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# An unusually robust triple bond: synthesis, structure and reactivity of 3-alkynylcyclopropenes

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**Abstract**—Several 1,2-diphenyl- and 1,2,3-triphenyl-3-alkynylcyclopropenes have been prepared in moderate to very good yields by the reaction of acetylenic nucleophiles with the appropriate cyclopropenylium salt. Single crystal X-ray structures of four of the cyclopropenes were obtained. Stereoselective reduction of the triple bond failed in all cases, whereas model compounds lacking the cyclopropene moiety were reduced successfully. A rational for this lack of reactivity is proposed. The solution-phase thermochemistry of the 3-alkynyl-1,2,3-triphenylcyclopropenes was explored, affording 3-alkynyl-1*H*-indenes in moderate to good yields.


## 1. Introduction

Recently we described the syntheses of an iridabenzene[1] and an iridabenzene valence isomer[2] starting from a nucleophilic 3-vinylcyclopropene.[3] Key to this new technique was stereospecific preparation of the requisite organic ligand, a (*Z*)-3-(2-iodoethenyl)cyclopropene (**1**). Although this cyclopropene could be prepared in high yield and excellent stereoselectivity,[1] we sought additional versatile routes for ligand synthesis. As an alternative to the Wittig approach, we presumed that selective reduction of a triple bond (Fig. 1) could be a viable method to access the needed ligands since a number of stereospecific and high yielding reagents have been reported in recent years.[4] This pathway was particularly attractive in our studies because of the ease of preparing the ethynylcyclopropene precursors. Although reports of 3-alkynylcyclopropenes are limited,[5] there are many preparations of cyclopropenes involving cyclopropenylium ions and various nucleophiles.[6] Cyclopropenylium ions are highly electrophilic and their reactions with nucleophiles ordinarily proceed in high yields.[7] We surmised that reaction of an acetylenic Grignard reagent with a cyclopropenylium ion, stereoselective reduction of the triple bond, and halodesilation[8] of the terminal substituent would give the (*Z*)-3-(2-haloethenyl)cyclopropenes needed for metallabenzene and valence isomer formation. We report herein the synthesis of a family of 3-alkynylcyclopropenes, their solid-state structures, and the surprising inertness of the triple bond towards reduction. We also describe the thermal reactivity of several derivatives.

## 2. Results and discussion

### 2.1. Cyclopropene synthesis

For our studies we focused on the use of 1,2,3-triphenylcyclopropenylium bromide (**2a**)[9] and 1,2-diphenylcyclopropenylium perchlorate (**2b**)[10] as the synthesis and chemistry of these salts is well delineated.[7] For example, treatment of **2a** with the appropriate acetylenic nucleophile in THF at −78 °C afforded cyclopropenes **3a** and **4a** in very good yields (Scheme 1). The trimethylsilyl group of **3a** was removed readily by $K_2CO_3$ in MeOH and $Et_2O$ to give the

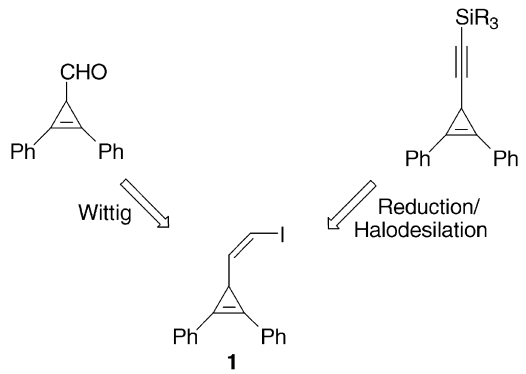


**Figure 1.** Synthetic approaches to (*Z*)-3-(2-haloethenyl)cyclopropenes.

*Keywords*: Alkynes; Cyclopropenes; Strained compounds; Thermochemistry.
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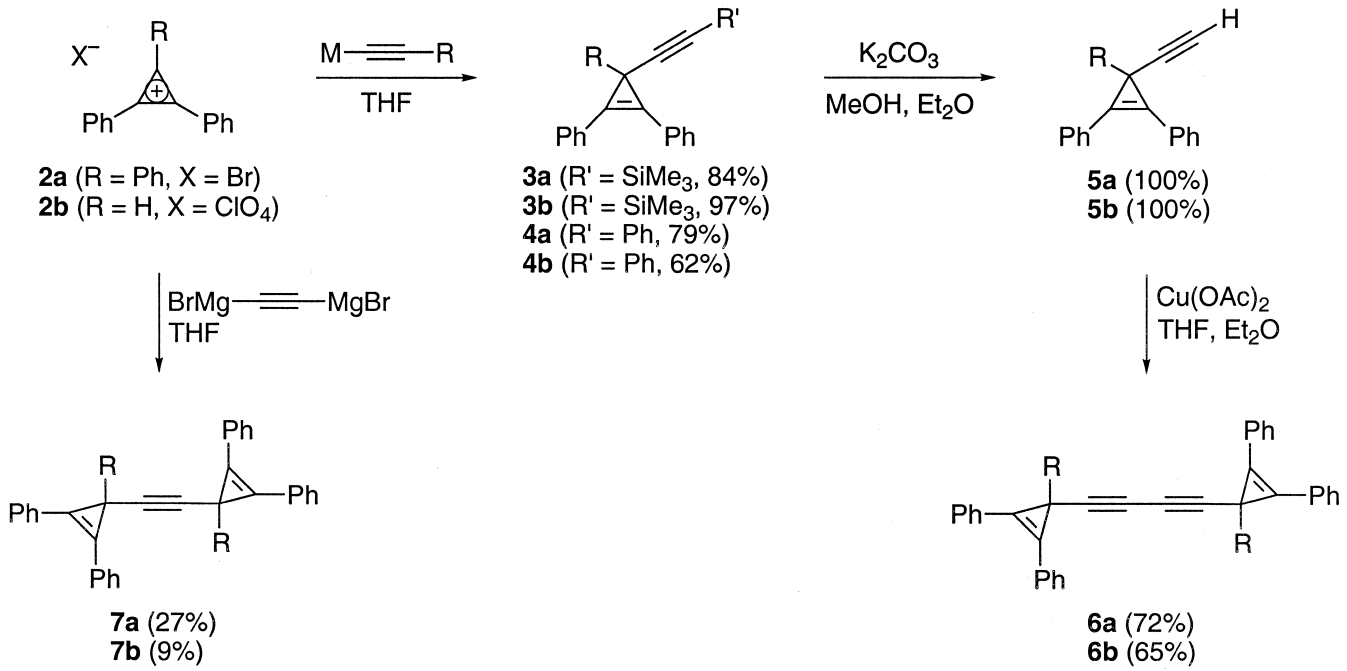



**Scheme 1.**

terminal acetylene **5a** in quantitative yield. Cyclopropene **5a** was then converted into a 1,4-bis(cyclopropenyl)-1,3-butadiyne system (**6a**) using a modified Eglinton–Glaser reaction.[11] The corresponding ethynyl-linked biscyclopropene **7a** was prepared in modest yield by treating **2a** with 0.5 equiv. of ethynyldimagnesium dibromide. The synthesis of the corresponding diphenylcyclopropenes **3b**–**7b**, which proceeded in an analogous fashion, has been described previously.[12]

## 2.2. Solid-state structures

Owing to the highly unsaturated and inherently reactive nature of cyclopropenes, we obtained single crystal X-ray structures for several derivatives (**3a**, **4b**, **6b**, **7a**). The molecular structures of **3a** and **4b** are shown in Figure 2.

**Table 1**. Selected bond lengths (Å) and bond angles (deg) for 3-alkynylcyclopropenes **3a**, **4b**, **6b**, **7a**, and the parent molecule

| | Parent[a] | 3a | 4b | 6b | 7a[b] |
|---|---|---|---|---|---|
| C(1)–C(2) | 1.278(2)[c] | 1.290(2) | 1.297(2) | 1.297(3) | 1.302(3) |
| C(1)–C(3) | 1.500(2) | 1.515(2) | 1.517(2) | 1.507(3) | 1.527(4) |
| C(2)–C(3) | 1.502(2) | 1.525(2) | 1.514(2) | 1.516(3) | 1.529(3) |
| C(3)–C(4) | 1.448(2) | 1.462(2) | 1.444(2) | 1.447(3) | 1.472(3) |
| C(4)–C(5) | 1.184(2) | 1.198(2) | 1.200(3) | 1.200(3) | 1.208(5)[d] |
| C(5)–R′ | [e] | 1.827(2) | 1.432(2) | 1.387(4) | [e] |
| C(1)–C(2)–C(3) | 65.2(1) | 64.5(1) | 64.8(1) | 64.3(2) | 64.7(2) |
| C(1)–C(3)–C(2) | 49.1(1) | 50.2(1) | 50.7(1) | 50.8(1) | 50.5(2) |
| C(1)–C(2)–C(Ph) | [e] | 154.6(2) | 153.1(1) | 154.6(2) | 151.5(3) |
| C(2)–C(1)–C(Ph) | [e] | 153.8(2) | 154.7(1) | 155.2(2) | 152.2(3) |
| C(3)–C(4)–C(5) | 179.0(1) | 178.1(2) | 175.9(1) | 178.6(2) | 177.0(4)[d] |
| C(4)–C(5)–R′ | [e] | 177.2(2) | 174.8(1) | 179.8(2) | [e] |

[a] Ref. 5e.
[b] Averages values for two independent molecules.
[c] Libration corrected value; see Ref. 5f.
[d] C(4)–C(4A) in **7a**.
[e] No comparable value.

Selected bond lengths and angles for all four systems, as well as comparison with the analogous values in the $C_5$ parent 3-ethynylcyclopropene,[5e] are given in Table 1. Typical of cyclopropenes in the solid state,[13] the carbon–carbon double bond lengths in the phenyl substituted derivatives are quite short (1.290–1.302 Å) and the $sp^3$ bond angles about C3 (50.2–50.8°) are highly constrained. The carbon–carbon triple bond lengths are in the normal range (1.198–1.208 Å). Almost all these values are longer or greater than in 3-ethynylcyclopropene,[5e] (C=C 1.255 Å, C≡C 1.184 Å, C1–C3–C2 49.4°), even if libration corrected values are considered.[5f] These increases are clearly due to the phenyl substituents which not only reduce the libration but also release the electron concentration and thus relieve some of the tension in the highly strained parent molecule.

Interestingly, the packing diagrams for **6b** and **7a** show several close intermolecular C–H···π contacts. For **6b**, the hydrogen on C3 sits 2.69 Å above/below the π-bond of the cyclopropene ring in the next molecule (Fig. 3). The intermolecular H3–C4 distance in **6b** is also quite short (2.78 Å). These contacts result in a packing motif that is reminiscent of one necessary for a topochemical diacetylene polymerization. However, H3 pushes the neighboring diynes apart, thus yielding 1,4-polymerization parameters ($d$=5.43 Å, $\gamma$=53°, and $S_1$=3.81 Å) that are somewhat outside the range typically observed for such monomers ($d$≈5 Å, $\gamma$≈45°).[14]

The crystal packing in **7a** is considerably more complex (Fig. 4). The individual molecules alternate their orientation and are offset with respect to one another. This arrangement is such that one of the *meta* protons of a cyclopropenyl phenyl group is pointed into the π-bond of a neighboring cyclopropenyl unit with a C–H···π contact of 2.72 Å (center of the double bond). In addition, the *ortho* and *para*

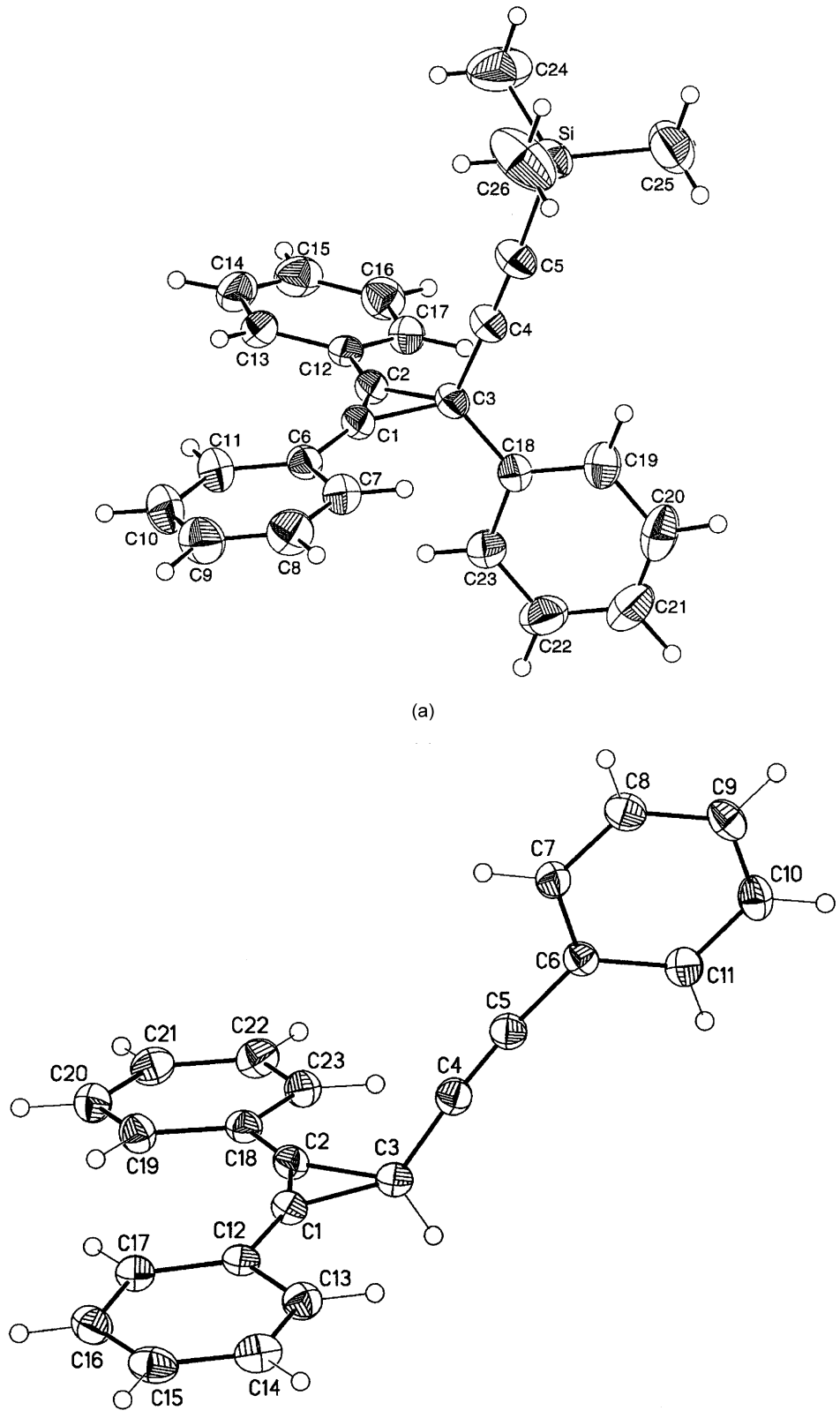



**Figure 2.** Molecular structures of cyclopropenes **3a** (top) and **4b** (bottom).

protons on the same cyclopropenyl phenyl group possess short C–H···π contacts (3.24 and 3.47 Å) with the two phenyl rings that are attached to the same neighboring cyclopropenyl unit.

### 2.3. Attempted reduction

With a number of 3-alkynylcyclopropenes now available, we attempted the stereospecific reduction of the triple bond.

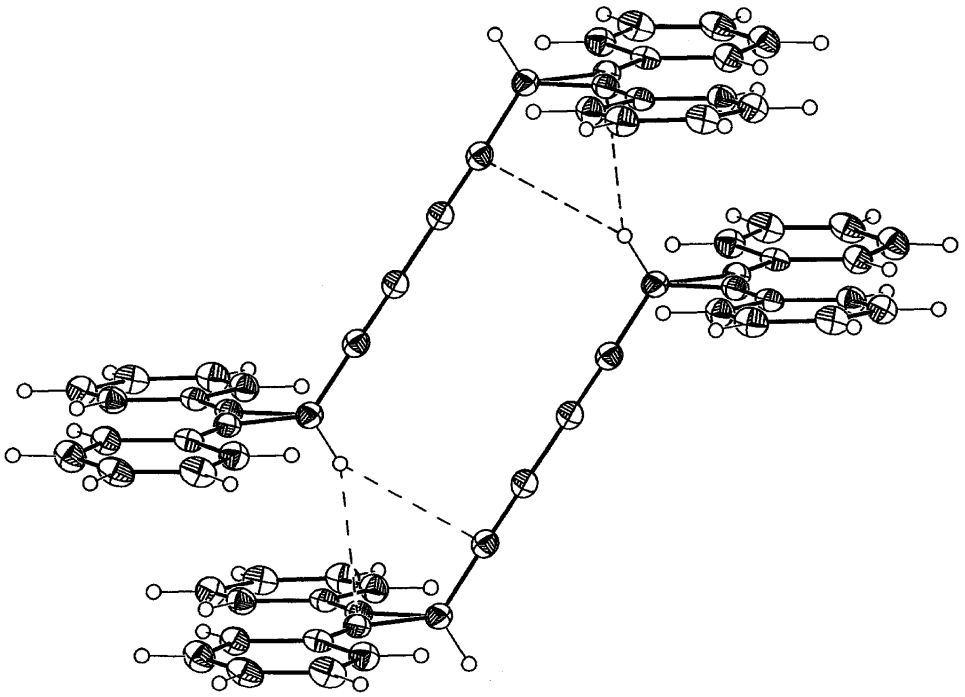


**Figure 3.** Crystal packing of cyclopropene **6b**.

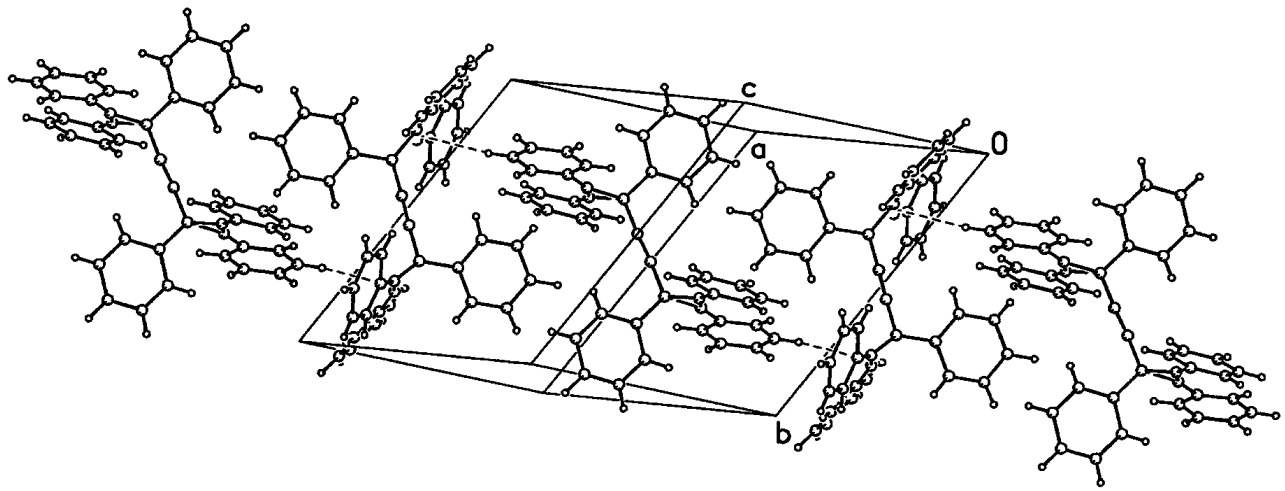
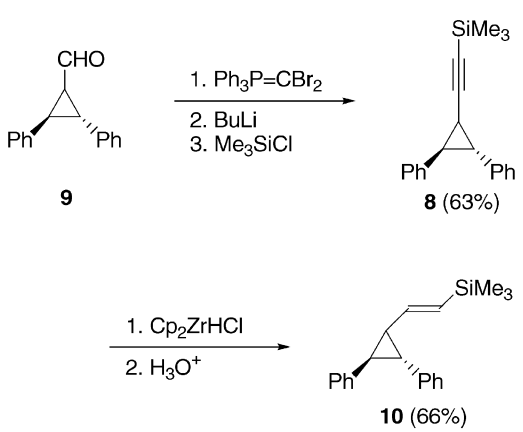



**Figure 4.** Crystal packing of cyclopropene **7a**.

Reaction of **3a** with Schwartz's reagent ($Cp_2ZrHCl$)[15] followed by aqueous work-up resulted in complete recovery of starting material. Use of '$Cp_2TiH$', generated in situ from $Cp_2TiCl_2$ and *i*-BuMgBr,[16] also resulted in recovery of **3a**. Careful hydrogenation with Lindlar's catalyst faired no better as the cyclopropene double bond was reduced preferentially. DIBAL-H (in a variety of solvents and temperatures) and $LiAlH_4$, both of which would give the undesired *E*-geometry, either failed to work or reduced the double bond preferentially. Examination of Figure 2(a) suggested that steric bulk might be the culprit for the unreactivity[17] and that use of **3b**, missing the Ph substituent at C3, would be more suitable. Unfortunately, exposure of **3b** to the various reagents and conditions described above also led to recovery of starting material or over-reduced products.



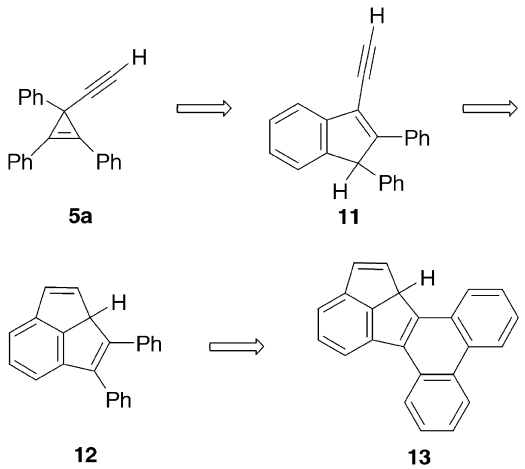

**Scheme 2.**

To what then can this surprising inertness of the triple bond in **3** be ascribed? Reagents and reaction conditions were ruled out as repetition of the above experiments with both (1-hexynyl)trimethylsilane and (2-phenylethynyl)trimethylsilane gave in every instance the correct product from *cis*-reduction ($J$=10–11 Hz). This result then suggested that electronics, and not sterics, were the cause of the unreactivity of the triple bond. To confirm this hypothesis, we prepared alkyne **8** (Scheme 2), the cyclopropane analog of **3b**. Exposure of aldehyde **9**[18] to the Corey–Fuchs procedure[19] and quench of the resultant acetylide ion with $Me_3SiCl$ gave **8** in 63% yield. Treatment of **8** with either $Cp_2ZrHCl$ or '$Cp_2TiH$' followed by aqueous work-up resulted in complete, stereospecific reduction of the triple bond, furnishing alkene **10** in 66% yield. Surprisingly, the expected *Z*-geometry about the double bond was instead *E*-, based on an alkene coupling constant of 14.2 Hz. Isomerization of *Z*-alkenylsilanes to *E*- is a relatively facile process, and we have encountered this problem before while investigating alternative syntheses of *Z*-2-(cyclopropenyl)ethenylsilanes.[20]

One possible explanation for the lack of reactivity of the triple bond in the alkynylcyclopropenes is due to hyperconjugation. The σ-bond to an sp hybridized carbon might be a reasonably good hyperconjugative electron acceptor for delocalization of the electron pair in the cyclopropenyl π-bond, since a resonance structure that is $(\text{cyclopropenium})^+$ $(\text{alkyne})^-$ seems reasonable. This in turn deactivates the triple bond to attack of the electrophilic reagents. Such hyperconjugation has been shown to occur in both difluorocyclopropanes[21] and fluorocyclopropenes.[22] Unfortunately, high level theoretical calculations on our molecules have not been illuminating.

## 2.4. Thermochemistry

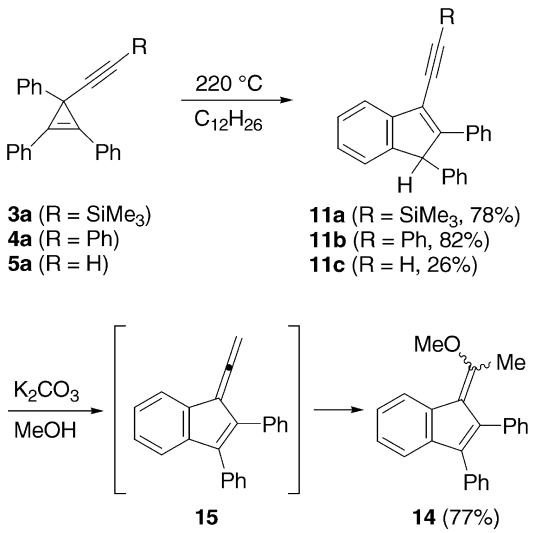
Given the current interest in 'buckybowls' and other related fullerene fragments,[23] we investigated the thermal chemistry of the 3-alkynyl-1,2,3-triphenylcyclopropenes as they might permit access to novel polycyclic aromatic hydrocarbons. After initially opening to the vinylcarbene,[6a,24] the alkynylated systems should undergo C–H insertion on the phenyl at C3 to yield indenes[25] such as **11** (Scheme 3).




**Scheme 3.**

Unlike the related 3-vinylcyclopropenes, which furnish cyclopentadienes via electrocyclic ring closure (in addition to indenes),[26] the distal alkyne carbon is too remote to undergo analogous reactivity.[5d] Brown rearrangement[23a] (vinylidene formation and subsequent C–H insertion) could lead to the cyclopent[cd]indene skeleton (**12**),[27] or with sufficient energy (pyrolysis or photolysis), to indene/phenanthrene hybrid **13**.[28]

Our initial attempts focused on the thermolysis of **3a**–**5a**. DSC analysis showed that these molecules underwent exothermic reaction around 225 °C. Heating dodecane solutions of the cyclopropenes to 220 °C for 2 h proceeded with complete conversion to indenes **11a**–**11c** (Scheme 4).[28] These compounds result from insertion of the resultant vinylcarbene into one of the *ortho* C–H bonds of the Ph substituent on C3 in **5**. Interestingly, indenes **11** do not undergo sigmatropic rearrangement under the reaction conditions to give the corresponding indenes with the double bond residing between the two Ph substituents, which would be the expected, thermodynamically preferred double bond configuration.[29] In an attempt to prepare a larger quantity of **11c**, desilylation of **11a** with $K_2CO_3$ in $MeOH/Et_2O$ unexpectedly furnished methoxyfulvene **14** as the sole product, isolated in 77% yield as a 14:1 mixture of regioisomers. This presumably occurs by base-induced isomerization to form unstable vinylidene **15**,[30] which then is attacked by the nucleophilic base and subsequently protonated. This instability/facile isomerization is possibly why **11c** was produced in low yield. Unfortunately, neither **12** nor **13** were observed in our experiments. Formation of these compounds will likely require temperatures greater than 500 °C, attainable only by flash vacuum pyrolysis.




**Scheme 4.**

## 3. Conclusions

In summary, we have prepared in very good yield a family of 3-ethynylcyclopropenes by the reaction of cyclopropenylium salts with acetylenic nucleophiles. The X-ray crystal structures of four of these compounds were determined, exhibiting short carbon–carbon double bonds and highly constrained bond angles at C3, both attributable to the

strained nature of the three-membered ring. Attempts to reduce the carbon–carbon triple bond in a stereoselective fashion failed to give the desired products, likely due to electronic effects resulting from hyperconjugation of the cyclopropene with the alkyne moiety. Thermolysis of the cyclopropenes gave alkynylindenes, the product of ring-opening with C–H insertion on the Ph substituent on C3. Treatment of the silyl-protected indene with base afforded an unstable vinylideneindene which reacted further to furnish a benzofulvene. Future studies will be directed toward the high temperature pyrolysis of the alkynylindenes and stereoselective reduction of alkynylstannanes.

## 4. Experimental

### 4.1. General

$^1$H and $^{13}$C NMR spectra were recorded in either $CDCl_3$ or $CD_2Cl_2$ using a Varian Inova 300 NMR ($^1$H: 299.94 MHz, $^{13}$C: 75.43 MHz) spectrometer Chemical shifts ($\delta$) are expressed in ppm downfield from $SiMe_4$ using the residual solvent as internal standard ($CDCl_3$–$^1$H: 7.27 ppm, $^{13}$C: 77.0 ppm; $CD_2Cl_2$–$^1$H: 5.32 ppm, $^{13}$C: 54.0 ppm). Coupling constants are expressed in Hz. IR spectra were recorded using a Nicolet Magna-FTIR 550 spectrometer. Melting points were determined on a Meltemp II apparatus and are uncorrected. DSC analyses were performed using a TA Instruments DSC 2920. Elemental analyses were performed by Robertson Microlit Laboratories, Inc.

Triphenylcyclopropenylium bromide (**2a**)[9] was prepared according to the literature. All other reagents were purchased from commercial suppliers and used as received. $CH_2Cl_2$ and pyridine were distilled from $CaH_2$ under an $N_2$ atmosphere prior to use. $Et_2O$ and THF were distilled from Na/benzophenone ketyl immediately prior to use. All other chemicals were of reagent quality and used as obtained from the manufacturers. Column chromatography was performed on Whatman reagent grade silica gel (230–400 mesh). Rotary chromatography was performed on a Chromatotron using silica gel (60 $PF_{254}$) plates (1–4 mm). Baker pre-coated silica gel plates were used for analytical (200×50×0.25 mm$^3$) thin layer chromatography. Reactions were carried out in an inert atmosphere (dry $N_2$ or Ar) when necessary.

**4.1.1. 3-(Trimethylsilylethynyl)-1,2,3-triphenylcyclopropene (3a).** Ethylmagnesium bromide was prepared from magnesium (0.30 g, 12 mmol) and dropwise addition of bromoethane (1.30 g, 12 mmol) in THF (20 mL). Once the addition of bromoethane was complete, the reaction was heated at reflux for 20 min. The suspension was then cooled to 0 °C under an atmosphere of $N_2$ and ethynyltrimethylsilane (1.38 g, 14 mmol) was added quickly via syringe. The resulting gray suspension was stirred at 0 °C for 15 min with the evolution of ethane gas. The mixture was then warmed to ambient temperature and stirred for an additional 15 min. THF (10 mL) was added to dissolve the solids.

In a separate flask triphenylcyclopropenyl bromide (**2a**, 869 mg, 2.5 mmol) in THF (175 mL) was cooled to −78 °C under $N_2$. The solution of alkynylmagnesium bromide was added to the cold suspension of **2a** using a double-ended needle under $N_2$ pressure over a 5 min period. The flask was rinsed with THF (10 mL) and the rinse was added to the suspension of **2a**. After stirring at −78 °C for 1 h, the cooling bath was removed and the mixture was stirred at ambient temperature for 12 h. Excess Grignard reagent was quenched with saturated aqueous $NH_4Cl$. The mixture was extracted with $Et_2O$, the phases were separated, and the aqueous phase was extracted again with $Et_2O$. The combined organics were washed with water, saturated $NaHCO_3$ solution, and brine. The organic layer was dried ($MgSO_4$), filtered through celite, and concentrated to give a yellow oil. Purification by preparative radial thin-layer chromatography (2 mm rotor, hexanes) furnished **3a** (765 mg, 84%) as a white solid, mp 150.6 °C (DSC). $^1$H NMR ($CDCl_3$): 7.70 (dd, $J$=7.6, 1.8 Hz, 4H), 7.52–7.34 (m, 8H), 7.26 (t, $J$=7.3 Hz, 2H), 7.18 (t, $J$=7.2 Hz, 1H), 0.18 (s, 9H). $^{13}$C NMR ($CDCl_3$): 142.19, 129.92, 129.88, 128.93, 128.03, 126.39, 126.10, 125.72, 111.79, 108.55, 82.84, 23.93, 0.31. IR (KBr): 2153, 1834. Calcd for $C_{26}H_{24}Si$: C, 85.66; H, 6.64. Found: C, 85.46; H, 6.67.

**4.1.2. 3-(Phenylethynyl)-1,2,3-triphenylcyclopropene (4a).** Use of phenylethyne (1.43 g, 14 mmol) in the procedure described above for **3a** gave after purification compound **4a** (728 mg, 79%) as a white solid, mp 155.5 °C (DSC). $^1$H NMR ($CDCl_3$): 7.76 (dd, $J$=7.9, 1.3 Hz, 4H), 7.60 (d, $J$=7.7 Hz, 2H), 7.51–7.37 (m, 8H), 7.33–7.25 (m, 5H), 7.19 (t, $J$=7.3 Hz, 1H). $^{13}$C NMR ($CDCl_3$): 142.52, 131.81, 131.59, 129.91, 129.84, 128.99, 128.10, 127.45, 126.48, 126.16, 125.80, 124.02, 112.16, 92.35, 78.47, 23.77. IR (KBr): 2215, 1829. Calcd for $C_{29}H_{20}$: C, 94.53; H, 5.47. Found: C, 94.44; H, 5.57.

**4.1.3. 3-Ethynyl-1,2,3-triphenylcyclopropene (5a).** Cyclopropene **3a** (547 mg, 1.5 mmol) was dissolved in $Et_2O$ (8 mL) and MeOH (20 mL). Anhydrous $K_2CO_3$ (221 mg, 1.6 mmol) was added and the resulting suspension was stirred at ambient temperature for 8 h. $Et_2O$ and water were added, the layers separated, and the aqueous phase extracted with $Et_2O$. The combined organics were washed with brine and dried ($MgSO_4$). The suspension was filtered through celite and concentrated to give **5a** (436 mg, 99%) as a pale yellow solid. Recrystallization from hexanes afforded a pure, colorless sample, mp 117.8 °C (DSC). $^1$H NMR ($CDCl_3$): 7.72 (d, $J$=8.0 Hz, 4H), 7.56–7.36 (m, 8H), 7.28 (t, $J$=7.2 Hz, 2H), 7.18 (t, $J$=7.2 Hz, 1H), 2.18 (s, 1H). $^{13}$C NMR ($CDCl_3$): 141.77, 129.86, 129.41, 129.02, 128.12, 126.11, 126.00, 125.88, 111.43, 86.42, 66.16, 22.86. IR (KBr): 3291, 2152, 1834. Calcd for $C_{23}H_{16}$: C, 94.48; H, 5.52. Found: C, 94.41; H, 5.59.

**4.1.4. 1,4-Bis(1,2,3-triphenylcycloprop-2-enyl)-1,3-butadiyne (6a).** Cyclopropene **5a** (117 mg, 0.4 mmol) and $Cu(OAc)_2$ (250 mg, 1.2 mmol) were suspended in pyridine (2 mL), water (1 mL) and dioxane (1 mL). The suspension was warmed with stirring to 45 °C and all solids dissolved to give a blue solution. A precipitate started to form after 20 min at 45–50 °C. After a total of 2 h of stirring at 45–50 °C, during which the blue color gradually changed to green, the flask was cooled to 0 °C and the precipitate was collected by filtration. The tan solid was washed with 10%

HCl solution and water, then dried in vacuo. Recrystallization from benzene (~3 mL) gave **6a** (84 mg, 72%) as small white cubes, mp 229 °C (melt with decomp.). $^1$H NMR ($CD_2Cl_2$): 7.69 (d, $J$=7.7 Hz, 8H), 7.51–7.38 (m, 16H), 7.26 (t, $J$=7.5 Hz, 4H), 7.17 (t, $J$=7.3 Hz, 2H). $^{13}$C NMR ($CD_2Cl_2$): 141.94, 130.39, 130.18, 129.62, 128.86, 126.63, 126.45, 126.32, 111.81, 80.49, 64.11, 24.31. IR (KBr): 2142, 1832. Calcd for $C_{46}H_{30}$: C, 94.81; H, 5.19. Found: C, 94.68; H, 5.41.

**4.1.5. Bis(1,2,3-triphenylcycloprop-2-enyl)ethyne (7a).** A 0.5 M solution of ethynyldimagnesium dibromide in THF was prepared according to the literature.[31] A portion of the solution (1.3 mL, 0.65 mmol) was diluted with THF (40 mL) and cooled to −78 °C under $N_2$. Cyclopropenylium salt **2a** (434 mg, 1.25 mmol) was added to the cold Grignard solution and the reaction was stirred for 2 h. The reaction was warmed to ambient temperature and stirred for an additional 12 h. $Et_2O$ and saturated $NH_4Cl$ solution were added. The phases were separated and the organic phase was washed with saturated $NaHCO_3$ solution, water, and brine. The organic phase was dried ($MgSO_4$), filtered through celite, and concentrated. The residual material was chromatographed (preparative radial thin-layer chromatography, 2 mm rotor, 9:1 petroleum ether/EtOAc) affording a pale yellow solid. Recrystallization from boiling hexanes (~10 mL) yielded **7a** (97 mg, 27%) as white needles, mp 190 °C (melt with decomp.). $^1$H NMR ($CDCl_3$): 7.71 (d, $J$=7.6 Hz, 8H), 7.45–7.32 (m, 12H), 7.19 (t, $J$=7.3 Hz, 4H), 7.10 (t, $J$=7.2 Hz, 2H). $^{13}$C NMR ($CDCl_3$): 143.37, 129.86, 129.02, 128.86, 127.91, 126.82, 126.23, 125.46, 112.58, 80.94, 23.54. IR (KBr): 1828. Calcd for $C_{44}H_{30}$: C, 94.59; H, 5.41. Found: C, 94.61; H, 5.47.

**4.1.6. 2-(*trans*-2,3-Diphenylcyclopropyl)ethynyltrimethylsilane (8).** $CBr_4$ (2.12 g, 6.4 mmol), $PPh_3$ (3.53 g, 13.4 mmol), and dry $CH_2Cl_2$ (25 mL) were combined and stirred at room temperature for 20 min, forming a deep orange-red solution. After cooling to 0 °C, aldehyde **9** (1.34 g, 6 mmol) in $CH_2Cl_2$ (2 mL) was added dropwise and the mixture stirred at 0 °C for 30 min, then room temperature for 3 h. The suspension was diluted with $Et_2O$ (100 mL), filtered through celite, and the solids washed with additional $Et_2O$ (30 mL). After concentration, the residue was passed over a short silica gel column using hexanes (100 mL). Concentration of the solution gave the crude dibromoalkene (1.95 g, 86%) as a viscous yellow oil. $^1$H NMR ($CDCl_3$): 7.41–7.21 (m, 10H), 5.87 (d, $J$=9.0 Hz, 1H), 2.87 (dd, $J$=9.0, 6.2 Hz, 1H), 2.63 (t, $J$=5.7 Hz, 1H), 2.37 (td, $J$=9.0, 5.1 Hz, 1H). $^{13}$C NMR ($CDCl_3$): 140.25, 137.05, 136.66, 128.90, 128.59, 128.54, 126.87, 126.48, 88.07, 33.13, 32.83, 30.43.

To a stirred solution of the above dibromoalkene (1.89 g, 5 mmol) and dry $Et_2O$ (40 mL) at 0 °C was added butyllithium (5 mL, 2.5 M, 12.5 mmol) dropwise. After stirring at 0 °C for 15 additional min, freshly distilled $Me_3SiCl$ (2.17 g, 20 mmol) in $Et_2O$ (3 mL) was added. The mixture was allowed to stir and warm to room temperature over 1 h. The reaction was quenched by addition of saturated $NH_4Cl$ solution (10 mL). The aqueous layer was removed and the organics dried ($MgSO_4$), filtered, and concentrated. Purification by preparative radial thin-layer chromatography (4 mm rotor, hexanes) afforded **8** (1.07 g, 63% from **9**) as a white solid, mp 51.6–52.5 °C. $^1$H NMR ($CDCl_3$): 7.46–7.22 (m, 10H), 2.87 (t, $J$=6.0 Hz, 1H), 2.63 (dd, $J$=8.6, 6.3 Hz, 1H), 2.37 (dd, $J$=8.6, 5.5 Hz, 1H), 0.11 (s, 9H). $^{13}$C NMR ($CDCl_3$): 139.97, 137.15, 128.50, 128.31, 127.75, 126.52, 126.44, 126.23, 104.74, 86.10, 33.47, 33.43, 20.39, −0.14. IR (KBr): 2164, 1598. Calcd for $C_{20}H_{22}Si$: C, 82.70; H, 7.63. Found: C, 82.47; H, 7.67.

**4.1.7. (*E*)-2-(*trans*-2,3-Diphenylcyclopropyl)ethenyltrimethylsilane (10).** Cyclopropane **8** (49 mg, 0.17 mmol) was placed in a flame-dried round bottom flask and dissolved in dry THF (3 mL). $Cp_2ZrHCl$ (53 mg, 0.20 mmol) was added in three portions and the reaction was stirred at room temperature for 1 h. Wet pentane (3 mL) was added to the mixture, which was then stirred for an additional 2 h. Concentration of the mixture and flash chromatography of the residue over silica (hexanes) gave alkene **10** (33 mg, 66%) as colorless oil. $^1$H NMR ($CDCl_3$): 7.42–7.21 (m, 10H), 5.76 (dd, $J$=14.2, 10.1 Hz, 1H), 5.52 (d, $J$=14.2 Hz, 1H), 2.81 (dd, $J$=9.1, 6.1 Hz, 1H), 2.59 (t, $J$=5.6 Hz, 1H), 2.37 (td, $J$=9.6, 5.1 Hz, 1H), 0.19 (s, 9H). $^{13}$C NMR ($CDCl_3$): 146.38, 141.40, 137.84, 129.22, 129.15, 128.49, 128.19, 126.31, 126.22, 125.99, 34.12, 33.07, 31.45, 0.19. HRMS calcd for $C_{20}H_{24}Si$: 292.1647. Found: 292.1653.

**4.1.8. 1,2-Diphenyl-3-(trimethylsilylethynyl)-1*H*-indene (11a).** A solution of cyclopropene **3a** (50 mg, 0.137 mmol) in dodecane (2 mL) was heated in a ~220 °C sand bath for 2 h. The dodecane was removed under vacuum and the residue purified by column chromatography (hexanes/$CH_2Cl_2$, 3:1), giving **11a** (39 mg, 78%) as a beige powder, mp 127.0–127.5 °C. $^1$H NMR ($CDCl_3$): 7.95 (br d, $J$=7.0 Hz, 2H), 7.57 (d, $J$=7.3 Hz, 1H), 7.39–7.09 (m, 11H), 5.13 (s, 1H), 0.36 (s, 9H). $^{13}$C NMR ($CDCl_3$): 152.20, 146.74, 143.04, 139.94, 133.53, 128.83, 128.28, 128.04, 127.96, 127.94, 127.18, 126.78, 126.33, 123.54, 121.39, 120.49, 103.83, 100.17, 56.78, −0.06. IR (KBr): 2140, 1596. Calcd for $C_{26}H_{24}Si$: C, 85.66; H, 6.64. Found: C, 85.53; H, 6.48.

**4.1.9. 1,2-Diphenyl-3-(phenylethynyl)-1*H*-indene (11b).** Thermolysis of **4a** (60 mg, 0.163 mmol) as described above gave **11b** (49 mg, 82%) as a light yellow powder, mp 148.5–149.1 °C. $^1$H NMR ($CDCl_3$): 8.05 (d, $J$=8 Hz, 2H), 7.76–7.69 (m, 3H), 7.52–7.36 (m, 6H), 7.32–7.20 (m, 8H), 5.25 (s, 1H). $^{13}$C NMR ($CDCl_3$): 151.42, 146.87, 143.19, 139.97, 134.77, 131.73, 128.83, 128.46, 128.28, 128.18, 127.95, 127.88, 127.20, 126.77, 126.36, 123.26, 120.48, 97.40, 84.71, 56.91. IR (KBr): 2203, 1597. Calcd for $C_{29}H_{20}$: C, 94.53; H, 5.47. Found: C, 94.26; H, 5.33.

**4.1.10. 1,2-Diphenyl-3-ethynyl-1*H*-indene (11c).** Thermolysis of **5** (50 mg, 0.171 mmol) as described above gave **11c** (13 mg, 26%) as a pale yellow solid, mp 113–114 °C. $^1$H NMR ($CDCl_3$): 7.96 (d, $J$=7.2 Hz, 2H), 7.79 (d, $J$=7.8 Hz, 1H), 7.40–7.25 (m, 4H), 7.21–7.08 (m, 7H), 5.01 (s, 1H), 2.24 (s, 1H). $^{13}$C NMR ($CDCl_3$): 152.23, 146.17, 143.21, 140.79, 134.49, 129.66, 128.01, 128.07, 128.17, 127.70, 127.02, 126.36, 123.37, 121.23, 120.02, 103.03, 101.32, 59.93. IR (KBr): 3297, 2142, 1597. Calcd for $C_{23}H_{16}$: C, 94.48; H, 5.52. Found: C, 94.27; H, 5.41.

**4.1.11. 1-(α-Methoxyethylidene)-2,3-diphenylindene (14).** Indene **11a** (29 mg, 0.08 mmol) was subjected to the protiodesilylation reaction conditions described for the preparation of **5a**. Purification of the crude material by column chromatography (hexanes/$CH_2Cl_2$, 1:1) furnished **14** (20 mg, 77%) as a yellow solid, mp 170.5–171.0 °C. $^1$H NMR ($CDCl_3$): 8.21 (br d, $J$=7.0 Hz, 1H), 7.39 (br d, $J$=7.3 Hz, 1H), 7.33–7.16 (m, 12H), 3.97 (s, 3H), 1.91 (s, 3H). $^{13}$C NMR ($CDCl_3$): 162.26, 140.17, 138.57, 137.43, 137.27, 135.71, 135.06, 130.60, 129.83, 127.94, 127.72, 126.63, 126.23, 125.29, 124.96, 124.25, 120.85, 119.48, 55.02, 15.97. IR (KBr): 2935, 2840, 1610, 1592. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.61; H, 6.07.

### 4.2. X-ray crystal structures

Data for **3a** were obtained on an Enraf-Nonius CAD-4 Turbo diffractometer; solution and refinement (C atoms anisotropic, H atoms riding) were accomplished with teXsan (v. 1.7 for SGI workstations). Data for **4b**, **6b**, and **7a** were obtained on a Siemens SMART diffractometer; solution and refinement (C atoms anisotropic, H atoms riding) were performed on $F^2$ with SHELXTL program suite (v. 5.03). Crystallographic data (excluding structure factors) for the reported structures have been deposited with the Cambridge Crystallographic Data Center as supplementary publications no. CCDC-217174 (**3a**), 216916 (**4b**), 216917 (**6b**), and 216918 (**7a**).

**4.2.1. Compound 3a.** $C_{26}H_{24}Si$, $M_r$=364.56, colorless tablet, 0.20×0.05×0.04 mm$^3$, monoclinic, space group $P2_1/c$, $a$=3.8508(2), $b$=21.5422(3), $c$=21.4937(8) Å, $\beta$=91.860(2)°, $V$=1782.06(9) Å$^3$, $Z$=4, $\rho_{calc}$=1.298 g cm$^{-3}$, Mo $K_\alpha$ radiation ($\lambda$=0.71069 Å), $\mu$=0.74 cm$^{-1}$, $F$(000)=720, $T$=−114 °C, $2\theta_{max}$=45°, 2657 independent reflections scanned, 548 reflections in refinement ($I \geq 3\sigma(I)$), 113 parameters, $R$=0.085, $R_w$=0.089.

**4.2.2. Compound 4b.** $C_{23}H_{16}$, $M_r$=292.36, colorless plate, 0.28×0.24×0.13 mm$^3$, monoclinic, space group $P2_1/c$, $a$=10.3133(1), $b$=19.7581(1), $c$=8.1048(1) Å, $\beta$=100.070(1)°, $V$=1626.08(3) Å$^3$, $Z$=4, $\rho_{calc}$=1.194 g cm$^{-3}$, Mo $K_\alpha$ radiation ($\lambda$=0.71073 Å), $\mu$=0.068 mm$^{-1}$, $F$(000)=616, $T$=−115 °C, $2\theta_{max}$=56.7°, 3166 independent reflections scanned, 2276 reflections observed ($I \geq 2\sigma(I)$), 208 parameters, $R1$=0.0509, $wR2$=0.1179.

**4.2.3. Compound 6b.** $C_{34}H_{22}$, $M_r$=430.52, colorless plate, 0.27×0.22×0.06 mm$^3$, monoclinic, space group $P2_1/c$, $a$=15.3093(12), $b$=4.1431(3), $c$=18.9043(15) Å, $\beta$=106.678(2)°, $V$=1148.6(2) Å$^3$, $Z$=2, $\rho_{calc}$=1.245 g cm$^{-3}$, Mo $K_\alpha$ radiation ($\lambda$=0.71073 Å), $\mu$=0.070 mm$^{-1}$, $F$(000)=452, $T$=−115 °C, $2\theta_{max}$=49.4°, 1666 independent reflections scanned, 1223 reflections observed ($I \geq 2\sigma(I)$), 154 parameters, $R1$=0.0523, $wR2$=0.1238.

**4.2.4. Compound 7a.** $C_{44}H_{30}$, $M_r$=558.68, colorless plate, 0.21×0.18×0.05 mm$^3$, triclinic, space group $P1$, $a$=10.3207(2), $b$=12.9619(1), $c$=14.4042(3) Å, $\alpha$=64.213(1), $\beta$=79.148(1), $\gamma$=67.475(1)°, $V$=1602.14(5) Å$^3$, $Z$=2, $\rho_{calc}$=1.158 g cm$^{-3}$, Mo $K_\alpha$ radiation ($\lambda$=0.71073 Å), $\mu$=0.066 mm$^{-1}$, $F$(000)=588, $T$=−115 °C, $2\theta_{max}$=49.9°, 4720 independent reflections scanned, 2880 reflections observed ($I \geq 2\sigma(I)$), 397 parameters, $R1$=0.0627, $wR2$=0.1482.

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## References and notes

1. (a) Gilbertson, R. D.; Weakley, T. J. R.; Haley, M. M. *J. Am. Chem. Soc.* **1999**, *121*, 2597–2598. (b) Gilbertson, R. D.; Lau, T. L. S.; Lanza, S.; Wu, H.-P.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **2003**, *22*, 3279–3289.
2. Gilbertson, R. D.; Weakley, T. J. R.; Haley, M. M. *Chem. Eur. J.* **2000**, *6*, 437–441.
3. See also: (a) Wu, H.-P.; Lanza, S.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **2002**, *21*, 2824–2826. (b) Jacob, V.; Weakley, T. J. R.; Haley, M. M. *Angew. Chem. Int. Ed.* **2002**, *41*, 3470–3473. (c) Wu, H.-P.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **2002**, *21*, 4320–4322. (d) Jacob, V.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **2002**, *21*, 5394–5400.
4. Larock, R. C. *Comprehensive organic transformations*; 2nd ed. Wiley-VCH: New York, 2000.
5. (a) Domnin, I. N.; Ivanov, A. L.; Fovorskaya, I. A. *Zh. Org. Khim.* **1986**, *22*, 1780–1783. (b) Ivanov, A. L.; Domnin, I. N. *Zh. Org. Khim.* **1988**, *24*, 2547–2552. (c) Maier, G.; Rang, H.; Emrich, R. *Liebigs Ann.* **1995**, 153–160. (d) Haley, M. M.; Biggs, B.; Looney, W. A.; Gilbertson, R. D. *Tetrahedron Lett.* **1995**, *36*, 3457–3460. (e) Baldridge, K. K.; Biggs, B.; Bläser, D.; Boese, R.; Haley, M. M.; Maulitz, A. H.; Siegel, J. S. *Chem. Commun.* **1998**, 1137–1138. (f) Dunitz, J. D. *Chem. Commun.* **1999**, 2547–2548. (g) Maier, G.; Neudert, J.; Wolf, O.; Pappusch, D.; Sekiguchi, A.; Tanaka, M.; Matsuo, T. *J. Am. Chem. Soc.* **2002**, *124*, 13819–13826.
6. (a) Halton, B.; Banwell, M. G. Cyclopropenes. In *The chemistry of the cyclopropyl group*; Rappaport, Z., Ed.; Wiley: New York, 1987; pp 1223–1339. (b) Baird, M. S. In *Cyclopropenes—synthesis by construction of the system. Methods of organic chemistry*; de Meijere, A., Ed.; Thieme: Stuttgart, 1996; Vol. E17d, pp 2695–2744.
7. (a) Komatsu, K.; Yoshida, Z. In *Cyclopropenylium salts. Methods of organic chemistry (Houben-Weyl)*; de Meijere, A., Ed.; Thieme: Stuttgart, 1996; Vol. E17d, pp 3079–3192. (b) Komatsu, K.; Kitagawa, T. *Chem. Rev.* **2003**, *103*, 1371–1427.
8. There are a number of possible procedures for dehalosilation with retention of the *Z*-geometry; see Ref. 4, pp 432–434 and 749–750.
9. Xu, R.; Breslow, R. *Organic Syntheses*; Freeman, J. P., Ed.; Wiley: New York, 1998; Coll. Vol. IX, pp 730–732.

10. Donaldson, W. A.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4846–4859.
11. (a) Glaser, C. *Chem. Ber.* **1869**, *2*, 422–424. (b) Eglinton, G.; McRae, W. *Adv. Org. Chem.* **1963**, *4*, 225–328. (c) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem. Int. Ed.* **2000**, *39*, 2632–2657.
12. Gilbertson, R. D.; Weakley, T. J. R.; Haley, M. M. *J. Org. Chem.* **2000**, *65*, 1422–1430.
13. Boese, R. *Advances in strain in organic chemistry*; Halton, B., Ed.; JAI: London, 1992; Vol. 2, pp 191–254.
14. Enkelmann, V. *Adv. Polym. Sci.* **1984**, *63*, 91–136, and references cited therein.
15. (a) Schwartz, J.; Labinger, J. A. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 333–340. (b) Swanson, D. R.; Nguyen, D.; Noda, Y.; Negishi, E.-I. *J. Org. Chem.* **1991**, *56*, 2590–2591. (c) Lipshutz, B. H.; Keil, R.; Barton, J. C. *Tetrahedron Lett.* **1992**, *33*, 5861–5864.
16. Sato, F.; Ishikawa, H.; Sato, M. *Tetrahedron Lett.* **1981**, *22*, 85–88.
17. We have encountered other systems where substituents at C3 have also impeded subsequent reactivity. For example, see: Gilbertson, R. D.; Weakley, T. J. R.; Haley, M. M.; Weiss, H.-C.; Boese, R. *Organometallics* **1998**, *17*, 3105–3107.
18. (a) Huber, M. K.; Dreiding, A. S. *Helv. Chim. Acta* **1974**, *57*, 748–750. (b) Komendantov, M. I.; Panasyuk, T. B. *Zh. Org. Khim.* **1985**, *21*, 1437–1442.
19. Corey, E. J.; Fuchs, P. W. *Tetrahedron Lett.* **1972**, 3769–3772.
20. (a) For a recent example, see: Mori, A.; Takahisa, E.; Nishihara, Y.; Hiyama, T. *Can. J. Chem.* **2001**, *79*, 1522–1524. (b) Gilbertson, R. D.; Haley, M. M. Unpublished results.
21. Getty, S. J.; Hrovat, D. A.; Xu, J.-D.; Barker, S. A.; Borden, W. T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1689–1701.
22. Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 3347–3350.
23. (a) Brown, R. F. C. *Eur. J. Org. Chem.* **1999**, 3211–3222. (b) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209–219. (c) Hagen, S.; Hopf, H. *Top. Curr. Chem.* **1998**, *196*, 45–89. (d) Mehta, G.; Rao, H. S. P. *Advances in strain in organic chemistry*; Halton, B., Ed.; JAI: London, 1997; Vol. 6, pp 139–187.
24. Baird, M. S. *Chem. Rev.* **2003**, *103*, 1271–1294.
25. For the only known alkynylindene, see: Padwa, A.; Austin, D. J.; Gareau, Y.; Kassir, J. M.; Xu, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2637–2647.
26. (a) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N.; Loza, R. *J. Org. Chem.* **1978**, *43*, 1481–1492. (b) Zimmerman, H. E.; Aasen, S. M. *J. Org. Chem.* **1978**, *43*, 1493–1506.
27. For a closely related cyclopent[cd]indene, see: Dürr, H.; Fuchs, V. *Tetrahedron Lett.* **1976**, 4049–4052.
28. Structure assignments for **11a–b** were confirmed by COSY, HMBC, and HMQC NMR experiments; **11c** was assigned by analogy.
29. Pettit, W. A.; Wilson, J. W. *J. Am. Chem. Soc.* **1977**, *99*, 6372–6379.
30. Wentrup, C.; Benedikt, J. *J. Org. Chem.* **1980**, *45*, 1407–1409.
31. Brandsma, L. *Preparative acetylenic chemistry*; Elsevier: Amsterdam, 1988; pp 28–29.