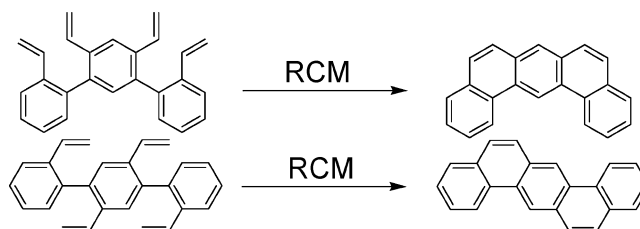# Polycyclic Aromatic Hydrocarbons by Ring-Closing Metathesis

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A strategy for the synthesis of polycyclic aromatic hydrocarbons (PAHs) by the ring-closing olefin metathesis (RCM) of pendant olefins on a phenylene backbone has been developed. RCM of 2,4′,6′,2″-tetravinyl-[1,1′;3′,1″]terphenyl and 2,2′,5′,2″-tetravinyl-[1,1′;4′,1′]terphenyl affords in high yield the isomeric [*a,j*] and [*a,h*] dibenzanthracenes, respectively. In contrast with other intramolecular annulation methods, such as Friedel−Crafts acylations, this reaction is completely regioselective. Since RCM is reversible and PAHs are often thermodynamic sinks, this strategy is an effective and general method for the preparation of PAHs. Density functional theory calculations support these results. Carbon disulfide is a suitable solvent for these reactions.

Introduction

Interest in the preparation of polycyclic aromatic hydrocarbons (PAHs) has been stimulated by the desire to understand their mechanisms of carcinogenesis and by the discovery of fullerenes and nanotubes. Numerous synthetic procedures for the construction of polycyclic aromatic systems have been described in the literature. This area has been recently reviewed[1] and described in a monograph.[2] Classic methods include the Pschorr synthesis,[3] the Elbs reaction,[4] alkylation of activated carbonyl compounds,[5] dimerization or trimerization of acetylenes and arynes,[6,7] Diels−Alder cycloaddition,[8] Wagner−Meerwein rearrangements,[9] annulation of *o*-quinones,[10] cyclodehydrohalogenation,[11] cyclodehydration methods,[12] flash vacuum pyrolysis,[13,14] photocycliza-

tion,[15,16] Scholl cyclodehydrogenation,[17] Wittig olefination,[15,18] and diaryl coupling.[19,20]

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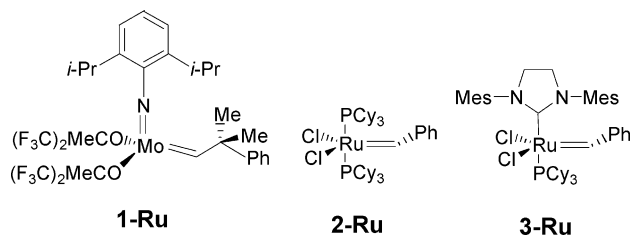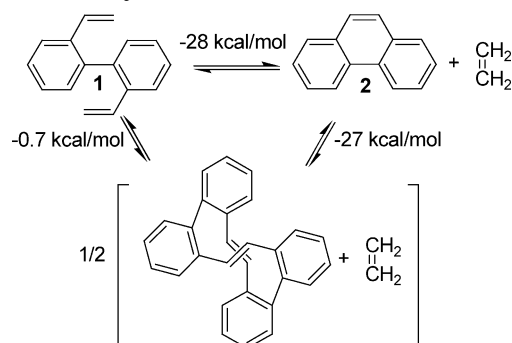
FIGURE 1. RCM catalysts.

Strategies involving transition metal catalysis are attractive because of the mild reaction conditions. For example, palladium-catalyzed cross-coupling is popular for the formation of aryl–aryl σ-bonds.[19] Ring-closing olefin metathesis (RCM) has emerged as a powerful tool for the preparation of double bonds in cyclic organic compounds[21] but has only recently been applied to PAHs.[22] The popularity of RCM is enhanced by the commercial availability of metal alkylidene catalysts such as those developed by Schrock[23] (**1-Mo**) and Grubbs[24] (**2-Ru**, **3-Ru**) (Figure 1).

In Katz's seminal paper on the mechanism of olefin metathesis, 2,2′-divinylbiphenyl (**1**) was converted to phenanthrene.[25] This reaction was run as a mechanistic probe and only allowed to proceed to ∼1% conversion. The yield of phenanthrene was not reported. A recent report by Iuliano and co-workers[22] demonstrates the preparative utility of RCM to generate functionalized phenanthrenes from 2,2′-divinylbiphenyl derivatives.

We hypothesized that RCM could be a useful method for the preparation of larger polycyclic aromatic hydrocarbons since it is reversible[26] and aromatic rings are

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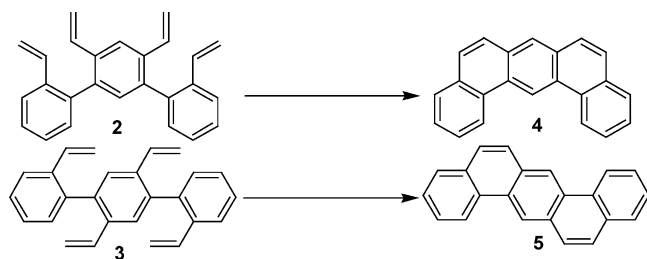
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SCHEME 1. Cyclization versus Dimerization

often thermodynamic sinks. The potential to form multiple aromatic rings in a single step was especially intriguing. The formation of multiple cyclopentenyl rings from 1,2-polydienes by RCM was reported by Coates and Grubbs.[27] We report herein computational and experimental results for the RCM of **1** to afford phenanthrene and for the double RCM of 2,4′,6′,2″-tetravinyl-[1,1′;3′,1″]-terphenyl (**2**) and 2,2′,5′,2″-tetravinyl-[1,1′;4′,1″]terphenyl (**3**) to afford dibenz[*a,j*]anthracene (**4**) and dibenz[*a,h*]-anthracene (**5**), respectively.

We also sought to develop reaction conditions that would circumvent the poor solubility of many PAHs. Carbon disulfide is an unusually effective solvent for many PAHs (for example, it is the best solvent for C_{60}[28]) but has received little attention as a medium for transition metal catalyzed reactions due to its perceived tendency to poison metal catalysts. We report effective olefin metathesis using Schrock's catalyst **1-Mo** in CS_2.

Results and Discussions

Two thermodynamic criteria should be satisfied for this RCM approach to be useful for the synthesis of large PAHs. First, the desired product should be a thermodynamic sink. Second, if multiple rings are to be formed in a single reaction, the energies of their formation should be additive. Quantitative knowledge of reaction energies is useful for the designed synthesis of high-energy PAHs, such as fullerenes[14] or Pascal's crowded PAHs.[7]

We used density functional theory (B3LYP/6-31G*, ΔG_{298}) calculations to quantitatively evaluate these criteria. To examine the first condition, the intramolecular reaction of **1** to afford phenanthrene and ethylene was compared to its dimerization (Scheme 1). The cyclization is calculated to be exergonic by −28 kcal/mol. In the dimerization, trans/trans (two conformations), cis/cis, and cis/trans isomers were considered. The trans/trans twisted conformation is lowest in energy, but its formation was exergonic by only −0.7 kcal/mol. All other isomers were less stable by at least 3 kcal/mol. Cyclization to the aromatic ring is therefore favored over dimerization or other processes, such as acyclic diene metathesis (ADMET) by ∼27 kcal/mol.

Next, we examined the RCM of the isomeric tetravinyl terphenyls **2** or **3** to give isomeric dibenzanthracenes **4** or **5** (Scheme 2). These reactions are calculated to be

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SCHEME 2. Double RCM

SCHEME 3. Preparation of Isomeric Tetravinylterphenyls[a]

[a] [a] Br_2, I_2, dark, 0 °C, 16 h, 58% (**6**) and 67% (**10**); [b] NBS, CCl_4, hν, reflux 9 h, 88%; [c] $AgNO_3$, H_2O, EtOH, reflux 0.5 h, 96%; [d] $(Ph)_3PCH_3Br$, KO*t*Bu, THF, 25 °C, 16 h, 61%; [e] $Pd(PPh_3)_4$, *o*-styrenyl boronic acid, aq. Na_2CO_3, DME, EtOH, reflux 16 h, 93% (**2**) and 94% (**3**); [f] NBS, benzene, initiator, reflux 8 h, 44%; [g] PPh_3, paraformaldehyde, KO*t*Bu, DMF, THF, 90%.

exergonic by −57 and −60 kcal/mol, respectively, releasing almost exactly twice as much energy as the RCM of biphenyl **1**. The energy released from multiple RCM reactions in the same molecule is additive, suggesting the feasibility of multiple cyclizations.

These computational results motivated us to prepare substrates to test this methodology. First, we reinvestigated Katz's initial work with **1**. Treating this compound with Grubbs' catalyst **2-Ru** gave phenanthrene in quantitative yield, in agreement with the recent work of Iuliano.[22]
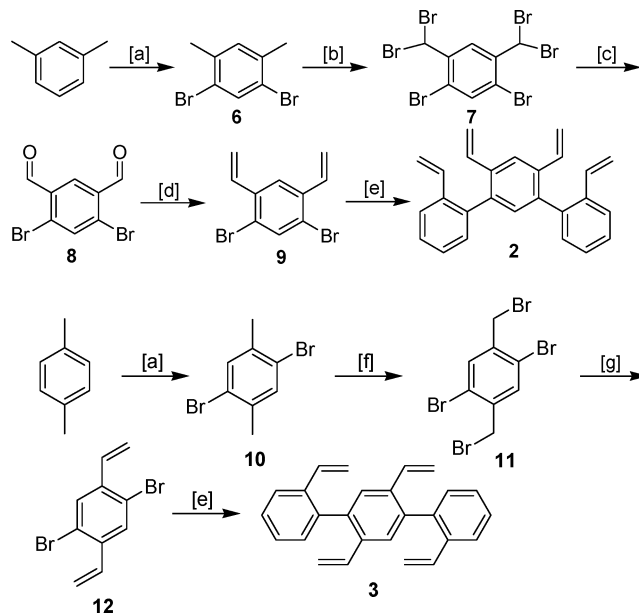
To demonstrate the efficiency of this reaction for one-step multiple cyclizations, we sought to prepare **4** and **5**[29,30] from the RCM of **2** and **3**, respectively, as illustrated in Scheme 2.

The preparation of the tetravinylterphenyls **2** and **3** is outlined in Scheme 3. Initial electrophilic bromination using the method of Schlüter[31] of *m*-xylene smoothly afforded the dibromoxylene[32] **6** on 0.5 mol scale. Subsequent polybromination of **6** under forcing conditions gave bis(benzalbromide) **7** in good yield. We were unable to cleanly monobrominate the two benzylic positions of **6** (i.e., prepare 1,5-dibromo-2,4-bis-bromomethylbenzene) using any of a wide range of conditions. Dialdehyde **8**[33] was obtained by silver nitrate-promoted hydrolysis of **7** in excellent yield. Double Wittig olefination with methylenetriphenyl phosphorane gave 1,5-dibromo-2,4-divinylbenzene **9**.

Likewise, electrophilic bromination of *p*-xylene afforded the dibromoxylene **10**.[31] In contrast to **6**, **10** could be cleanly converted to the bis(benzylbromide)[34] **11**. Double Wittig olefination with *para*-formaldehyde gave 1,4-dibromo-2,5-divinylbenzene **12**.

After optimization, Suzuki coupling[35] of **9** or **12** with *o*-styrenylboronic[36] acid provided the isomeric tetravinylterphenyls **2** or **3** in high yield. Not surprisingly, terphenyls **2** and **3** both exhibited atropisomerism, with rotational barriers of 17 kcal/mol, measured by variable-temperature ^{1}H NMR (see Supporting Information).

With substrates **2** and **3** in hand, we focused our attention on the RCM. Simply treating the corresponding

TABLE 1. Comparison of Tetravinylterphenyl RCM with Different Catalysts[a]

catalyst	substrate	time (h)	yield (%)[b]
1-Mo	**2**	2.5	87
	3	1.5	95
2-Ru	**2**	8.5	88
	3	18.5	88
3-Ru	**2**	2.5	92
	3	3.5	92

[a] Reactions were performed at 25 °C at 5 mol % loading in C_6D_6 and for **1-Mo** and in CD_2Cl_2 for **2-Ru** and **3-Ru**. [b] Based on ^{1}H NMR using an internal standard.

tetravinylterphenyl with Grubbs' catalyst **2-Ru** in dry dichloromethane at 35 °C furnished the dibenzanthracenes **4** and **5** in 98% and 83% isolated yield, respectively, with no detectable side products. The yield of **5** is likely to be higher, but we did not obtain a second crop of crystals to minimize the handling of this highly carcinogenic compound.

The RCM of **2** and **3** to form **4** and **5**, respectively, was also investigated with **1-Mo** or **3-Ru**. The reaction using **1-Mo** and **3-Ru** was faster than using **2-Ru** (Table 1), but all three catalysts were effective.

The low solubility of many PAHs must be addressed to extend this methodology to larger systems. Although carbon disulfide is a good solvent for many large PAHs, sulfur-containing compounds are often considered to be incompatible with transition metal catalysts. Heck, Mioskowski, and co-workers[37] have, however, shown that metathesis of thiols and thioethers is possible using **3-Ru**.

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TABLE 2. Results of RCM in CS_2 with 1-Mo, 2-Ru, and 3-Ru[a]

catalyst	substrate	cat. load (mol %)	product	yield (%)[b]
1-Mo	**2**	10	**4**	68
	3	20	**5**	79
2-Ru	**1**	10	−	0
	2	10	−	0
3-Ru	**1**	10	phenanthrene	71

[a] Reactions were performed at 25 °C for 1 h and monitored by GC/MS. [b] Isolated yields.

Because of its promise to dissolve large PAHs, we attempted the RCM of **1** using **1-Mo**, **2-Ru**, and **3-Ru** in CS_2. The **2-Ru** catalyst was readily quenched, generating an inactive and uncharacterized purple precipitate. Schrock's catalyst worked better: in less than 15 min at 25 °C, **1-Mo** cleanly converted **1** to phenanthrene. The catalyst **3-Ru** proved also to be useful in CS_2. Within 1 h, **3-Ru** cleanly catalyzed the conversion of **1** to phenanthrene. However, within 3 h in CS_2 at 25 °C, **3-Ru** decomposed to an inactive mixture. We then investigated the use of **1-Mo** for the preparative scale multiple RCM of **2** to **4** and **3** to **5** in CS_2. The desired products were formed within 20 min at 25 °C in good yield (Table 2).

The stability of **1-Mo** and **3-Ru** in CS_2 was monitored by ^{13}C and ^1H NMR spectroscopy in CS_2 (see Supporting Information). For **1-Mo**, resonances at 284.8 (^{13}C) and 12.29 ppm (^1H) match literature values[38] for the molybdenum alkylidene carbon bearing hydrogen. The **1-Mo** spectra were unchanged after 36 h at 25 °C. For **3-Ru**, resonances at 221.8, 221.2 (^{13}C), and 19.43 ppm (^1H) match the literature values[39] for the imidazolinylidene ruthenium and alkylidene carbon atoms and for the alkylidene protons. After 36 h at 25 °C, the **3-Ru** spectra revealed decomposition to several products, with the alkylidene resonance vanishing and a new, unassigned resonance appearing at 10.4 ppm.

Conclusions

Calculations show that the RCM of divinyl substituents to give phenanthrene units is exergonic by 28 kcal/mol. The phenanthrene units are thermodynamic sinks, ~27 kcal/mol more stable than competing products. RCM is a synthetically useful method to generate multiple new benzenoid rings in a single step. Three commercially available catalysts, **1-Mo**, **2-Ru**, and **3-Ru**, are effective, although **2-Ru** is less reactive. RCM with catalyst **1-Mo** is effective in carbon disulfide.

Experimental Section

Caution: Benzylic bromides are lachrymators. Dibenzanthracenes are carcinogenic and should be handled with care in accordance with *NIH Guidelines for the Laboratory Use of Chemical Carcinogens*.[40] Carbon disulfide is highly flammable and possesses an extremely low autoignition temperature of 90 °C.

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2,2′-Divinylbiphenyl (1). A solution of 2-bromostyrene (0.109 mL, 1.00 mmol) and tetrakis(triphenylphosphine)-palladium(0) (0.035 g, 0.03 mmol) in dimethoxyethane (DME, 4.35 mL) was stirred for 10 min at 25 °C. To this solution, a solution of *o*-vinylbenzeneboronic acid (0.163 g, 1.10 mmol) in 1 mL of ethanol and a solution of Na_2CO_3 (0.212 g, 2.00 mmols) in 1 mL of water were added. The mixture was heated at reflux for 16 h. After cooling, DME was removed in vacuo and the residue was extracted with water and hexane. Silica gel column chromatography with hexane mobile phase and crystallization from hexane afforded colorless crystals (181 mg, 88%). EI-MS: *m/z* 206.0. The product was spectrally identical to previously reported samples.[21]

Phenanthrene from 1 in $CDCl_2$ Using 2-Ru. The internal standard 1,3,5-trimethoxybenzene (14 mg, 0.083 mmol), substrate **1** (15 mg, 0.073 mmol), and 0.80 mL of degassed and dry CD_2Cl_2 were combined. After recording an initial NMR spectrum, we added $Cl_2(PCy_3)_2Ru=CHPh$ (6 mg, 0.007 mmol). After 8 h at 25 °C, the ^1H NMR spectrum was recorded. Integration versus the internal standard provided the yield (87%).

Phenanthrene from 1 in CS_2 Using 1-Mo. A Schlenk flask was charged with **1** (58.5 mg, 0.284 mmol) and **1-Mo** (24 mg, 10 mol %). Carbon disulfide (11.7 mL) was transferred into the flask by bulb-to-bulb distillation. The solution was stirred at room temperature for 1 h and then quenched by pouring onto 5 g of silica gel. The product was eluted with toluene. Removal of solvent by rotary evaporation gave white crystals (36.2 mg, 71%). EI-MS: *m/z* 178.0. The product was spectrally identical to an authentic standard (Aldrich).

2,4′,6′,2″-Tetravinyl-[1,1′;3′,1″]terphenyl (2). A mixture of **9** (0.720 g, 2.50 mmol) and tetrakis(triphenylphosphine)-palladium(0) (0.173 g, 0.150 mmol) was dissolved in 22.0 mL of 1,2-dimethoxyethane and stirred at 25 °C for 10 min. To this was added a solution of *o*-vinylbenzene boronic acid (0.814 g, 5.50 mmol) in 7 mL of ethanol and a solution of sodium carbonate (1.06 g, 10.0 mmol) in 5 mL of water. The yellow solution was heated at reflux for 16 h. After cooling, the mixture was diluted with diethyl ether and water was added. The ether layer was collected, and the aqueous layer was washed with ether (2 × 30 mL). The organic layers were combined, dried over magnesium sulfate, and concentrated to 5 mL. The solution was diluted with hexane (20 mL). Flash chromatography (hexane/silica) afforded colorless viscous oil (0.780 g, 93%). ^1H NMR at 110 °C (DMSO-d_6): δ 7.95 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.41−7.33 (m, 4H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.84 (s, 1H), 6.49−6.39 (m, 4H), 5.77 (d, *J* = 17.5 Hz, 2H), 5.64 (d, *J* = 17.5 Hz, 2H), 5.19 (d, *J* = 11.0 Hz, 2H), 5.16 (d, *J* = 11.0 Hz, 2H). ^{13}C NMR (CDCl₃): δ 139.3, 139.2, 139.1, 139.0, 136.6, 136.5, 135.8, 135.4, 135.2, 133.3, 132.8, 130.7, 127.9, 127.6, 127.5, 125.3, 125.1, 121.8, 121.6, 115.1, 115.0, 114.9. UV (hexane, nm): $λ_{max}$ 252 (ε 50 200). EI-MS: *m/z* 334.0. Exact Mass Calcd for $C_{26}H_{22}$: 334.1721. Found: 334.1715.

2,2′,5′,2″-Tetravinyl-[1,1′; 4′,1″]terphenyl (3). This was prepared by the reaction of **12** (0.144 g, 0.500 mmol) with *o*-vinylbenzene boronic acid (0.163 g, 1.10 mmol) in the same manner as described for **2**. After chromatography, colorless crystals were obtained from hexane (0.157 g, 94%). mp 124−126 °C. ^1H NMR at 110 °C (DMSO-d_6): δ 7.31 (d, *J* = 7.5 Hz, 2H), 7.03−6.96 (m, 6H), 6.82 (d, *J* = 7.0 Hz, 2H), 6.05 (dd, *J* = 11.5, 17.5 Hz, 2H), 5.95 (dd, *J* = 11.0, 17.5 Hz, 2H), 5.27 (d, *J* = 17.5 Hz, 2H), 5.18 (d, *J* = 17.5 Hz, 2H), 4.76 (d, *J* = 11.5 Hz, 2H), 4.69 (d, *J* = 11.0 Hz, 2H). ^{13}C NMR (300 MHz, CDCl₃): δ 139.7, 139.2, 136.6, 136.6, 135.5, 134.9, 130.9, 128.0, 127.77, 127.2, 125.1, 115.0. UV (methylene chloride, nm): $λ_{max}$ 229; EI-MS: (*m/z*) 334.0. Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.23; H, 6.75.

Dibenz[a,j]anthracene (4) by Reaction in CH_2Cl_2. Compound **2** (0.133 g, 0.40 mmol), $Cl_2(PCy_3)_2Ru=CHPh$ (6.6

(40) *NIH Guidelines for the Laboratory Use of Chemical Carcinogens*; NIH Publication No. 81-2385; National Institutes of Health: Washington, DC, 1981.

mg, 0.008 mmol), and dry dichloromethane (3.4 mL) were mixed and heated to 35 °C for 23 h. The solution was concentrated to 1 mL and purified by silica gel chromatography with 4% ethyl acetate in hexane to give **4** (109.1 mg, 98%). mp 197−198 °C (lit.[30] mp 195−197 °C). ^{1}H NMR (CDCl$_3$): δ 10.08 (s, 1H), 9.05 (m, 2H), 8.38 (s, 1H), 7.46−8.10 (m, 10 H), in agreement with reported values.[29]

Dibenz[*a,j*]anthracene (4) by Reaction in CS$_2$. Compound **2** (28.9 mg, 0.086 mmols) and **1-Mo** (6 mg, 10 mol %) were added to a Schlenk flask. Freshly distilled CS$_2$ (6 mL) was added, and the solution was stirred for 1 h under nitrogen. The solution was then poured onto silica gel and eluted with hexane. The solvent was removed to give white crystals (16.4 mg, 68%) that were spectrally identical to previous reports.[29]

Dibenz[*a,h*]anthracene (5) by Reaction in CH$_2$Cl$_2$. This was prepared from **3** (0.100 g, 0.30 mmol) and Cl$_2$(PCy$_3$)$_2$Ru= CHPh (0.040 g, 0.049 mmol) in dichloromethane (6.0 mL) in the same manner as **4**. Recrystallization gave pure **4** (0.069 g, 83%) as colorless crystals. ^{1}H NMR (CDCl$_3$): δ 9.16 (s, 2H), 8.88 (d, 2H), 7.63−7.99 (m, 10 H). The product was spectrally identical to an authentic standard (Aldrich).

Dibenz[*a,h*]anthracene (5) by Reaction in CS$_2$. A solution of **3** (52.4 mg, 0.157 mmol) and **1-Mo** (24 mg, 20 mol %) in CS$_2$ (9.3 mL) was stirred in a Schlenk flask for 1 h. The solution was poured over silica gel and eluted with toluene. Removal of the solvent afforded **5** (34 mg, 79%). The product was spectrally identical to an authentic standard (Aldrich).

1,5-Dibromo-2,4-dimethylbenzene (6). To an ice-cooled solution of iodine (0.20 g, 0.79 mmol) in neat *m*-xylene (19.7 mL, 0.16 mol) was added bromine (54.6 g, 0.34 mol) dropwise over 1 h in the absence of light. After 16 h at room temperature, 20% aqueous KOH (100 mL) was added. The mixture was shaken under slight warming until the disappearance of the yellow color and was then allowed to cool. The aqueous layer was decanted, and the remaining solids were washed with water (4 × 50 mL). Recrystallization from absolute ethanol gave **6** (24.4 g, 58%) as white crystals. mp 71−72 °C. ^{1}H NMR (CDCl$_3$): δ 7.68 (s, 1H), 7.10 (s, 1H), 2.31 (s, 6H).

1,5-Dibromo-2,4-bis(dibromomethyl)benzene (7). *N*-Bromosuccinimide was added in three equal portions (3 × 3.82 g, 0.063 mol) over 9 h to a solution of **6** (2.64 g, 0.010 mol) in refluxing CCl$_4$ (60 mL) under incandescent irradiation (100 W). The mixture was cooled to room temperature and filtered through a sintered glass frit, and the residue was washed twice with hexane. The filtrate was evaporated in vacuo. Recrystallization from hexane afforded **7** (5.09 g, 88%) as tan crystals. mp 115−118 °C. ^{1}H NMR (CDCl$_3$): δ 8.66 (s, 1H), 7.71 (s, 1H), 6.97 (s, 2H). ^{13}C NMR (CDCl$_3$): δ 141.5, 136.0, 133.7, 121.3, 37.8. UV (MeOH, nm): λ$_{max}$ 229 (ε 41 000). EI-MS: *m/z* 499.0. Anal. Calcd for C$_8$H$_4$Br$_6$: C, 16.58; H, 0.70. Found: C, 16.82; H, 0.88.

4,6-Dibromobenzene-1,3-dicarbaldehyde (8). To a solution of **7** (15.6 g, 0.027 mol) in 95% ethanol (625 mL) was added a solution of AgNO$_3$ (19.2 g, 0.113 mol) in water (125 mL), and the mixture was stirred at reflux for 30 min. The solution was allowed to cool, AgBr was filtered off, and the cake was washed with 95% ethanol (3 × 20 mL). The filtrate was evaporated to dryness under reduced pressure. The residue was washed with water until neutral and dried in vacuo to yield **8** (7.53 g, 96%) as a white solid. mp 192−193 °C (lit.[33] mp 192 °C). ^{1}H NMR (CDCl$_3$): δ 10.32 (s, 2H), 8.39 (s, 1H), 8.04 (s, 1H); the observed chemical shifts were not in agreement with reported values.[33] ^{13}C NMR (DMSO-*d*$_6$): δ 189.9, 138.4, 133.0, 130.8, 130.5. EI-MS: *m/z* 291.0.

1,5-Dibromo-2,4-divinylbenzene (9). Potassium *tert*-butoxide (2.83 g, 0.025 mol) was added to methyltriphenylphosphonium bromide (9.77 g, 0.027 mol) dissolved in 180 mL of tetrahydrofuran. The yellow solution was stirred for 5 min and placed in an ice bath, and **8** (3.50 g, 0.012 mol) was slowly added. The reaction mixture was stirred overnight at 25 °C. The solvent was evaporated in vacuo, and the residue was filtered through silica gel using hexane. The solvent was

removed, and purification by column chromatography using hexane provided **9** (2.10 g, 61%) as white crystals. mp 84−86 °C. ^{1}H NMR (CDCl$_3$): δ 7.76 (s, 1H), 7.68 (s, 1H), 6.96 (dd, *J* = 10.8, 17.4 Hz, 2H), 5.75 (d, *J* = 17.1 Hz, 2H), 5.41 (d, *J* = 11.1 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 137.2, 136.3, 135.2, 124.7, 123.0, 117.5. UV (hexane, nm): λ$_{max}$ 245 (ε 27,600). EI-MS: *m/z* 288.0. Anal. Calcd for C$_{10}$H$_8$Br$_2$: C, 41.71; H, 2.80. Found: C, 42.02; H, 2.86.

1,4-Dibromo-2,5-dimethylbenzene (10). This was prepared from *p*-xylene (23.1 mL, 0.19 mol), iodine (0.30 g, 1.18 mmol), and bromine (19.8 mL, 0.385 mol) in the same manner as described for **6**, yielding **10** (33.3 g, 67%) as white crystals. mp 72−74 °C; ^{1}H NMR (CDCl$_3$): δ 7.39 (s, 2H), 2.33 (s, 6H).

1,4-Dibromo-2,5-bis(bromomethyl)benzene (11). A mixture of **10** (20.4 g, 77.1 mmol), *N*-bromosuccinimide (28.3 g, 0.159 mol), and 1,1′-azobis(cyclohexanecarbonitrile) (0.010 g, 0.041 mmol) in benzene (380 mL) was heated at reflux for 8 h. The solvent was removed in vacuo, and recrystallization with absolute ethanol afforded **11** (14.4 g, 44%) as white crystals. mp 156−158 °C. ^{1}H NMR (CDCl$_3$): δ 7.66 (s, 2H), 4.51 (s, 4H).

1,4-Dibromo-2,5-divinylbenzene (12). A mixture of **11** (4.40 g, 10.4 mmol) and triphenylphosphine (6.83 g, 26.0 mmol) in dimethylformamide (50 mL) was heated at reflux for 18 h. The solvent was removed, and tetrahydrofuran (80 mL) and paraformaldehyde (7.04 g) were added. Potassium *tert*-butoxide (3.51 g, 31.3 mmol) in tetrahydrofuran (15 mL) was then transferred in the reaction vessel, turning the mixture cloudy and light yellow. The solvent was evaporated, and the residue was separated using a silica column with hexane. Removal of solvent and recrystallization from absolute ethanol afforded **12** (2.70 g, 90%) as white crystals. mp 81−83 °C. ^{1}H NMR (CDCl$_3$): δ 7.71 (s, 2H), 6.95 (dd, *J* = 12, 18 Hz, 2H), 5.71 (d, *J* = 15 Hz, 2H), 5.40 (d, *J* = 12 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 138.4, 134.7, 130.8, 122.7, 117.9. UV (methylene chloride, nm): λ$_{max}$ 276 (ε 24 000); EI-MS (*m/z*): 288.0; Anal. Calcd for C$_{10}$H$_8$Br$_2$: C, 41.71; H, 2.80. Found: C, 42.01; H, 2.72.

Phenanthrene from 1 in CS$_2$ (NMR Scale). The vinyl compound (**1**, 10 mg) was placed into either a J-Young tube or a thick-walled NMR tube. A sealed capillary containing dry, degassed CDCl$_3$ or C$_6$D$_6$ was inserted into the tube. In a glovebox, 10 mol % of catalyst (∼3 mg of **1-Mo** or 4 mg of **2,3-Ru**) was added. To the tube, 200 μL of CS$_2$ was distilled via bulb-to-bulb distillation using a vacuum line and liquid nitrogen. The tube was then sealed under vacuum and allowed to warm to room temperature. The ^{1}H NMR was taken after 15 min.

General Procedure for Preparative CS$_2$ Reactions. The pendant vinyl compound (30−50 mg of **1**, **2**, or **3**) was placed into a Schlenk flask, evacuated, and back-filled with nitrogen. In a glovebox, 10 mol % of catalyst was then added to the flask. The carbon disulfide (∼8 mL) was added by bulb-to-bulb distillation under vacuum. The final concentration of the solution was ∼6 mg of substrate per 1 mL of CS$_2$. The reaction was stirred at room temperature for 1 h. The solution was poured onto silica gel in a filter and washed with hexane or toluene. The solvent was then removed by rotary evaporation. Products were analyzed by GC/MS and ^{1}H NMR.

Supporting Information Available: Computational methods, geometries, energies, experimental procedures, and ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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