

## Elaboration of Diaryl Ketones into Naphthalenes Fused on Two or Four Sides: A Naphthoannulation Procedure

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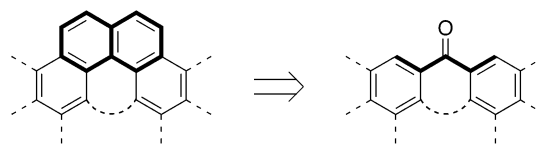
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**Abstract:** Transition metal-catalyzed double ring closures of 1,1-diaryl-2,2-diethynylethylenes yield polycyclic aromatic hydrocarbons and heterocycles that contain a newly formed naphthalene ring system embedded in a larger polycyclic network. The diynes required for this procedure are readily synthesized from diaryl ketones by the Corey–Fuchs olefination and subsequent Sonogashira coupling with trimethylsilylacetylene followed by desilylation. This procedure provides easy access to new compounds such as 3,11-di-*tert*-butyl[4]helicene and 1,8,9-perinaphthothioxanthene. Double naphthoannulation of 9,10-anthraquinone by this procedure closes four new benzene rings in a single operation to give coronene, although the yield in this case is presently low.

### Introduction

Polycyclic aromatic hydrocarbons (PAHs) and related compounds that contain one or more heteroatoms (primarily O, N, or S) pervade many branches of chemistry and the allied sciences.<sup>1</sup> They abound, for example, in the soot and smoke from burning coal and from the incomplete combustion of other fossil fuels, wood and tobacco;<sup>2</sup> environmental chemists are especially concerned about compounds of this class that exhibit carcinogenic activity, e.g., benzo[*a*]pyrene.<sup>3</sup> In a completely different arena, much of the molecular photophysics that is known today has come from studies on the absorption and emission properties of polycyclic aromatic  $\pi$ -systems.<sup>4</sup> Questions about the aromaticity of PAHs and related heterocycles have occupied theoreticians for decades,<sup>5</sup> and new questions keep emerging.<sup>6</sup> In these and numerous other branches of chemistry, laboratory syntheses of polycyclic aromatic compounds have been crucial to the advancement of our understanding. No scientific endeavors have stimulated as much interest in the development of new methods for the synthesis of such compounds, however, as the recent discovery of fullerenes and the



**Figure 1.** A new strategy for constructing naphthalenes.

current quest for new carbon-rich materials related to C<sub>60</sub>, graphite, and nanotubes.<sup>7</sup> We report here a procedure for synthesizing the bicyclic naphthalene ring system in an unconventional manner that annulates both of the new benzene rings onto preexisting arenes.

In the course of studies on the reactivity of large PAHs, we needed a method to build fused naphthalenes starting from diaryl ketones (Figure 1).

To the best of our knowledge, the only previous construction of a fused naphthalene ring system by a strategy similar to this is the one reported by Zimmermann et al. in their novel synthesis of corannulene (Scheme 1).<sup>8</sup> In that work, flash vacuum pyrolysis (FVP) of the bis(trimethylsilylethynyl)olefin **1a** on a 20–40 mg scale gave 1.5–3.0 mg of corannulene (ca. 15% yield). Attempts by Zimmermann et al. to investigate FVP of the desilylated compound (**1b**) were thwarted, unfortunately, by rapid polymerization of the parent hydrocarbon.

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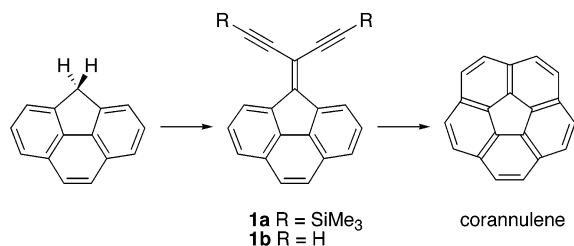
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(7) (a) Taylor, R. *Lecture Notes on Fullerene Chemistry: A Handbook for Chemists*; Imperial College Press: London, 1999. (b) Simpson, C. D.; Brand, J. D.; Berresheim, A. J.; Przybilla, L.; Rader, H. J.; Müllen, K. *Chemistry* **2002**, *8*, 1424–1429. (c) Haddon, R. C., Ed. *Acc. Chem. Res.* **2002**, *35*(12): special issue on Carbon Nanotubes.

(8) (a) Zimmermann, G.; Nuechter, U.; Hagen, S.; Nuechter, M. *Tetrahedron Lett.* **1994**, *35*, 4747–4750. (b) For evidence that thermal cyclizations of such 1,1-diaryl-2,2-dialkynylethylenes involve the intermediacy of “isobenzzenes,” see: Hopf, H.; Berger, H.; Zimmermann, G.; Nuechter, U.; Jones, P. G.; Dix, I. *Angew. Chem.* **1997**, *109*, 1236–1239; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1187–1190.

## Scheme 1

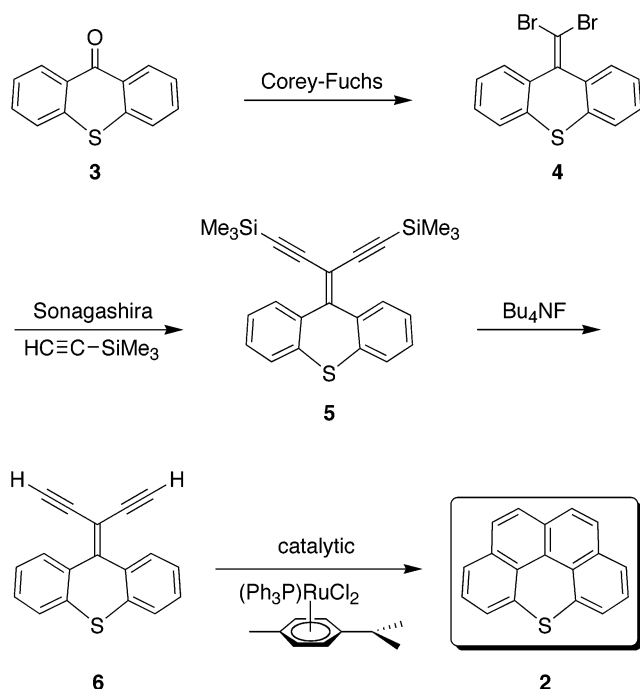


Our synthesis puts together analogous 1,1-diethynylethylenes in a different way and then cyclizes them by solution methods, rather than by gas-phase FVP.

## Results and Discussion

Our synthesis of the previously unknown 1,8,9-perinaphthothioxanthene (**2**, Scheme 2) illustrates the four steps we use

## Scheme 2

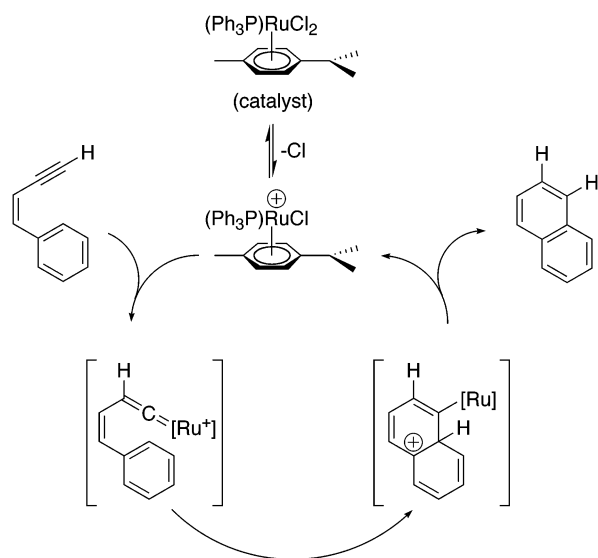


to accomplish the overall naphthoannulation outlined in Figure 1. It begins with a Corey–Fuchs olefination<sup>9</sup> of the starting ketone, thioxanthenone (**3**). The resulting 1,1-dibromoalkene (**4**) is then transformed into the corresponding 1,1-bis(trimethylsilyl)ethynylalkene (**5**) by a double Sonogashira coupling<sup>10</sup> with trimethylsilylacetylene; subsequent desilylation with tetra-*n*-butylammonium fluoride provides the parent diyne (**6**). To make two new benzene rings out of the two 1-aryl-1-buten-3-yne moieties in **6** we employed the ruthenium-catalyzed cycloisomerization protocol developed by Merlic.<sup>11</sup> Thus, slow addition of **6** to a solution of (Ph<sub>3</sub>P)Ru(cymene)Cl<sub>2</sub> (0.2 equiv) in refluxing 1,2-dichloroethane gives 1,8,9-perinaphthothioxanthene (**2**) in 95% yield. An X-ray crystal structure of this

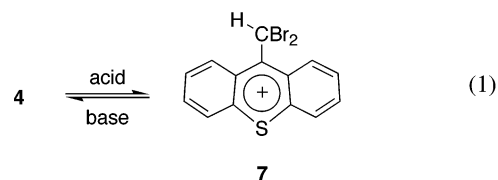
new ring system can be found in the Supporting Information; the molecule is planar, as expected, with long C–S bonds, as shown in Scheme 2.

The ruthenium-catalyzed cycloisomerization reaction of 1-aryl-1-buten-3-yne has previously been shown by deuterium-labeling studies to involve initial formation of a ruthenium–vinylidene.<sup>11</sup> Merlic has also provided evidence that the subsequent carbon–carbon bond-forming step exhibits the electronic characteristics of an electrophilic aromatic substitution;<sup>11</sup> however, the final steps of the mechanism remain the subject of speculation (Scheme 3).

## Scheme 3



Three aspects of the particular reaction sequence shown in Scheme 2 deserve further comment. First, we found the Corey–Fuchs olefination of thioxanthenone (**3**) to be rather sluggish, presumably owing to the special stability of the “aromatic” heteroannulenone ring system.<sup>12</sup> Fortunately, forcing conditions (150 °C/sealed vessel, 48–72 h) produced the 1,1-dibromoalkene (**4**) without complications. Second, alkene **4** was observed to capture adventitious acid (e.g., the traces of acid in CDCl<sub>3</sub>) to produce what we believe to be the thiopyrylium ion **7** (eq 1).<sup>13</sup>



A set of small, low field signals arising from the thiopyrylium ion **7**<sup>14</sup> can be seen in most NMR spectra of **4**, but neutralization regenerates the alkene with no deleterious consequences.<sup>15</sup> Finally, we found the unprotected parent diyne (**6**) to be rather

(9) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769–3772.

(10) (a) Sonogashira, K. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley: Hoboken, NJ, 2002; Vol. 1, pp 493–529. (b) Sonogashira, K. *J. Organomet. Chem.* **2002**, 653, 46–49. (c) Sonogashira, K. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 1998, pp 203–229.

(11) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, 118, 11319–11320.

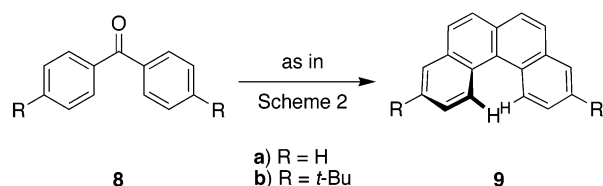
(12) (a) Bouanani, H.; Gayoso, J. *Bull. Soc. Chim. Fr.* **1974**, 545–552. (b) ref 5d, pp 79–81 and references therein.

(13) For references to pyrylium and thiopyrylium ions, see: (a) Balaban, A. T.; Dinculescu, A.; Dorofeenko, G. N.; Fischer, G. V.; Kablik, A. V.; Mezheritskii, V. V.; Schroth, W. *Advances in Heterocyclic Chemistry*; Supplement 2: Pyrylium Salts: Synthesis, Reactions, and Physical Properties; Academic Press: New York, 1982. (b) Reference 5c, Chapter 8.

(14) Small, but unobscured, <sup>1</sup>H NMR signals for thiopyrylium ion **7** (400 MHz, CDCl<sub>3</sub>): 7.98 (dm, *J* = 9.6 Hz), 7.41–7.51 (m), 6.68 (s, CHBr<sub>2</sub>).

(15) Further evidence for the thiopyrylium ion **7** follows from the similarity of its behavior to that of the oxygen analogue (ref 17).

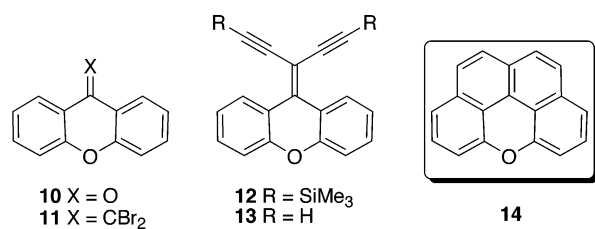
Scheme 4



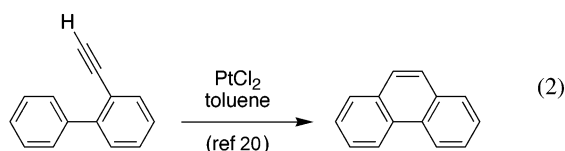
labile and prone to easy polymerization (cf **1b**<sup>8a</sup>). Diyne **6** can be prepared in essentially quantitative yield by desilylation of **5** and survives long enough at room temperature for routine spectroscopic characterization, but we typically use it immediately for the next step. The 95% yield reported above for the synthesis of 1,8,9-perinaphthothioxanthene (**2**) actually corresponds to the overall yield of **2** for the two steps from **5**.

When the same four-step reaction sequence is carried out on acyclic diaryl ketones, e.g., benzophenone (**8a**) and 4,4'-di-*tert*-butylbenzophenone (**8b**), [4]helicenes (**9**) are produced (Scheme 4). Despite the steric strain of the final products, the yields for the cyclization steps in these syntheses are still quite decent (60% in both cases, over two steps from the corresponding silylated diynes).

Xanthenone (**10**), like thioxanthenone (**3**), is sluggish in the Corey–Fuchs olefination, and the resulting dibromoalkene (**11**) is even more susceptible to protonation by traces of acid than is its sulfur counterpart (**4**).<sup>12,13,16,17</sup> Nevertheless, the corresponding 1,1-bis(trimethylsilylethynyl)alkene (**12**) can be readily obtained as before and cleanly desilylated to the parent diyne (**13**). At this point, however, we encountered a serious shortcoming of the ruthenium-catalyzed cycloisomerization reaction. In keeping with Merlic's view that the carbon–carbon bond-forming step involves electrophilic attack on the aromatic ring<sup>11</sup> and the fact that ether oxygen atoms strongly deactivate positions meta to their point of attachment,<sup>18</sup> exposure of **13** to solutions of (Ph<sub>3</sub>P)Ru(cymene)Cl<sub>2</sub> under a variety of conditions promoted polymerization of the diyne and gave no more than 10% yield of cyclized product (**14**).<sup>19</sup> The reaction was further complicated by the formation of a second, inseparable, product that has the same molecular weight as **14** (GC–MS).



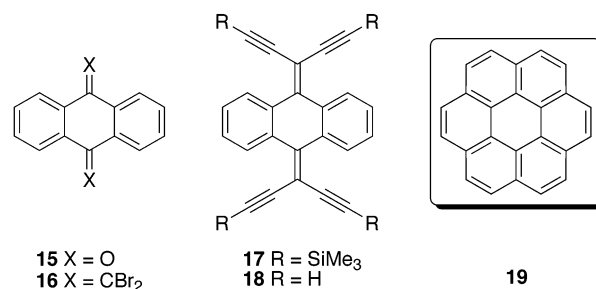
To contend with this problem, we explored the use of other catalytic systems introduced recently by Fürstner for the cyclization of *o*-ethynylbiphenyls to phenanthrenes (eq 2).<sup>20</sup>



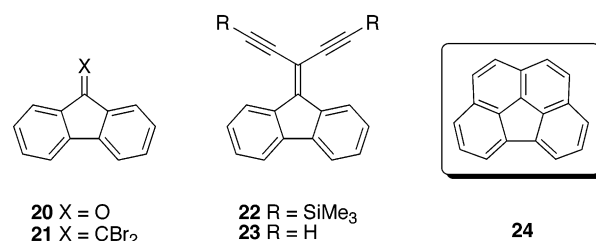
Thus, it was found that catalytic PtCl<sub>2</sub> in hot toluene will also convert the 1,1-diethynylalkene **13** into 1,8,9-perinaphthoxanthene (**14**), albeit only in about 15% yield. Neither the Ru-catalyzed reaction nor the Pt-catalyzed alternative proceeds

in high yield, but the absence of isomeric side products in the latter makes it the more attractive choice. Better conditions for the cyclization of **13** must be found, obviously, to make this synthesis of **14** practical; however, we did succeed in preparing enough pure **14** to obtain an X-ray crystal structure (planar; see Supporting Information) and to record the first <sup>1</sup>H and <sup>13</sup>C NMR spectra of this previously uncharacterized compound.<sup>19</sup> Factors other than electronic deactivation by the meta oxygen atom that may also contribute to the low yield for cycloisomerization of **13** are discussed in the following section.

Finally, in an effort to expand the power of this naphthoannulation strategy, we applied the four-step procedure to anthraquinone (**15**). Gratifyingly, the conversions to **16**, **17**, and **18** all worked satisfactorily, and the final closure with (Ph<sub>3</sub>P)Ru(cymene)Cl<sub>2</sub> (0.2 equiv) does indeed produce coronene (**19**).<sup>21</sup> The yield in the final 4-fold cycloisomerization, unfortunately, is only in the 15–20% range at the present stage of optimization.

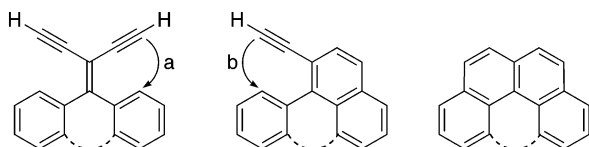


**Limitations of the Transition Metal-Catalyzed Cycloisomerizations.** The low yields associated with cyclizations *meta* to an ether oxygen (**13** → **14**) and with the ambitious double naphthoannulation of anthraquinone (**18** → **19**) have already been mentioned above. One additional system we investigated that fails completely in the final cycloisomerization step is fluorenone (**20**). As usual, the conversions to the requisite intermediates (**21**, **22**, and **23**) all worked satisfactorily, but none of the catalysts examined in this case promoted double cyclization to the known hydrocarbon **24**.<sup>22</sup> We do not see even the product of one cyclization; only polymers are obtained.



The factors that determine the success or failure of these cycloisomerizations are all kinetic in origin and not thermodynamic. Even for the cycloisomerizations that give quite strained products (e.g., **23** → **24**), the final ring closure is calculated to

- (16) Small, but unobscured, <sup>1</sup>H NMR signals for pyrylium ion **11** (400 MHz, CDCl<sub>3</sub>): 8.46 (dd, *J* = ca 8.8, 2.0 Hz), 7.48 (dd, *J* = ca 8.8, 2.0 Hz), 6.63 (s, CHBr<sub>2</sub>).
- (17) Addition of CH<sub>3</sub>OH to the NMR tube causes the signals for the small amount of pyrylium ion derived from **11** to disappear, and new signals corresponding to those of a methyl ether grow in.
- (18) Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: New York, 1990; pp 47, 88, and later chapters.
- (19) Naphtho[2,1,8,7-*klmn*]xanthene (**14**) was first prepared in 1941 from coal tar pitch by Kruber, O. *Chem. Ber.* **1941**, *74*, 4B, 1688–1692, but no spectroscopic characterization has subsequently been reported.
- (20) Fürstner, A.; Mamane, V. *J. Org. Chem.* **2002**, *67*, 6264–6267.



**Figure 2.** Distances for (a) first closure (b) second closure.

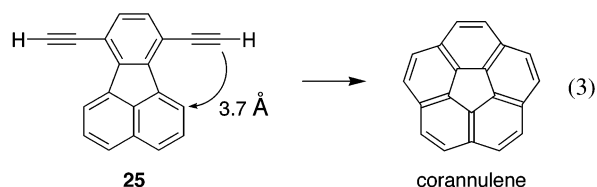
be exothermic by more than 40 kcal/mol, and the first cyclization is calculated to be exothermic by more than 60 kcal/mol.<sup>23</sup> Apparently, bimolecular processes that lead to higher-molecular weight polymers dominate the reactions whenever some structural feature slows down the desired cyclizations.

Without a good picture for the transition state of the rate-limiting step in these transition metal-catalyzed cycloisomerizations it is difficult to explain why some naphthoannulations work so well (e.g., **6** → **2**) while others fail. We have noticed, however, that there is an inverse correlation between the success of the naphthoannulation and the calculated distance<sup>23</sup> that separates the terminal acetylenic carbon atom in the starting material from the aryl carbon atom to which it will become bonded (distances a and b in Figure 2).<sup>24,25</sup>

In the most successful cycloisomerization reported here (**6** → **2**), those distances are 3.34 and 3.33 Å, respectively, whereas in the barely viable oxygen analogue (**13** → **14**), those distances are 3.35 and 3.42 Å, respectively. The demands in the first step are comparable in these two cases, but the second step in the oxygen heterocycle may be too slow to compete effectively with polymerization. In the double naphthoannulation of anthraquinone (**18** → **19**), the distances for the four cyclization steps, following the energetically most favorable pathway, are 3.22, 3.32, 3.39, and 3.39 Å, respectively. The longest distances in this case fall between those in the sulfur heterocycle (**6**) and those in the oxygen heterocycle (**13**), and the overall yield likewise falls between those two extremes. In the naphthoannulation of fluorenone (**23** → **24**), the distances for the two cyclization steps are much longer (3.46 and 3.80 Å, respectively), and the reaction fails completely.

From these admittedly sparse data, we tentatively conclude that cycloisomerizations of the sort reported here may be limited to those in which the distances between the atoms to be joined are less than about 3.40 Å. In the benzophenone systems, which successfully lead to [4]helicenes (Scheme 4), relatively free rotation of the phenyl groups brings the atoms to be joined well within 3.40 Å of one another. In light of this empirical “distance rule,” it is no surprise that diyne **25** fails to cyclize to corannulene under the transition metal-catalyzed cycloisomerization conditions reported here (eq 3). The success of flash

vacuum pyrolysis in this case undoubtedly stems from the increased magnitude of out-of-plane distortions at elevated temperatures.<sup>26</sup>



## Conclusions

A four-step procedure is reported for the transformation of diaryl ketones into polycyclic aromatic hydrocarbons and heterocycles that contain a newly formed, fused naphthalene ring system. The transition metal-catalyzed double ring closures of 1,1-diaryl-2,2-diethynylethylenes in the final step appear to work best for those compounds in which the distances between the atoms to be joined are less than about 3.35–3.40 Å.

## Experimental Section

General procedures for the four steps of the naphthoannulation sequence are reported below, using the transformations illustrated in Scheme 2 as examples. Full details for all reactions can be found in the Supporting Information.

**General Procedure 1: Corey–Fuchs Olefination.** An oven-dried sealable 150-mL pressure vessel was charged with thioxanthene-9-one (**3**, 1.875 g, 8.833 mmol), carbon tetrabromide (5.885 g, 17.74 mmol), and a magnetic stirring bar. The vessel was purged with nitrogen gas, 50 mL of anhydrous benzene was added, and the mixture was stirred for 5 min. Triphenyl phosphine (9.313 g, 35.51 mmol) was then added, and the vessel was sealed. The reaction mixture was heated at 150 °C for 44 h in a wax bath with vigorous stirring. The vessel was cooled to room temperature before opening, and the contents were rinsed into a round-bottom flask with dichloromethane. The crude product was then preadsorbed onto neutral alumina and chromatographed on an alumina column with hexanes as the eluent. The hexane fractions were dried over magnesium sulfate and concentrated to dryness on a rotary evaporator to give 1.739 g (53% yield) of 9-(dibromomethylene)-9H-thioxanthene (**4**) as an off-white powder that was pure by <sup>1</sup>H NMR analysis: mp 117–119 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.78 (dm, *J* = 7.2 Hz, 2H), 7.51 (dm, *J* = 7.6 Hz, 2H), 7.30 (td, *J* = 7.4 Hz and *J* = 1.8 Hz, 2H), 7.26 (td, *J* = 7.6 Hz and *J* = 1.6 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 140.49, 135.49, 134.11, 129.37, 127.91, 127.22, 126.08, 92.409. Anal. Calcd. for C<sub>14</sub>H<sub>8</sub>Br<sub>2</sub>S: C, 45.68; H, 2.19. Found: C, 45.89; H, 1.89.

**General Procedure 2: Sonogashira Coupling.** Dibromide **4** (1.1025 g, 2.995 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (226 mg, 0.321 mmol), and copper(I) iodide (145 mg, 0.764 mmol) were added to a sealable vessel that contained 30 mL of triethylamine. The solution was stirred and purged with nitrogen for 5 min. Trimethylsilyl acetylene (1.95 mL, 13.8 mmol) was then added by syringe, and the vessel was sealed. The reaction mixture was heated at 95 °C in a wax bath with stirring for 21 h. The vessel was then cooled to room temperature and opened, and the contents were diluted with 100 mL of dichloromethane. The resulting solution was washed successively with two 100-mL portions of saturated aqueous ammonium chloride solution and two 100-mL portions of distilled water. The organic layer was then dried over magnesium sulfate, and the crude product was preadsorbed onto silica gel. The sample was chromatographed on a silica gel column with a

(21) Coronene (**19**): *Chem. Abstr.* Registry No. 191-07-1. Available from Aldrich Chemical Co. (catalog no. C8,480-1).

(22) Benzo[ghi]fluoranthene (**24**): *Chem. Abstr.* Registry No. 203-12-3. Available from Fluka Chemical Co. (catalog no. BCR-139).

(23) Calculations were performed at the B3LYP/6-31G\*/AM1 level of theory, using the Spartan package of programs (Linux v. 02: Wavefunction, Irvine, CA).

(24) A more accurate estimation of relative transition-state geometries would be given by comparisons among the proposed vinylidene intermediates (Scheme 3); however, geometry calculations on transition metal–vinylidene complexes are less reliable, and the trend should be qualitatively no different.

(25) Distance-reactivity relationships of this sort have been noted for other types of cyclization reactions; see, for example: (a) Nicolaou, K. C.; Dai, W. *M. Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387–1416. (b) Nicolaou, K. C.; Smith, A. L. *Acc. Chem. Res.* **1992**, *25*, 497–503. (c) Chen, W.-C.; Zou, J.-W.; Yu, C.-H. *J. Org. Chem.* **2003**, *68*, 3663–3672. (d) Gaffney, S. M.; Capitani, J. F.; Castaldo, L.; Mitra, A. *Int. J. Quantum Chem.* **2003**, *95*, 706–712.

(26) (a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082–7084. (b) Scott, L. T.; Cheng, P.-C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 10963–10968.

2% ethyl acetate:98% hexane solution until a brown-yellow band eluted. The fractions containing the product were then combined and concentrated to dryness on a rotary evaporator to give 895 mg (74% yield) of 9-[bis(trimethylsilylethynyl)methylene]-9H-thioxanthene (**5**) as a brown solid which was pure by  $^1\text{H}$  NMR analysis: mp 199–201 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.11 (dm,  $J = 8.0$  Hz, 2H), 7.46 (dm,  $J = 6.8$  Hz, 2H), 7.27 (td,  $J = 7.2$  Hz and  $J = 1.6$  Hz, 2H), 7.23 (td,  $J = 7.6$  Hz and  $J = 1.6$  Hz, 2H), 0.17 (s, 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  148.61, 133.59, 133.47, 129.68, 128.28, 126.24, 125.37, 103.18, 102.50, 99.18, –0.21. HRMS ESI ( $m/z$ ):  $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{26}\text{-NaSi}_2\text{S}$ , 425.1191; found 425.1196.

**General Procedure 3: Desilylation.** The bis(trimethylsilyl)diyne **5** (314 mg, 0.780 mmol) was dissolved in 5 mL of dichloromethane. A separate solution of tetrabutylammonium fluoride trihydrate (1.012 g, 3.208 mmol) in 5 mL of dichloromethane was also prepared. The two solutions were combined, and the resulting mixture was stirred at ambient temperature. After TLC showed no remaining starting material (ca 15 min), the solution was filtered through a short pad of silica gel, which was subsequently washed with additional dichloromethane. The combined dichloromethane solutions were dried over magnesium sulfate and then concentrated nearly to dryness on a rotary evaporator, taking care not to apply excessive heat. The unprotected 9-(diethynylmethylene)-9H-thioxanthene (**6**) is sensitive to heat and polymerizes readily, and thus, no attempt was made to obtain an accurate mass. According to  $^1\text{H}$  NMR analysis, **6** was formed with complete conversion as the only product and in essentially quantitative yield. After the NMR analysis, this product was immediately subjected to the next reaction without further purification.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.08 (m, 2H), 7.50 (m, 2H), 7.30 (m, 4H), 3.12 (s, 2H).

**General Procedure 4: Double Cyclization.** The crude product from the previous reaction (**6**) was diluted to a volume of 6 mL with 1,2-dichloroethane, and the resulting solution was drawn into a 10 mL syringe equipped with a long needle. A separate solution of  $\text{RuCl}_2\text{-}(\text{PPh}_3)(\eta^6\text{-}p\text{-cymene})^{27}$  (141 mg, 0.248 mmol) and ammonium hexafluorophosphate (84 mg, 0.51 mmol) in 16 mL of 1,2-dichloroethane was

heated to 75 °C under nitrogen in a three-neck flask equipped with a reflux condenser and a septum. The solution of **6** was then added at a rate of 0.5 mL/h with a syringe pump. Heating was continued for an additional 13 h after completion of the addition, for a total reaction time of 25 h. The reaction mixture was then cooled to room temperature, diluted with dichloromethane, and filtered through a short pad of silica gel, which was washed with several additional portions of dichloromethane. The crude product was then adsorbed onto silica gel and subjected to column chromatography on silica gel with hexanes as the eluent. The first yellow band was collected. The fractions were combined, dried over magnesium sulfate, and concentrated to dryness on a rotary evaporator to give 190 mg of naphtho[2,1,8,7-*klmn*]-thioxanthene (**2**) as yellow needles (95% yield over 2 steps), which were pure by  $^1\text{H}$  NMR analysis: mp 149–151 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.64 (s, 4H), 7.44 (dd,  $J = 8.0$  Hz and  $J = 1.2$  Hz, 2H), 7.28 (t,  $J = 7.2$  Hz, 2H), 7.16 (dd,  $J = 7.2$  Hz and  $J = 1.2$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  134.12, 132.02, 128.38, 128.06, 127.61, 127.26, 126.85, 126.36, 124.87, 120.96. HRMS ESI ( $m/z$ ):  $[\text{M}]^+$  calcd for  $\text{C}_{18}\text{H}_{10}\text{S}$ , 258.0503; found 258.0498.

**X-ray Structures.** Four X-ray crystal structures on compounds reported here have been deposited at the Cambridge Crystallographic Data Centre: **2** (CCDC 226047), **9b** (CCDC 226048), **14** (CCDC 226049), **18** (CCDC 226050).

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**Supporting Information Available:** Experimental details for all the reactions reported herein, analytical and spectral characterization data for all new compounds (PDF), and crystallographic information for compounds **2**, **9b**, **14**, and **18** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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