 6.6$ Hz), 2.80 (t, 2H, $J = 6.6$ Hz), 1.86 (m, 1H); the following peaks are overlapping in both isomers: δ 7.39–7.31 (m,

5H), 4.13 (m,1H), 1.71 (m,1H), 1.38–1.14 (m, 8H), 0.92–0.84 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 150.4, 144.2, 135.1, 130.9, 130.3, 129.2, 129.2, 129.1, 127.6, 127.5, 127.2, 87.5, 47.9, 43.5, 40.3, 34.7, 31.6, 29.5, 28.4, 14.0, 1.0; Mass Spec (EI): 500 (M, 14), 374 (18), 373 (100), 275 (100), 246 (23), 147 (33), 134 (13), 115 (111); HRMS: calcd for $C_{16}H_{22}I_2S$ 499.9532, found 499.9548. Integration of the alkene peaks revealed that this is a 17:83 *Z*:*E* mixture.

*Reaction of carbene complex **4f**-trans with iodine*. General procedure 3 was followed using carbene complex **4f**-*trans* (0.043 g, 0.10 mmol) and iodine (0.026 g, 0.10 mmol). Chromatographic purification afforded a colorless compound identified as an inseparable mixture of diiodides **27f** and **38f** (0.025 g, 76% yield). Diiodide **38f** (peaks for the major component of the mixture, **27f** are not listed). ^{1}H NMR ($CDCl_3$): Major (*Z*) isomer: δ 6.01 (d, 1H, $J = 8.9$ Hz); minor (*E*) isomer: δ 6.57 (d, 1H, $J = 9.4$ Hz); the following peaks are overlapping in both isomers: δ 7.39–7.31 (m, 5H), 3.20 (dd, 2H, $J = 5.9$, 3.8 Hz), 2.50 (m, 1H), 1.50–1.20 (m, 6H), 0.92–0.84 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 143.7, 134.5, 131.1, 129.2, 127.9, 95.5, 41.0, 1.7 (peaks for compound **27f** have been subtracted out). Integration of the alkene peaks revealed that **27f** is an 84:16 *Z*:*E* mixture, and that **38f** is a 96:4 *Z*:*E* mixture.

*Reaction of diiodide **27b** with n-butyllithium followed by protonation – Proof of alkene stereochemistry*. To a solution of diiodide **27b** (0.075 g, 0.16 mmol) in THF (30 mL) under nitrogen at −78 °C was added via syringe *n*-butyllithium (0.12 mL of a 1.6 M hexane solution, 1.9 mmol) and the mixture was stirred at −78 °C for 5 min after completion of the addition. Water (1 mL) was added and the solution was allowed to warm to room temperature. The reaction mixture was poured into a separatory funnel containing water and ether. The ether layer was dried over sodium sulfate and the solvent was removed on a rotary evaporator. Final purification was achieved by flash chromatography on silica gel using pure hexane as the eluent to afford the monoidodo vinyl sulfide **43** (0.024 g, 44% yield). Iodo vinyl sulfide **43**: ^{1}H NMR ($CDCl_3$): major (*trans*) isomer: δ 6.08 (d, 1H, $J = 14.8$ Hz), 5.68 (dd, 1H, $J = 14.8$, 8.7 Hz), 3.86 (td, 1H, $J = 11.3$, 4.2 Hz), 2.44 (m, 1H); minor (*cis*) isomer: δ 6.14 (d, 1H, $J = 8.7$ Hz), 5.52 (t, 1H, $J = 8.7$ Hz), 3.95 (td, 1H, $J = 11.6$, 4.1 Hz), 2.93 (m, 1H); the following peaks are overlapping in both isomers: δ 7.34–7.09 (m, 5H), 2.52–2.36 (m, 1H), 1.95 (m, 1H), 1.98–1.64 (m, 2H), 1.52–1.04 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 140.0, 137.8, 136.0, 129.2, 129.1, 126.3, 123.5, 123.0, 51.7, 48.1, 40.5, 40.2, 38.1, 37.3, 33.8, 33.3, 29.7, 28.5, 25.2, 25.1; Mass Spec (EI): 344 (M^+, 30), 217 (37), 181 (100), 149 (21), 123 (32), 109 (21); HRMS: calcd for $C_{14}H_{17}IS$ 344.0096, found 344.0096. Integration of the alkene peaks revealed that this is a 70:30 *trans*:*cis* mixture.

*Preparation of carbene complex **4i** and subsequent reaction with iodine*. General procedure 2 was followed using carbene acylate **1b** (0.500 g, 1.28 mmol), 2-methylthiophenol (0.152 mL, 1.28 mmol), and acetyl chloride (0.91 mL, 1.28 mmol). After chromatographic purification a red solid identified as carbene complex **4i** (0.119 g, 22% yield) was obtained. This solid was immediately used in the next experiment. General procedure 3 was followed using carbene complex **4i** (0.016 g, 0.038 mmol) and iodine (0.010 g. 0.040 mmol). After chromatographic purification a colorless oil identified as compound **27i** (0.018 g, 99% yield) was obtained. Diiodide **27i**: ^{1}H NMR ($CDCl_3$): major (*Z*) isomer: 5.87 (d, 1H, $J = 8.8$ Hz), minor (*E*) isomer: 6.59 (d, 1H, $J = 9.5$ Hz); the following peaks are overlapping in both isomers: 7.45–7.10 (m, 4H), 4.00 (dt, 1H, $J = 10.8$, 4.0 Hz); 2.78 (tdd, 1H, 10.8, 8.8, 3.8 Hz), 2.53–2.30 (m, 2H) overlapping with 2.40 (s, 3H), 2.05 (qd, 1H, 10.8, 3.8 Hz), 2.85 (m, 2H), 1.53 (m, 2H); ^{13}CNMR (ppm): 147.4, 139.7, 132.6, 130.6, 128.3, 126.6, 92.3, 77.2, 56.1, 39.9, 34.9, 33.5, 32.5, 29.7, 28.3, 24.8, 20.6; Mass Spec (EI): 484 (M^+, 9), 441 (2), 357 (100), 229 (78), 127 (51); HRMS: calcd for $C_{15}H_{18}I_2S$ 483.9219, found 483.9213. Integration of the alkene peaks revealed that this product is a 91:9 *Z*:*E* mixture.

*Preparation of carbene complex **4j** and subsequent reaction with iodine*. General procedure 2 was followed using carbene acylate **1b** (0.550 g, 1.41 mmol), 3-methylthiophenol (0.168 mL, 1.41 mmol), and acetyl chloride (0.100 mL, 1.41 mmol). After chromatographic purification a red solid identified as carbene complex **4j** (0.241 g, 40% yield). Carbene complex **4j**: ^{1}H NMR ($CDCl_3$): δ 7.40–7.10 (m, 4H), 2.72 (br s, 3H), 2.38 (s, 3H), 2.35 (m, 1H), 2.00 (m, 2H), 1.53 (m, 2H), 1.20 (m, 2H), 0.86 (t, 2H). This solid was immediately used in the next experiment. General procedure 3 was followed using carbene complex **4j** (0.148 g, 0.35 mmol) and iodine (0.093 g. 0.037 mmol). After chromatographic purification a colorless oil identified as diiodide **27j** (0.166 g, 100% yield) was obtained. Diiodide **27j**: ^{1}H NMR ($CDCl_3$): major (*Z*) isomer: δ 6.06 (d, 1H, $J = 9.2$ Hz), 4.05 (td, 1H, $J = 11.0$, 3.8 Hz), 2.80 (tdd, 1H, $J = 11.0$, 9.2, 3.8 Hz), 2.38 (s, 3H); minor (*E*) isomer: δ 6.63 (d, 1H, $J = 9.4$ Hz), 4.02 (td, 1H, $J = 11.0$, 3.8 Hz), 3.25 (tdd, 1H, $J = 11.0$, 9.4, 3.8 Hz), 2.39 (s, 3H); the following peaks are overlapping both isomers:7.35–7.10 (m, 4H), 2.55 (br d, 1H, $J = 11.0$ Hz), 2.20–1.30 (m, 7H); ^{13}CNMR ($CDCl_3$): δ 156.6, 139.0, 130.9, 128.9, 127.5, 56.3, 52.1, 40.0, 39.9, 35.4, 34.8, 33.6, 32.3, 28.3, 24.9, 24.8, 21.4. Integration of the alkene peaks revealed that this product is a 69:31 *Z*:*E* mixture.

*Preparation of carbene complex **4k** and subsequent reaction with iodine*. General procedure 2 was followed using carbene acylate **1b** (0.533 g, 1.37 mmol), ethanethiol (0.101 mL, 1.37 mmol), and acetyl chloride (0.097 mL, 1.37 mmol). After chromatographic purification a

red solid identified as carbene complex **4k** (0.494 g, 41% yield). The NMR spectrum of this compound was significantly broadened; this material was utilized immediately in the next reaction. General procedure 3 was followed using carbene complex **4k** (0.111 g, 0.31 mmol) and iodine (0.082 g. 0.032 mmol). After chromatographic purification a colorless oil identified as compound **27k** (0.107 g, 82% yield) was obtained. Diiodide **27k**: ^{1}H NMR ($CDCl_3$): major (*Z*) isomer δ 5.85 (d, 1H, $J = 8.9$ Hz), 3.92 (td, 1H, $J = 11.0$, 4.0 Hz); minor (*E*) isomer: 6.43 (d, 1H, $J = 9.5$ Hz), 3.89 (td, 1H, $J = 11.0$, 4.0 Hz) 3.09 (tdd, 1H, $J = 11.0$, 9.5, 4.0 Hz); the following peaks are overlapping in both isomers: δ 2.85–2.58 (m, 3.5H), 2.48 (dq, 1H, $J = 11.0$, 4.0 Hz), 2.20–1.05 (m, 6H) overlapping with 1.25 (t, 3H, $J = 7.4$ Hz – two sets of lines); ^{13}CNMR (ppm): 154.6, 147.4, 95.2, 90.6, 77.6, 76.9, 76.3, 56.0, 51.7, 39.9, 39.8, 35.6, 34.9, 33.1, 32.3, 32.0, 30.6, 28.2, 24.8, 14.9, 14.3; MS (EI): 422 (M^+, 6), 336 (2), 295 (100), 227 (40), 167 (29), 127 (30); HRMS: calcd for $C_{10}H_{16}I_2S$ 421.90622, found 421.9067. Integration of the alkene peaks revealed that this product is a 51:49 *Z*:*E* mixture.

*Preparation of carbene complex **4l** and subsequent reaction with iodine*. General procedure 2 was followed using carbene acylate **1b** (0.314 g, 0.81 mmol), 2-propanethiol (0.075 mL, 0.81 mmol), and acetyl chloride (0.057 mL, 0.81 mmol). After chromatographic purification a red solid identified as carbene complex **4l** (0.092 g, 36% yield). The NMR spectrum of this compound was significantly broadened; this material was utilized immediately in the next reaction. General procedure 3 was followed using carbene complex **4l** (0.078 g, 0.24 mmol) and iodine (0.064 g. 0.025 mmol). After chromatographic purification a colorless oil identified as compound **27l** (0.092 g, 87% yield) was obtained. Diiodide **27l**: ^{1}H NMR ($CDCl_3$): major (*Z*) isomer: δ 5.87 (d, 1H, $J = 8.9$ Hz), 4.02 (td, 1H, $J = 11.0$, 4.0 Hz), 2.72 (tdd, 1H, $J = 11.0$, 8.9, 4.0 Hz); minor (*E*) isomer: δ 6.42 (d, 1H, $J = 9.4$ Hz), 3.91 (td, 1H, $J = 11.0$, 4.0 Hz), 3.09 (tdd, 1H, $J = 11.0$, 9.4, 4.0 Hz); the following peaks are overlapping in both isomers: δ 3.26 (septet, 1H, $J = 6.5$ Hz), 2.47 (dq, 1H, $J = 11.0$, 4.0 Hz), 2.15–1.50 (m, 6H), 1.40–1.18 (m, 6H); ^{13}CNMR ($CDCl_3$): δ 154.8, 149.1, 100.8, 95.1, 56.2, 51.7, 41.8, 49.9, 39.9, 39.8, 35.7, 34.8, 33.3, 32.3, 28.2, 24.8, 23.1, 22.9, 22.2, 21.6; Mass Spec (EI): 436 (M^+, 10), 309 (100), 267 (54), 199 (48), 139 (53); HRMS: calcd for $C_{11}H_{18}I_2S$ 435.9219, found 435.9256. Integration of the alkene peaks revealed that this product is a 52:48 *Z*:*E* mixture.

*Reaction of alkoxycarbene complex **44** with iodine*. General procedure 3 was followed using carbene **44** (0.080 g, 0.29 mmol) and iodine (0.083 g, 0.33 mmol). Chromatographic purification using 19:1 hexane: ethyl acetate afforded a colorless compound identified as iodoester **46** (0.029 g, 41% yield). Methyl 4-iodobutanoate (**46**): ^{1}H NMR ($CDCl_3$): δ 3.67 (s, 3H), 3.22 (t, 2H, $J = 6.7$ Hz), 2.40 (t, 2H, $J = 7.0$ Hz), 2.11 (tt, 2H, $J = 7.0$, 6.7 Hz). The spectral data were consistent with those previously reported for this compound [40].

*Reaction of carbene complex **47** with iodine*. General procedure 3 was followed using carbene complex **47** [25] (0.073 g, 0.222 mmol) and iodine (0.059 g, 0.233 mmol). Chromatographic purification afforded a colorless compound identified as 1-iodo-1-thiophenylethylene (**48**) (0.0257 g, 44% yield). The product turns black upon brief standing at room temperature. 1-iodo-1-thiophenylethylene (**48**). ^{1}H NMR ($CDCl_3$): δ 7.56–7.39 (m, 5H), 6.34 (d, 1H, $J = 2.1$ Hz), 6.09 (d, 1H, $J = 2.1$ Hz), ^{13}C NMR ($CDCl_3$): δ 132.5, 130.0, 129.4, 128.7, 127.6, 95.1; IR (CH_2Cl_2): 3156 (m), 3056 (w), 1644 (m), 1465 (vs), 1381 (m), 1263 (m), 1100 (m) cm^{-1}: Mass Spec (CI): 262 (M, 6), 135 (100), 134 (37), 127 (60), 110 (59), 109 (57): HRMS: Calc for C_8H_7IS 261.9313, found 261.9331.

*Reaction of carbene complex **49** with iodine*. General procedure 3 was followed using carbene complex **49** [15] (0.331 g, 0.849 mmol) and iodine (0.216 g, 0.849 mmol). Chromatographic purification afforded a colorless solid identified as 1,2-bis(thiophenyl)stilbene (**50**) (0.088 g, 56% yield). 1,2-bis(thiophenyl)stilbene (**50**). mp 54–55 °C. ^{1}H NMR ($CDCl_3$): δ 8.08–8.02 (m, 4H), 7.62 (m, 2H), 7.45–7.42 (m, 14H); ^{13}C NMR ($CDCl_3$): δ 189.9, 136.6, 135.0, 133.5, 129.4, 129.1, 128.7, 127.4; IR (CH_2Cl_2): 3069 (s), 3038 (w), 1681 (vs), 1581 (s), 1450 (s), 1206 (s), 1175 (s), 1025 (m); Mass Spec (EI): 396 (M^+, 89), 287 (52), 210 (43), 178 (65), 105 (100); HRMS: calcd for $C_{26}H_{20}S_2$ 396.1001, found 396.0994. Note: The Carbon-13 spectrum for this compound has been calculated and the peak at δ 189.9 is not consistent with the proposed structure. We however feel that in a compound where the NMR is of such limited utility (all protons/carbons aromatic), the mass spectrum is the best indication of structure. High resolution analysis of key fragment ions is also consistent with this structure. Peak at 289 ($M-C_6H_5S$): calcd for $C_{20}H_{15}S$ 287.0894, found 287.0918. Peak at 178 (diphenylacetylene): calcd for $C_{14}H_{10}$ 178.0782, found 178.1770.

*Sonogashira coupling of diiodide **27a** with 1-hexyne*. A mixture of diiodide **27a** (0.150 g, 0.361 mmol), palladium chloride (0.005 g, 0.028 mmol), triphenylphosphine (0.010 g, 0.038 mmol), 1-hexyne (0.22 mL, 1.901 mmol), and copper(I) iodide (0.007 g, 0.037 mmol) in diethylamine (5 mL) was stirred for 20 h at 45 °C. The solvent was evaporated, and the residue was dissolved in ethyl acetate. The resulting suspension was filtered through Celite and solvent was removed on a rotary evaporator. Flash chromatography of the residue using pure hexane as the eluent afforded a colorless oil identified as dienyne **51** (0.080 g, 92% yield). This oil quickly darkened. Dienyne **51**. ^{1}H NMR ($CDCl_3$): δ 7.41 (br d, 2H, $J = 6.4$ Hz), 7.31 (m, 3H), 6.78 (dt, 1H, $J = 17.2$, 10.4 Hz), 6.48 (d, 1H, J = 10.4 Hz), 5.27 (d, 1H,

$J = 17.2$ Hz), 5.19 (d, 1H, $J = 10.4$ Hz), 2.28 (t, 2H, $J = 6.8$ Hz), 1.38 (quintet, 2H, $J = 6.8$ Hz), 1.26 (sextet, 2H $J = 6.8$ Hz), 0.83 (t, 3H, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$): δ 137.3, 134.4, 133.4, 132.5, 129.0, 127.8, 120.1, 119.1, 99.6, 76.7, 30.6, 22.0, 19.5, 13.8. Mass Spec (ESI): 265 (M + Na).

*Stille coupling of diiodide **17a** and tributyl(phenylethynyl)stannane*. Diiodide **27a** (0.250 g, 0.600 mmol) was dissolved in DMF (5 mL) at 25 °C. To the solution was added bis(acetonitrile)palladium(II) chloride (0.008 g, 0.03 mmol) and the solution was stirred for 5 min at 25 °C. Tributyl(phenylethynyl)stannane (0.282 g, 0.721 mmol) was added and the solution immediately turned black. The reaction was stirred an additional 30 min and the diluted with ether (25 mL). The mixture was placed in a separatory funnel and washed with water. The ether layer was dried over sodium sulfate and the solvent was removed on a rotary evaporator. The residue was purified by flash chromatography on silica gel using pure hexane as the eluent. Three fractions were isolated. The product in the first fraction was the starting alkynylstannane (0.025 g, 6% recovery). The product in the second fraction was the starting diiodide **27a** (0.105 g, 46% recovery). The product in the third fraction was identified as enyne **51** (0.084 g, 34% yield). Enyne **51**: ^{1}H NMR ($CDCl_3$): δ 7.49–7.62 (m, 2H), 7.38–7.21 (m, 8H), 6.16 (t, 1H, $J = 7.3$ Hz), 3.23 (t, 2H, $J = 7.3$ Hz), 3.02 (q, 2H, $J = 7.3$ Hz); ^{13}C NMR ($CDCl_3$): δ 139.4, 132.1, 131.5, 128.9, 128.6, 128.2, 127.6, 122.4, 119.7, 96.3, 90.0, 84.7, 35.3, 3.0; Mass Spec (EI): 390 (M^+, 29), 263 (100), 254 (34), 218 (14), 153 (25), 152 (19), 129 (54), 127 (25), 109 (32); HRMS: calcd for $C_{18}H_{15}IS$ 389.9939, found 389.9936.

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