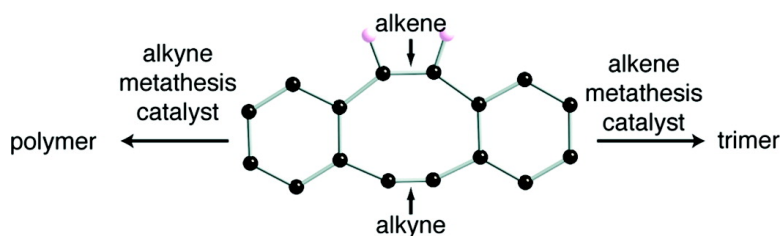


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## Reactions of Strained Hydrocarbons with Alkene and Alkyne Metathesis Catalysts

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We recently reported the synthesis and ROMP reactivity of (5Z,11E)-Dibenzo[a,e]cyclooctatetraene;<sup>1</sup> here we investigate the reactivity of the strained ene-yne cycle (**1**) with alkene and alkyne metathesis catalysts. The significant result is that alkyne metathesis allows for a rapid polymer growth to yield a polymer with alternating alkene and alkyne linkages along the polymer backbone. In contrast, the olefin metathesis catalyst provides discrete trimers such as an unusual hexasubstituted Dewar benzene derivative.

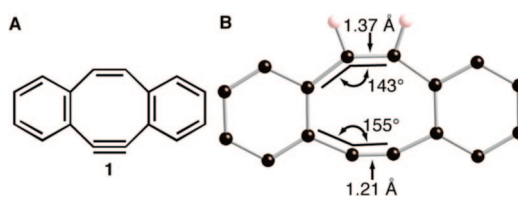
We synthesize **1** following the procedure of Sondheimer and co-workers.<sup>2,3</sup> Figure 1B shows the calculated<sup>4</sup> structure for **1**. It is apparent from the angles and distances that the strain is distributed between both the double and triple bonds. The double bond in **1** is opened outward to an angle of  $\sim 143^\circ$ . Our interest in the ring-opening metathesis polymerization of **1** is to determine how and where alkyne and alkene metathesis polymerization catalysts will react with this unusual and strained polyfunctional hydrocarbon.

We first investigated the reaction of **1** with alkyne metathesis catalysts as shown in Scheme 1.<sup>5,6</sup> We add Schrock's tungsten catalyst to the solution of **1**;<sup>7</sup> the mixture begins to darken immediately, changing from bright yellow to dark brown. After the reaction was stirred overnight, we add methanol to quench the reaction mixture and precipitate the polymer **2**. We can reduce the double and triple bonds of the **2** to make **3**, an ortho-phenylene ethylene. We have prepared polymer **3** by an independent method,<sup>1</sup> and their NMR spectra are identical.

We used GPC to characterize the molecular weight of **2** and **3**. We showed previously<sup>1</sup> that GPC with polystyrene standards is a reliable method for estimating the polydispersity and degree of polymerization of **3**. We observe that the molecular weights of **2** and **3** are the same ( $\sim 20\,000$  amu), as are their polydispersities (2.4) (see Supporting Information, Figure S1.). When we use relatively large amounts of the catalyst ( $\sim 1:1::\text{catalyst}:\text{monomer}$ ), we note (by NMR) that all the monomer is consumed before all the catalyst can initiate. Several studies have used bisalkynes in ring-closing alkyne metathesis reactions to form macrocycles instead of polymers.<sup>8</sup> In the case of **1**, the cis olefin that remains after polymerization prevents the catalytic site from biting back into the chain to terminate in macrocycle formation.

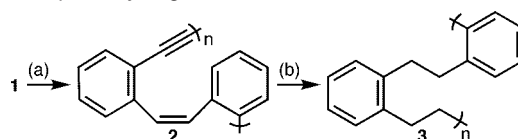
The  $^1\text{H}$  coupling constant of the symmetric olefin (measured from  $^{13}\text{C}$  satellites) is 14.5 Hz.<sup>9</sup> This coupling constant agrees well with the coupling constant for the cis olefin in a related stereoregular polymer.<sup>1</sup> The release of the strain is evident in the resonances associated with the alkyne (from  $\sim 108$  ppm in the monomer to  $\sim 93$  ppm in the polymer). The excitation and emission wavelengths are also red-shifted compared to structurally similar oligophenylene ethynylenes that have been made up to six repeating units in length.<sup>10</sup>

We next turn our attention to olefin metathesis reactions of **1**. Surprisingly, we find discrete trimeric compounds (**4** and **5**) as shown in Scheme 2. In general these reactions produce a multitude



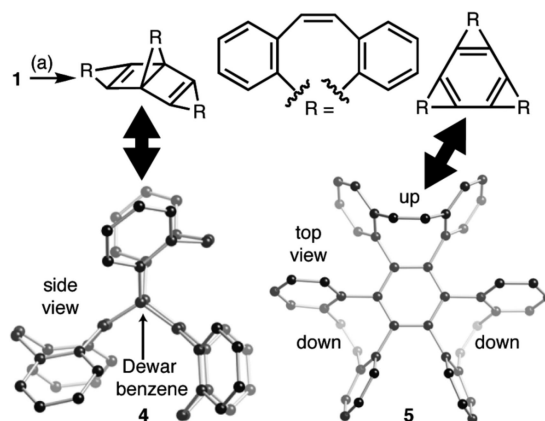
**Figure 1.** (A) Structure and (B) DFT model of **1**. Hydrogens on the benzo-substituents have been removed.

**Scheme 1.** Polymerization of **1** with Alkyne Metathesis Catalysts and Subsequent Hydrogenation<sup>a</sup>



<sup>a</sup> Key: (a) tris(*t*-butoxy)(2,2-dimethylpropylidene)(VI)tungsten. (b) 10% Pd/C, 3 atm H<sub>2</sub>.

**Scheme 2.** Olefin Metathesis Catalysts with **1** Produce Trimers **4** and **5**. Side-View of **4** and Top-View of **5** Taken from Their Crystal Structures. Hydrogens Are Removed to Clarify the View<sup>a</sup>



<sup>a</sup> Key: (a) [(Cl)<sub>2</sub>(PCy<sub>3</sub>)NHC]Ru=CHPh or CpRu(II)(CH<sub>3</sub>CN)<sub>3</sub>•PF<sub>6</sub>, CH<sub>2</sub>Cl<sub>2</sub>.

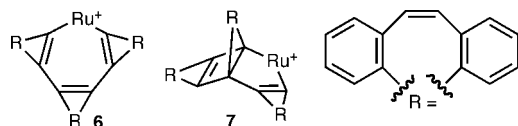
of products and are very difficult to characterize. When we use the later generation of catalysts from Grubbs and co-workers<sup>11</sup> that bear the N,N-heterocyclic carbene ligands, we were able to isolate the unusual hexasubstituted Dewar benzene **4**.<sup>12</sup> The molecular structure of **4** from the crystal is shown in Scheme 2. It contains an unsaturated six-membered bridge over the central carbons of the Dewar benzene. Each of the eight-membered rings and the strap over the top fold in a common direction to form a structure reminiscent of a paddle-wheel. We were not able to isomerize **4** to the benzene isomer with either light or heat.<sup>13</sup> Density functional

theory (DFT) calculations show that the Dewar and benzene isomers are essentially isoenergetic when the backbone is fully benzannulated.

We were puzzled as to how the alkene metathesis catalyst was effecting the formation of the Dewar benzene **4**. There are examples of benzene formation from trimerization with metathesis catalysts and where the Dewar form is simply more stable than the benzene form.<sup>14</sup> Alternatively, a degradation product of the catalyst could be producing a ruthenium complex that could act similarly to cyclopentadienyl complexes of ruthenium. These complexes are well-known to dimerize and trimerize alkynes.<sup>15</sup>

We report here, however, the first use of CpRu(II) compounds to catalyze formation of Dewar benzenes. We allow **1** to react CpRu(II)(CH<sub>3</sub>CN)<sub>3</sub>•PF<sub>6</sub>, and we subsequently isolate **4** in 14% yield. The major product from this reaction, however, is the previously unknown **5** in 61% yield. This new triannulenyne is substantially more stable than its unbenzannulated parent and can be stored on the shelf for months.<sup>16</sup> It is interesting to note that we could not detect **5** in the complex reaction mixture with the metathesis catalysts. The molecular structure of **5** determined crystallographically is shown in Scheme 1C. It has an unusual structure where one of its eight-membered rings folds to one side of the benzene plane and the other two point in the opposite direction. DFT calculations show the benzene form to be more stable by ~67 kcal/mol than the corresponding Dewar form.

The Dewar isomer **4** was unexpected and, because this along with the more conventional isomer **5** is formed by the catalytic action of CpRu<sup>+</sup>, raises the question of the mechanism by which the transformation occurs. A mechanism that would account for the formation of both **4** and **5** likely involves intermediates **6** and **7**. It is easy using well-precedented organometallic reactions to produce these intermediates.<sup>17,18,19</sup> Reductive elimination of the hydrocarbon from **6** gives isomer **4**. Similarly, the metallacyclopentene **7** eliminates to give the Dewar isomer **4**. It provides an addition to the previously proposed mechanism for alkyne trimerization and allows us to follow the relative relationship of the phenyl rings through the reaction.



Detailed above are the reactions of the strained ene-yne, **1**, with alkene and alkyne-metathesis catalysts. We find that alkyne metathesis catalysts form polymers. These polymers represent a new type of a nanostructured hydrocarbon. Furthermore, they may serve as starting materials for formation of sizable graphene pieces through further reaction. The alkene metathesis catalysts do not produce polymers but lead to unusual structures **4** and **5**.

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Office of Basic Energy Sciences, US DOE (no. DE-FG02-01ER15264). We thank the MRSEC Program of the National Science Foundation under Award Number DMR-0213574 and by the New York State Office of Science, Technology and Academic Research (NYSTAR) for financial support for M.L.S. The National Science Foundation (Grant CHE-0619638) is thanked for acquisition of the X-ray diffractometer.

**Supporting Information Available:** Experimental details for the synthetic procedures, DFT structures/calculations, <sup>1</sup>H and <sup>13</sup>C NMR spectra comparing monomer and polymer, and cif files for **4** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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