In pursuit of conjugation in one-dimension:
Synthetic studies of oligomeric and polymeric organic materials

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ABSTRACT

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Chapter 1. Ring-Opening Alkyne Metathesis Polymerization of Dibenzocyclooctynes

A molybdenum(VI) propylidyne substituted with bidentate phenoxides will react with dibenzocyclooctynes in living ring-opening alkyne metathesis polymerization (ROAMP). The corresponding monodentate phenoxides do not yield well-controlled polymerizations. However, if the substrate in the ROAMP reaction is an aliphatic cyclooctyne, uncontrolled, non-living polymerizations take place in all cases.

Chapter 2. Ring-Opening Alkyne Metathesis via a Tungstenatetrahedrane Intermediate

A cyclopropenone-modified dibenzocyclooctyne will undergo a single ring opening alkyne metathesis reaction in the presence of Schrock’s tris(tert-butoxy)tungsten(VI) neopentyldiyne—a highly active alkyne metathesis catalyst. Despite the enormous amount of ring strain present in and related diphenycyclooctadiynes, these compounds do not readily undergo ring-opening alkyne metathesis polymerization (ROAMP), even with the most active alkyne metathesis catalysts available. The ring-opening of 1 proceeds via a tungstenatetrahedrane intermediate. Because of its sluggish reactivity, we were able to
follow the ring-opening reaction by NMR to gain mechanistic insight into this remarkable behavior.

Chapter 3. Functionalization of Diphenyloligoenes

Bromine and carboxylic acid substituted α,ω-diphenyl-µ,ν-dicyano-oligoenes (DPDC\textit{n}) were synthesized up to 9 and 7 olefin units in length, respectively. The carboxylic acid functionalized oligoenes (DPDC\textit{n}-CO\textsubscript{2}H) are aligned through hydrogen bonding to DMF in the solid state. These can also be used to direct monolayer formation of Fe\textsubscript{3}O\textsubscript{4} on single crystalline, 100 Gallium Arsenide.
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Dedication

To my mom and dad, for teaching me about hard work and humor.
Chapter 1. Ring-Opening Alkyne Metathesis Polymerization of Dibenzocyclooctynes

1.1 A Brief History of Alkyne Metathesis

In 1968, Bailey et al. reported that 2-pentyne will disproportionate to 2-butyne and 3-hexyne when passed over a heterogeneous mixture of tungsten(VI) oxide and silica. Six years later, the first homogeneous catalyst system for this alkyne metathesis reaction was reported by the Mortreux group, and a year after that Katz proposed the currently well-accepted metallacyclobutadiene mechanism for the transformation (Scheme 1).

![Scheme 1 - 1: The alkylidyne/metallacyclobutadiene mechanism for acetylene metathesis.](image)

Evidence in favor of this mechanism was provided by the Schrock group through their demonstration of the utility of both high-valent metal alkylidyynes and metallacyclobutadienes in promoting alkyne metathesis.

Since that time, a variety of alkyne metathesis catalysts and pre-catalysts based on the metal-carbyne structure have since been reported. These systems cover range of activity, stability, and functional group tolerance. Notable among these are Mortreux’s molybdenum(0) carbonyl system (1), which employs various phenols as activating ligands, Schrock’s ubiquitous tris(tert-butoxy)(2,2-dimethylopropyldyne) tungsten(VI) (2), Moore’s molybdenum(VI) propylidyne pre-catalyst (3), and Fürstner’s triphenylsilyloxybrombenzylidyne...
(4)\(^1\) (Figure 1-1). Because of these advances, alkyne metathesis has been developed into a useful synthetic tool in the form of alkyne cross metathesis (ACM) and the related acyclic diyne metathesis polymerization (ADIMET). ACM and ADIMET have been used in the synthesis of natural products,\(^{25,26}\) unique inorganic and organic materials,\(^{27,28}\) and conjugated polymers.\(^{29–32}\)

There are, however, remarkably few examples of ring-opening alkyne metathesis polymerization (ROAMP), and there remains a need for reliable and robust ROAMP methods.\(^{18,19,24,33–40}\) This is in contrast to the related olefin ring-opening metathesis polymerization (ROMP), which today is one of the most ubiquitous and easily controlled living polymerization reactions.\(^{41}\) ROMP can be used as a stand-alone method or in conjunction with other polymerization reactions to yield a diverse array of polymeric materials for a wide number of applications.\(^{41–43}\) With the number of synthetically accessible, complex cycloalkynes on the rise, ROAMP too has the potential to produce a variety of heretofore-unavailable polymeric architectures (Figure 1-2).\(^{44–47}\) Furthermore, the highly reactive acetylene functionality primes these polymers for a diverse array of post-synthetic modifications, from click-chemistry to enyne and aryl-yn cyclizations.

**Figure 1 - 1: Popular Alkyne Metathesis Catalysts.**
A controlled ROAMP reaction should follow the same reaction pattern of any living polymerization. For all polymerization reactions, the degree of chain extension is related to the relative rates of initiation, propagation, termination, and chain-transfer reactions. For a living polymerization the rate of initiation should be much faster than the rate of propagation to ensure that all chains are activated before propagation begins. Termination and chain-transfer events must be eliminated.41

For ROAMP (Scheme 1-2), if the rate of reaction between the polymerization initiator and the cyclic alkyne \( k_i \) is much faster than subsequent reactions with the resulting linear alkyne, the rate of chain-transfer and termination \( k_{CT} \) should be negligible. In theory this can be achieved by adjusting the metathesis activity of the initiator and by introducing strain into the cyclic
alkyne. Of these two factors, controlling the relative rates of initiation and propagation ($k_p$)—that is, ensuring that the very first ring opening reaction is faster than the rest—proves to be the more challenging. How best to accomplish it is the subject of ongoing study some of which will be discussed below.

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1.2 The Status of ROAMP Today

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Scheme 1 - 3: Schrock’s synthesis of polycyclooctyne (poly-5) via ROAMP and ADIMET.

The first example of ROAMP was demonstrated by the Schrock group in 1987 (Scheme 1 - 3). This was several years after the demonstration of living olefin ROMP by the Grubbs group. In that communication and the full paper that followed it two years later, the authors reported that both tungsten and molybdenum alkylidynes would initiate the ring-opening of cyclooctyne (5). However, they either obtained polymers (using W$_2$(OtBu)$_6$, 6) that were of exceptionally high poly-dispersity (PDI = 4 - 7) or oligomers and macrocycles. Polymers of similar molecular weight and polydispersity were obtained using cross metathesis. The authors reasoned that the linear alkynes formed in the polymerization were vulnerable to cross-metathesis catalyzed by the propagating polymer, contributing to the large PDIs and producing macrocycles in the expected, free-energy controlled distribution. Attempts to use less active alkylidynes to initiate the reaction resulted only in the isolation of stable metallacyclobutadiene
intermediates. The authors therefore concluded that living ROAMP was not possible with the alkyne metathesis catalysts available at the time.

Scheme 1 - 4: Bazan’s polymerization of tetrasilylcyclooctadiynes.

Almost a decade later, the Bazan group reported the polymerization of Tetrasilacycloocta-3,7-diynes (7) using tungsten based alkyne metathesis catalysts. They found that these silicon containing cyclooctynes were far more stable and far less reactive than cyclooctyne in the alkyne metathesis reaction. Both features were likely due to steric protection provided by the alkyl groups on silicon. When ethyl groups were used, only highly active, in situ generated tungsten methylidyynes could initiate the polymerization. The authors were able to manipulate this reactivity to produce regioregular polymers of alternating alkynes and di-silanes in respectable molecular weights and PDI (poly-7, MW: 31000, PDI: 1.4). In these polymers, the substituents on silicon alternated between ethyl and methyl indicating a head-to-tail ring-opening reaction (Scheme 1-4).

Scheme 1 - 5: Nuckolls’s polymerization of 8 with Schrock’s Catalyst.
The next example of ROAMP did not come until 2008 when Matt Carnes, then a graduate student in the Nuckolls lab explored the metathesis reactivity of the highly unstable ene-yne, 8.\textsuperscript{48} Despite the fact that the alkyne in 8 is strained to 155° (calculated by density functional theory—B3LYP/6311G**), its polymerization with the highly reactive 2 (Schrock’s catalyst) was sluggish (>18 hours at 80 °C). The polydispersity of the resulting polymer was high (PDI: 2.4), which the authors attributed to the high rate of propagation over initiation.

Scheme 1 - 6: Tamm’s polymerization of cyclooctyne with imidazolin-2-iminato functionalized tungsten(VI) complexes.

In 2010, the Tamm group reported that an imidazolin-2-iminato modified tungsten benzylidyne, 9, and alkylidyne, 10, were capable as initiators of the ROAMP of cyclooctyne.\textsuperscript{36} The polymers produced were of high molecular weight and generally low PDIs, depending on the amount of catalyst used and the substrate concentration (for their best conditions, $M_n$: 33000, PDI: 1.4, polymer yield 70%). Linear polymers were only obtained when the reaction was run in neat cyclooctyne. Dilution with toluene lead to the formation of cyclic oligomers, indicating that the newly formed linear alkynes were still reactive with the propagating polymer chains.

That same year, Felix Fischer, a postdoctoral researcher in the Nuckolls lab, demonstrated the first example of living ROAMP.\textsuperscript{35} For this he employed a series of dibenzocyclooctynes (11-13) that were far more stable than previously polymerized cyclooctynes. In addition to Schrock’s
catalyst, Fischer screened an assortment of alkoxide, phenoxide, and amide ligands for the activation of the widely used molybdenum(VI) propylidyne \([\text{N(tBu)(Ar)}]_3\text{Mo}[\text{CCH}_2\text{CH}_3]\) (3). 

Scheme 1 - 7: Nuckolls's Polymerization of dibenzocyclooctynes with various initiators.

In that screen he found that the use of 2-nitrophenol, yielded polymer with remarkably lower polydispersity (PDI = 1.1) than any other ligand albeit at about five times the molecular weight than expected for the initiator loading, an indication that not all the molybdenum was activated for polymerization. Nevertheless, he went on to show that the polymers propagating chain-ends continued to be active, and that monomer could be added to yield a linear increase the polymer molecular weight without increasing the polydispersity—a hallmark of living polymerizations.

1.3 Preliminary Screens of Bidentate Phenoxides

Our motivation for the research described below was the potential chelating ability of the nitro substituent in 2-nitrophenol. We speculated that this might be responsible for its remarkable ability to promote a living ROAMP. When compared with other phenolic ligands screened there was no clear trend with respect to pKa or stericics. This suggested that the nitro group played a role beyond its effects on the electronic and physical structure of the phenolate. As an ortho
substituent, it could bind to the free coordination site on the propagating molybdenum (VI) complex. This binding would in turn stabilize the molybdenum center and inhibit insertion of the next cyclooctyne monomer, slowing the rate of chain propagation with respect to initiation.

Scheme 1 - 8: Synthesis of salicylimine ligands.

Scheme 1 - 9: Polymerization of 13 with salicylimine ligands and 3.

<table>
<thead>
<tr>
<th>Entry #</th>
<th>Ligand</th>
<th>high $M_n$</th>
<th>low $M_n$</th>
<th>high PDI</th>
<th>low PDI</th>
</tr>
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<td>1</td>
<td>14: $R_1 = R_2 = R_3 = R_4 = H$</td>
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<td>--</td>
<td>1.2</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>15: $R_1 = R_3 = R_4 = H$, $R_2 = Me$</td>
<td>703,000</td>
<td>--</td>
<td>1.2</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>16: $R_1 = R_2 = R_3 = H$, $R_4 = NO_2$</td>
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<td>5,900</td>
<td>1.5</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>17: $R_1 = R_2 = R_3 = H$, $R_4 = OMe$</td>
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<td>5,300</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>6</td>
<td>18: $R_2 = R_3 = R_4 = H$, $R_1 = NO_2$</td>
<td>383,000</td>
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<td>1.1</td>
<td>1.7</td>
</tr>
<tr>
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<td>1.3</td>
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<td>1.3</td>
</tr>
<tr>
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<td>1.6</td>
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<tr>
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<td>1.5</td>
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<td>--</td>
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</tbody>
</table>

Table 1 - 1: Number averaged molecular weight and polydispersity index for polymerizations of 13 with various salicylimine ligands.
In order to establish whether other ortho-substituents capable of donating electron density to the metal center were effective in controlling the polymerization of dibenzocyclooctynes, we screened a series of salicylimine ligands for the activation of initiator 3 in the polymerization of monomer 13 (cf. Figures 1 - 1 and Scheme 1 - 7). Salicylimines have already been used in olefin metathesis catalysts, including those capable of ROMP, and have shown themselves to be effective competitive inhibitors of alkene binding.49–53 We hypothesized that, as for these alkylidene complexes, the imine nitrogen could act as a reversibly binding σ-donor to the alkylidyne. These ligands were synthesized by the condensation of a salicylaldehydes with a number of different amines and anilines (Scheme 1-8). Table 1 - 1 shows the number average molecular weights (M_n) and polydispersities for the polymerization of dibenzocyclooctyne 13. Many of the ligands used yielded polymers with bi-modal molecular weight distributions, indicating that more than one catalytic species was present in solution.

From this screen we established that N-phenyl salicylimine, 14, gave consistently lower PDIs, but still with much higher than expected Mn. NMR analysis confirms that there are multiple molybdenum species present in solution. When the reaction was cooled to –78 °C, however, we found that the M_n dropped to 6000—exactly that which was expected for a 5:1 monomer to initiator loading. We concluded that at lower temperatures, all metal centers present in solution were able to initiate before the beginning of the propagation reaction.

1.4 Polymerizations of a Simplified Monomer with Bidentate Phenoxides
To further investigate this temperature and ligand dependence we switched to the simpler and more soluble tri-isopropylsilyl (TIPS) protected, dibenzocyclooctyne, 28. The synthesis of 28 is also less laborious (Scheme 1-9). We start with nickel-catalyzed Negishi-like homocoupling of commercially available 1-(bromomethyl)-3-methoxybenzene (29). The resulting diarylethane, 30, is subjected to Freidel-Crafts alkylation with tetrachlorocyclopropene to yield cyclopropenone 31 upon hydrolysis of the resulting dichlorocyclopropene. Deprotection of the methoxy groups with boron tribromide, followed by protection with TIPS gives cyclopropenone 32. Finally, photolysis of the carbonyl yields 28 in just five steps from commercially available material. Dibenzocyclooctyne 28 is stable indefinitely when stored below 0 °C.

Scheme 1 - 10: Synthesis of dibenzocyclooctyne 28.

For structural confirmation and additional insight into its three-dimensional conformation, we obtained a crystal structure of the related dibromo-dibenzocyclooctyne, 33 (Figure 1-2). 33 is synthesized in the same manner as 13 with the exception of the final protection step, where dodecyl is replaced with TIPS. 33 is chiral in the solid state and crystalizes in the monoclinic, P2_1/c space group as a racemic co-crystal, with two molecules per unit cell.
Figure 1 - 3: Crystal structure of dibenzocyclooctyne 33. Methyls and hydrogens are excluded for clarity. C23-C24-C25 Bond angle: 155.7°; C23-C24 bond distance: 1.20 Å. Thermal ellipsoids represent 50% probability.

In the polymerization of 28, we compared the activity of 3 activated by 14 with 2-nitrophenol, 34, as well as related phenols 35 – 37, both at room temperature and at –78 °C. 35 and 36 are electronically similar to 34 and 14, respectively, but cannot chelate to 3. Cresol (37) was chosen to rule out steric contributions to activity, although it should be noted that both 2-trifluoromethyl phenol and 1-naphthalenol were screened in the previous study.35

Figure 1 - 4: Phenols screened in the following study.

1 The following work has been published, and is recounted here with permission from the American Chemical Society, which allows inclusion of journal articles into dissertations. See reference 34.
In each polymerization reaction three equivalents of phenol were mixed with one equivalent of 3 in toluene (yielding initiator complexes 3-14, 3-34 – 3-37). This mixture was then added to a rapidly stirred solution of 5 equivalents of 28 in toluene. Aliquots were taken at 15, 30, 45, 60, 90, and 120 seconds. We confirmed by NMR that all monomer was consumed within the first 30 seconds of the reaction. We also observe no change in the polydispersity or molecular weight of the polymers after the initial polymerization.²

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**Figure 1 - 5:** GPC traces from polymerizations of 28 with 3 activated by phenols 14, 36 – 37. Reactions run at a) –78 °C; and, b) room temperature.

Figure 1 - 5 shows the GPC traces for polymerizations of 28 quenched with methanol after 15 seconds. When the reaction is run at -78 C, both 3-14 and 3-34 yield polymers with low PDI

² Detailed GPC and NMR data are given in the experimental section of this chapter.
and the expected Mn for a 5:1 monomer to initiator loading. Mass spectrometric analysis of poly-28 formed in the presence of 3-14 is consistent with the formation of oligomers ranging from the trimer to the nonamer and terminated at either end with a butynyl and a methyl group. The other three initiator complexes all yield polymers with excessively high Mn and broad molecular weight distributions. At room temperature, 3-14 again yields low molecular weight polymer with a narrow weight distribution (PDI = 1.2). However, 3-34 yields polymers with low PDI (1.3) but with an order of magnitude higher molecular weight than expected. Polymerizations with 3-35 – 3-37 again yield high molecular weight polymers with PDI > 3.0. We made several attempts to increase the monomer-initiator loading beyond 5:1, but we have not observed an increase in molecular weight. We again believe this is likely due to solubility properties of the polymer or possibly to the lifetime of the metal center. Despite this, we are able to test whether the polymer in solution contains living chain ends in the polymerization of 28.

Figure 1 - 6: GPC of aliquots taken at 45, 90, 135, and 180 s from living polymerizations of.
2.5 equiv. of 28 were added at 60, 105, and 150 s.

Figure 1 - 6 shows the polymerization of 28 using 3-14 and 3-34 as initiators. After 45 seconds an aliquot is removed, and an additional 2.5 equivalents of monomer is added. This is repeated
twice more, and the resulting polymers were analyzed by GPC. In both cases, addition of additional monomer results in an increase in polymer molecular weight with no change in polydispersity. We therefore conclude that at low temperatures, both 3-14 and 3-34 initiate living polymerizations with dibenzocyclooctynes.

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1.5 Polymerizations of an aliphatic cyclooctyne

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In order to test the generality of our findings, we also screened initiators 3-14, 3-34 – 3-37 in the polymerization of functionalized cyclooctyne, 38 (Scheme 1-11) at -78 C. 38 is synthesized in the manner outlined by Dommerholt et al.\textsuperscript{55} In the final step the free alcohol is protected by a 4-chlorobenzoyl group in order to provide solubility as well as a UV active handle for GPC analysis.

![Scheme 1 - 12: Polymerization of 38.](image)

In the polymerization of 38, all five initiators yield polymers. However each of these polymers has significantly higher than expected $M_n$ ($M_n$ from 6000–10000; expected $M_n \sim 1500$) and PDIs ranging from 1.4–1.8. In most cases, these $M_n$ and PDIs continue to evolve over time (Figure 1-6). Between 15 and 120 seconds, a significant decrease in $M_n$ was observed for initiators 3-34 and 3-37, and in increase in $M_n$ was observed for initiators 3-35 and 3-38. Both
observations can presumably be attributed to cross metathesis. The polymers formed when \textbf{3-14} is used as an initiator, however, do not react further under the polymerization conditions.

We were not able to demonstrate that these polymers contain living chain ends, as we observe no increase in molecular weight when additional equivalents of \textbf{38} are added to the solution (see experimental for details).

\textbf{1.6 Discussion}

The experiments discussed above illustrate a number of properties in the ROAMP reaction of cyclooctynes. The difference in ROAMP reactivity for aliphatic cyclooctyne \textbf{38} when compared with \textbf{28} can be attributed to the structural similarity of the molybdenum(VI) propylidyne initiator and the molybdenum(VI) alkylidyne (poly-\textbf{38} in Figure 1 – 8) in the propagating species. This suggests that the structure of the metal-carbon bond is significant and that the reactivity of molybdenum (VI) alkylidyne is inherently different from that of molybdenum (VI)
benzylidyynes. The relative stability of benzylidyynes over alkylidyynes helps to explain this difference.\textsuperscript{56}

**Figure 1 - 8: Propagating polymers from the ROAMP of cyclooctynes.**

Because of their structural similarity, the addition rate of the first equivalent of 38 to the molybdenum propylidyne—the initiation, $k_{\text{init}}$—and the rate of subsequent additions of 38 to the growing **poly-38** ($k_{\text{prop}}$) are essentially equal ($k_{\text{init}} \sim k_{\text{prop}}$). This leads to an increase in both polydispersity and molecular weight of the resulting polymers. In contrast, the addition of the first equivalent of 28 to the molybdenum propylidyne leads to a thermodynamically more stable benzylidyne. Therefore, $k_{\text{prop}}$ is expected to be inherently smaller than the $k_{\text{init}}$ in the polymerization of dibenzocyclooctynes. Significantly, this effect only manifests itself in the presence of phenoxides with chelating ortho-substituents (14 and 34). In the case of non-chelating phenoxide ligands (35 – 37) both the initiation step and the propagation steps appear to proceed at similar rates. We speculate that this is due to the extremely high reaction rates, likely on the order of diffusion. This leads us to the conclusion that propagating molybdenum species must first bias the relative reaction rates of initiation and propagation before bidentate ligands can have an effect.

The difference in reactivity exhibited by the 2-nitrophenol complex (3-34) when compared with the salicylimine complex (3-14) can be rationalized in the context of ligand field theory. The imine will be a stronger $\sigma$-donor, and should therefore more effectively stabilize the
propagating metal center, as well as compete more successfully with the alkyne for the open coordination site. This explains both the higher PDI’s observed from 3-34 overall, and the difference in reactivity of 3-14 and 3-34 with dibenzocyclooctynes at room temperature. The difference in room temperature reactivity of dibenzocyclooctynes 28 and 13 is less clear. We speculate that this has much to do with the difference in solubility between the dodecyl and TIPS protected monomers and polymers, especially at the very high reaction rates observed. This could strongly influence the concentration dependent rates of initiation for the multiple metal complexes present in solution. At lower temperatures, the chelating ortho-substituent is also likely to be more tightly bound. This remarkable substrate dependence merits further study.

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1.7 Conclusion

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We have investigated the effect of bidentate phenoxides in the ring opening alkyne metathesis polymerization of cyclooctynes. We have found that these monomers behave differently based on the substitution alpha to the alkyne. The ROAMP of dibenzocyclooctynes can be controlled well by the addition of an ortho-chelating substituent to the phenolate ligand attached to a molybdenum(VI) propylidyne, while the ROAMP of cyclooctynes cannot. This study can be used as a guide in the selection of initiators for particular ROAMP substrates, and in the design of new ROAMP initiators.

I am grateful to the following people for their assistance on this project. Dr. Wes Sattler in Professor Ged Parkin’s group solved the crystal structure of 33. The screens of salicylimine ligands were carried out in collaboration with Professor Felix Fisher, currently of the University
of California Berkeley, during his postdoctoral research. Daniel Paley synthesized 3. Dr. Yashuhiro Itagaki and Mirko Palma assisted with MALDI-MS.

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1.8 Experimental Section

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General Materials and Methods:

All chemicals were purchased from Sigma-Aldrich, Fisher Scientific, TCI America, or Strem Chemicals and were used without further purification. When necessary, solvents were dried by passing through a column of activated alumina under an atmosphere of Ar or distilled from sodium and benzophenone. All reactions were performed in oven dried or flame dried glassware under an atmosphere of Ar. Flash chromatography was performed on a Teledyne ISCO CombiFlashRf using RediSepRf silica gel columns. $^1$H (400 or 500 MHz) and $^{13}$C (100 or 125 MHz) nuclear magnetic resonance spectra were recorded at 300 K (unless otherwise noted) on Bruker 400 and 500 FT NMR spectrometers. Spectra are referenced to the solvent residual peak (CDCl$_3$, $\delta = 7.26$ [H] and $\delta = 77.26$[C], toluene-d$_8$, $\delta = 2.09$[H]). Resonance peaks are categorized as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (b). Coupling constants ($J$) are given in Hz. Low-resolution LC mass spectra were recorded on a JEOL LCmate (ionization mode: APCI+); high-resolution mass spectra were recorded on a JMS-HX110 HF mass spectrometer (ionization mode: FAB+); MALDI-MS was recorded on a AB SCIEX Voyager DE MALDI. GPC was performed on a Varian PL-GPC 50 Plus equipped with a guard column and two Polypore (300 mm) columns calibrated to polystyrene standards. All GPC data was analyzed using a 254 nm wavelength UV detector. [([N(tBu)Ar)$_3$Mo≡CCH$_2$CH$_3$]$^{[11]}$ (Ar = 3,5-dimethyl benzene) = 3 and 12 were synthesized following literature procedures. 3 was weighed in
an Argon glove box prior to mixing with phenol. All NMR experiments with 3 were set up inside an argon Glove box and performed in Wilmad® quick pressure valve NMR tubes purchased from Sigma-Aldrich. The single crystal x-ray diffraction data of 33 was collected on a

*Synthesis of Monomers and ligands:*

![Diagram of 1,2-bis(3-methoxyphenyl)ethane (30)](image)

1,2-bis(3-methoxyphenyl)ethane (30) NiBr₂(PPh₃)₂ (2.03 g, 2.73 mmol), activated Zinc powder (5.37 g, 82.1 mmol), and Et₄N⁺I⁻ (14.1 g, 54.7 mmol), were combined under Argon in a round bottomed flask. THF (60 mL) was added to the mixture, followed by 3-(bromomethyl)anisole, 29 (11.0 g, 54.7 mmol) in 25 mL THF. The reaction was stirred at room temperature, and monitored by TLC until all 29 had disappeared. Upon the reactions completion, hexanes (100 mL) was added, and the mixture is filtered and washed several times with hexanes. The filtrate was collected, concentrated in vacuo, and purified by flash column chromatography (5% EtOAc in Hexanes) to yield 30 as a yellow oil (5.87 g, 24.4 mmol, 89.3%). Structure was confirmed by ¹H NMR, and is consistent with that reported in reference 33. ¹H NMR (300 MHz, CDCl₃) 7.23 – 7.13 (m, 2H), 6.84 – 6.65 (m, 6H), 3.75 (s, 6H), 2.88 (s, 4H).
4,9-dimethoxy-6,7-dihydro-1H-dibenzo[\(a,e\)]cyclopropa[c][8]annulen-1-one (31) was synthesized as described in reference 33. Starting with 5.70 g (23.7 mmol) of 30 yielded 3.69 g 31 (12.6 mmol, 53.3%). Structure confirmed by \(^1\)H NMR and is consistent with that reported in reference 33: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.92\ (d, J = 9.2\ \text{Hz, 1H}), 6.99 - 6.83\ (m, 2H), 3.88\ (s, 3H), 3.35\ (d, J = 10.5\ \text{Hz, 1H}), 2.59\ (d, J = 10.5\ \text{Hz, 1H}).

4,9-di(triisopropylsilyl)oxy-6,7-dihydro-1H-dibenzo[\(a,e\)]cyclopropa[c][8]annulen-1-one (32)

A 500 mL round bottom flask was charged under an Ar atmosphere with 31 (3.4 g, 11.6 mmol) in dry CH\(_2\)Cl\(_2\) (150 mL) and cooled to \(-78\ \text{°C}\). BBr\(_3\) (7.69 mL, 81.4 mmol) was added dropwise and the resulting mixture stirred for 30 min at \(-78\ \text{°C}\) and thawed to 24 °C. After completion the mixture was cooled to \(-78\ \text{°C}\), quenched with MeOH (60 mL), and concentrated on a rotary evaporator to yield the deprotected diphenol (3.06 g) as a pale brown solid which was used in the next step without further purification.

A 100 mL round bottom flask was charged under an N\(_2\) atmosphere with (3.06 g, 11.6 mmol), and triisopropylsilyl chloride (6.14 mL, 29.0 mmol) in dry DMF (25 mL). Triethylamine (8.1 mL, 58.0 mmol) was added. The resulting mixture was stirred for 16 h at 24°C, quenched with H\(_2\)O (100 mL), and extracted with diethyl ether (3 x 100 mL). The combined organic phases were washed with saturated aqueous NaCl solution (2 x 25 mL), dried (MgSO\(_4\)), and concentrated on a rotary evaporator. Column chromatography (SiO\(_2\); EtOAc/hexane 5\(\rightarrow\)15%) yielded 33 (5.11 g, 73%) as a colorless solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.83\ (d, J = 8.0\ \text{Hz, 1H}).\)
Hz, 2H), 6.83-6.80 (m, 4H), 3.31-3.23 (m, 2H), 2.61-2.54 (m 2H), 1.28-1.20 (m, 6H), 1.07 (d, J = 7.5, 36H) ppm; $^{13}$C NMR, (100 MHz, CDCl$_3$): $\delta =$ 159.4, 153.7, 147.9, 142.4, 135.6, 121.2, 118.1, 116.8, 17.1, 12.7 ppm; HR-MS: m/z (%): 577.35 [M+H] C$_{34}$H$_{53}$O$_3$Si$_2$ calc. 576.35

3,8-di(triisopropylsilyl)-5,6-dihydro-11,12-didehydrodibenzo[a,e]-[8]annulen (28) A 50 mL Pyrex round bottom flask was charged under an Ar atmosphere with 32 (1.06 g, 1.44 mmol) in THF/MeOH (30 mL, 2:1) and was irradiated (medium pressure Hg lamp) at 24°C for 90 min. The solvent was concentrated on a rotary evaporator. Column chromatography (SiO$_2$; hexane/CH$_2$Cl$_2$ 19:1) yielded 28 (637 mg, 62%) as a pale yellow oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 7.13 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 2.5 Hz, 2H), 6.74 (dd, J = 8 Hz, J = 2.5 Hz, 2H), 3.19-3.11 (m, 2H), 2.46-2.38 (m, 2H), 1.32-1.22 (m, 6H), 1.11 (d, J = 7.5 Hz, 36H) ppm; $^{13}$C NMR, (100 MHz, CDCl$_3$): $\delta =$ 155.7, 155.1, 126.6, 121.8, 117.5 116.6, 110.7, 36.6, 18.0, 12.8 ppm; HR-MS: m/z (%): 548.35 [M] C$_{34}$H$_{52}$O$_2$Si$_2$ calc. 576.35

5,8-dibromo-4,9-di(triisopropylsilyl)-6,7-dihydro-1H-dibenzo[a,e]cyclopropa[c]-[8]annulen-1-one: A 100 mL round bottom flask was charged under an Ar atmosphere with 4 (1.0 g, 2.4 mmol), and triisopropylsilyl chloride (1.3 mL, 5.9 mmol) in dry DMF (25 mL). Triethylamine (1.0 mL, 7.1 mmol) was added dropwise. The resulting mixture was stirred for 16 h at 24°C, quenched with H$_2$O (100 mL), and extracted with diethyl ether/ethyl acetate (1:1, 3 x 100 mL).
The combined organic phases were washed with saturated aqueous NaCl solution, dried (MgSO₄), and concentrated on a rotary evaporator. Column chromatography (SiO₂; hexane/AcOEt) yielded the cyclopropenone (1.06 g, 60%) as a colorless solid. ¹H NMR (400 MHz, CDCl₃): δ = 1.15-1.18 (d, J = 8.0, 36H), 1.27- 1.38 (m, 6H), 2.20-2.27 (m, 2H), 4.08-4.20 (m, 2H), 6.85-6.97 (d, J = 8.4, 2H), 7.79-7.81 (d, J = 8.4, 2H) ppm; ¹³C NMR, (100 MHz, CDCl₃): δ = 13.0, 17.9, 35.6, 117.2, 117.6, 118.1, 133.7, 143.1, 147.0, 153.5, 156.5 ppm; HR-MS: m/z (%): 733.1755 (49.7) [M+H⁺], C₃₅H₅₁Br₂O₃Si₂⁺, calc. 733.1738.

4,7-dibromo-3,8-di(triisopropylsilyl)-5,6-dihydro-11,12-didehydrodibenzo[a,e]-[8]annulen  (36)

A 50 mL Pyrex round bottom flask was charged under an Ar atmosphere with 5 (1.06 g, 1.44 mmol) in THF/MeOH (30 mL, 2:1) and was irradiated (medium pressure Hg lamp) at 24°C for 90 min. The solvent was concentrated on a rotary evaporator. Column chromatography (SiO₂; hexane/CH₂Cl₂ 19:1) yielded 1b (637 mg, 62%) as a pale yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 1.14-1.16 (d, J = 7.4, 36H), 1.29-1.43 (sept, J = 7.4, 6H), 2.04-2.13 (m, 2H), 4.02-4.11 (m, 2H), 6.76-6.79 (d, J = 8.4, 2H), 7.09-7.12 (d, J = 8.4, 2H) ppm; ¹³C NMR, (100 MHz, CDCl₃): δ = 18.0, 35.2, 110.8, 116.7, 117.4, 117.9, 125.1, 135.0, 153.0, 153.5 ppm; HR-MS: m/z (%): 704.1727 (48.3) ([M], C₃₅H₅₀Br₂O₂Si₂, calc. 704.1716

CH₂Cl₂, 3 hrs, 24°C, 41%.
(1R,8S,9R)-Bicyclo[6.1.0]non-4-yn-9-ylmethanol 4-methoxybenzoyl ester (38) A 10 mL round bottom flask was charged with 12 (141 mg, 0.94 mmol), triethylamine (0.2 mL, 1.4 mmol), N,N-dimethylaminopyridine (6 mg, 0.049 mmol). 4-Methoxybenzoyl chloride (0.02 mL, 1.4 mmol) was added dropwise and the reaction was stirred for three hours. The reaction was quenched with NH4Cl, and extracted with CH2Cl2 (3 x 10 mL). The organic layer was washed with brine (10 mL), dried over MgSO4, and concentrated on a rotary evaporator. Column chromatography (SiO2, 0→10% EtOAc in Hexanes with 1% Et3N) yielded 38 (110 mg, 41%) as a waxy, colorless solid. 1H NMR (500 MHz, CDCl3): δ = 8.00 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 4.22 (d, J = 6.1 Hz, 2H), 3.86 (s, 3H), 2.43 (dq, J = 13.8, 2.8 Hz, 2H), 2.36 – 2.24 (m, 2H), 2.16 (dt, J = 14.0, 2.2 Hz, 2H), 1.40 (qd, J = 12.2, 3.3 Hz, 2H), 0.88 – 0.76 (m, 3H) ppm; 13C NMR (125 MHz, CDCl3): δ = 166.42, 163.27, 131.54, 122.96, 113.55, 98.76, 68.70, 55.39, 33.33, 23.63, 23.02, 21.37 ppm. HR-MS: m/z (%): 284.14 [M] C18H20O3 calc. 284.14

Typical procedure for the synthesis of salicylimine ligands:

(E)-2-((phenylimino)methyl)phenol (14) A 100 mL round bottomed flask was charged under a N2 atmosphere with salicylaldehyde (5.0 g, 41.0 mmol) in anhydrous ethanol (30 mL). Aniline
(3.73 g, 40.0 mmol) was added, and the solution was heated to 80°C for 20 hours. Upon cooling, a crystalline yellow solid precipitated from solution. This was filtered, washed with hexanes, and dried to yield 5 (6.9 g, 87%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 6.86-6.90 (dt, $J$ = 0.8, 7.6, 1H), 6.99-7.01 (m, 1H), 7.21-7.25 (m, 3H), 7.30-7.38 (m, 4H), 8.52 (s, 1H), 13.28 (s, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 117.1, 118.9, 119.0, 121.0, 126.7, 129.2, 132.2, 133.0, 148.2, 161.0, 162.5 ppm; LC-MS: m/z: 198.26 [M+H] C$_{13}$H$_{11}$NO.

(E)-2-((2,6-dimethylphenylimino)methyl)phenol (15) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.31 (s, 6H), 7.03-7.04 (m, 1H), 7.05-7.22 (m, 4H), 7.42-7.44 (m, 1H), 7.47-7.52 (m, 1H), 8.42 (s, 1H), 13.22 (s, 1H) ppm; $^{13}$C NMR, (100 MHz, CDCl$_3$): $\delta$ = 18.6, 117.4, 118.9, 119.1, 125.1, 128.4, 128.5, 132.3, 133.3, 148.3, 161.4, 166.9 ppm; LC-MS [M+H]: 226.27.

(E)-2-(((4-nitrophenyl)imino)methyl)phenol (16) $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ =  12.58 (s, 1H), 8.64 (s, 1H), 8.40 – 8.26 (m, 2H), 7.52 – 7.32 (m, 4H), 7.11 – 6.94 (m, 2H).
(E)-2-(((4-methoxyphenyl)imino)methyl)phenol (17) $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 13.44$ (s, 1H), 8.50 (s, 1H), 7.37 – 7.26 (m, 1H), 7.26 – 7.14 (m, 2H), 7.04 – 6.94 (m, 1H), 6.94 – 6.80 (m, 3H), 3.75 (s, 3H); $^{13}$C NMR, (100 MHz, CDCl$_3$): $\delta = 160.80$, 160.13, 158.64, 141.02, 132.46, 131.84, 131.83, 122.12, 119.20, 118.79, 116.91, 114.42, 114.39, 55.27.

(E)-4-nitro-2-((phenylimino)methyl)phenol (18) $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 14.48$ (s, 1H), 8.73 (s, 1H), 8.41 (d, $J = 2.8$ Hz, 1H), 8.28 (dd, $J = 9.2$, 2.8 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.41 – 7.29 (m, 3H), 7.11 (d, $J = 9.1$ Hz, 1H), 2.18 (s, 4H).

(E)-4-methoxy-2-((phenylimino)methyl)phenol (19)$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 12.80$ (s, 1H), 8.52 (s, 1H), 7.45 – 7.33 (m, 2H), 7.31 – 7.18 (m, 3H), 7.02 – 6.89 (m, 2H), 6.86 (dd, $J = 2.8$, 0.9 Hz, 1H), 3.76 (s, 3H); $^{13}$C NMR, (100 MHz, CDCl$_3$): 162.25, 155.25, 152.12, 148.36, 129.30, 129.28, 126.81, 121.06, 120.31, 118.69, 117.93, 117.90, 115.23, 77.32, 77.00, 76.68, 55.77.
(E)-4-nitro-2-(((4-nitrophenyl)imino)methyl)phenol (20) 1H NMR (300 MHz, CDCl₃): δ = 13.53 (s, 3H), 8.75 (s, 3H), 8.46 (d, J = 2.8 Hz, 3H), 8.42 – 8.29 (m, 9H), 7.50 – 7.38 (m, 6H), 7.17 (d, J = 9.2 Hz, 3H), 3.73 (s, 1H), 1.25 (t, J = 6.9 Hz, 1H).

(E)-4-methoxy-2-(((4-methoxyphenyl)imino)methyl)phenol (21) 1H NMR (400 MHz, CDCl₃): δ = 12.95 (s, 1H), 8.50 (s, 1H), 7.29 – 7.16 (m, 2H), 6.96 – 6.87 (m, 4H), 6.84 (dd, J = 2.1, 1.3 Hz, 1H), 3.78 (d, J = 11.4 Hz, 6H). 13C NMR, (100 MHz, CDCl₃): δ = 159.91, 159.89, 158.72, 155.04, 152.07, 152.05, 141.16, 122.18, 119.69, 118.88, 117.72, 115.04, 114.45, 114.41, 55.74, 55.73, 55.35.

(E)-4-methoxy-2-(((4-nitrophenyl)imino)methyl)phenol (22) 1H NMR (300 MHz, CDCl₃): δ = 12.15 (d, J = 2.1 Hz, 1H), 8.60 (s, 1H), 8.31 (dd, J = 9.2, 2.4 Hz, 2H), 7.43 – 7.31 (m, 2H), 7.13 – 6.96 (m, 2H), 6.92 (d, J = 3.0 Hz, 1H), 3.82 (s, 3H).
(E)-2-(((4-methoxyphenyl)imino)methyl)-4-nitrophenol (23) \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 14.71\) (s, 1H), 8.69 (s, 1H), 8.37 (d, \(J = 2.7\) Hz, 1H), 8.25 (dd, \(J = 9.2, 2.7\) Hz, 1H), 7.40 – 7.28 (m, 2H), 7.08 (d, \(J = 9.1\) Hz, 1H), 7.03 – 6.94 (m, 2H), 3.87 (s, 3H).

(\(E\))-2-((isopropylimino)methyl)phenol (24) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 13.67\) (s, 1H), 8.27 (t, \(J = 2.4\) Hz, 1H), 7.25 (ddd, \(J = 8.5, 7.2, 1.5\) Hz, 1H), 7.18 (dt, \(J = 7.6, 1.7\) Hz, 1H), 6.93 (dd, \(J = 8.4, 1.1\) Hz, 1H), 6.82 (td, \(J = 7.4, 1.1\) Hz, 1H), 3.48 (heptd, \(J = 7.0, 4.1\) Hz, 1H), 1.30 – 1.19 (m, 6H); \(^{13}\)C NMR, (100 MHz, CDCl\(_3\)): \(\delta = 161.89, 161.10, 131.73, 131.71, 130.92, 118.62, 118.16, 116.73, 59.71, 23.95\).

(\(E\))-2-((tert-butylimino)methyl)phenol (25) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.32\) (s, 9H), 6.81-6.84 (t, \(J = 7.6\) Hz, 1H), 6.92-6.94 (d, \(J = 8.4\) Hz, 1H), 7.22-2.78 (m, 2H), 8.31 (s, 1H), 14.35 (bs, 1H) ppm; \(^{13}\)C NMR, (100 MHz, CDCl\(_3\)): \(\delta = 29.6, 56.9, 117.3, 118.1, 118.9, 131.3, 132.0, 159.7, 162.1\); LC-MS [M+H]: 178.38.
(E)-2-((isopropylimino)methyl)-4-nitrophenol (26) $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.37 (s, 1H), 8.23 (d, $J$ = 2.8 Hz, 1H), 8.14 (dd, $J$ = 9.4, 2.9 Hz, 1H), 6.88 (d, $J$ = 9.4 Hz, 1H), 3.80 (pd, $J$ = 6.4, 0.9 Hz, 1H), 1.40 (d, $J$ = 6.5 Hz, 6H); $^{13}$C NMR, (100 MHz, CDCl$_3$): δ = 172.02, 161.77, 137.45, 129.02, 128.35, 120.05, 115.49, 57.21, 23.29, 23.27.

\[
\begin{align*}
\text{OH} & \quad \text{N} \\
\text{NO}_2 & \quad \text{OMe}
\end{align*}
\]

(E)-2-((isopropylimino)methyl)-4-methoxyphenol (27) $^1$H NMR (400 MHz, CDCl$_3$): δ = 13.11 (s, 1H), 8.26 (dd, $J$ = 5.8, 2.9 Hz, 1H), 6.88 (q, $J$ = 2.4, 2.0 Hz, 2H), 6.73 (dd, $J$ = 3.7, 2.0 Hz, 1H), 3.73 (dd, $J$ = 4.7, 2.3 Hz, 3H), 3.50 (tt, $J$ = 12.6, 5.5 Hz, 1H), 1.45 – 0.97 (m, 6H); $^{13}$C NMR, (100 MHz, CDCl$_3$): δ = 161.62, 161.60, 155.05, 151.68, 118.66, 118.29, 117.34, 114.50, 59.88, 55.59, 55.56, 23.95.

\[
\begin{align*}
\text{OH} & \quad \text{N} \\
\text{OH} & \quad \text{N}
\end{align*}
\]
(E)-4-((phenylimino)methyl)phenol (35) 1H NMR (500 MHz, Acetone): δ 8.45 (s, 1H), 7.84 (d, J = 8.6 Hz, 2H), 7.38 (dd, J = 8.7, 7.0 Hz, 2H), 7.25 – 7.12 (m, 3H), 6.97 (d, J = 8.6 Hz, 2H) ppm; 13C NMR (126 MHz, Acetone) δ 151.54, 150.57, 143.70, 121.69, 120.07, 119.74, 116.28, 111.82, 106.65. LC-MS: m/z: 198.19 [M+H] C13H11NO.

General Polymerization Procedures:

General Time-Resolved Polymerization procedure:

d28 A flame dried 5 mL Schlenk tube was charged under an Ar atmosphere with 4 (27.4 mg, 0.05 mmol) in dry toluene (3 mL) and cooled to −78°C. A mixture of 1 (6.7 mg, 0.01 mmol) and ArOH-3 (5.9 mg, 0.03 mmol) in toluene (1 mL) was added in one portion. Aliquots (0.3-0.5 mL) for time resolved GPC analysis were taken from the reaction mixture and quenched in MeOH (3 mL) at 15, 30, 45, 60, 90, and 120 seconds. The precipitated polymer was separated by filtration, rinsed with MeOH (25 mL), and dried under high vacuum. 1-3 mg of polymer was dissolved in THF, and this solution was filtered through a syringe filter and injected into the GPC. All other time-resolved polymerizations of 4 and 5 were carried out in the same way. If all fractions are combined, 14 mg (52%) of poly-28 are obtained.

Living Polymerization Experiment procedure:

d28 A flame dried 5 mL Schlenk tube was charged under an Ar atmosphere with 4 (27.4 mg, 0.05 mmol) in dry toluene (3 mL) and cooled to −78°C. A mixture of 1 (6.7 mg, 0.01 mmol) and ArOH-3 (5.9 mg, 0.03 mmol) in toluene (1 mL) was added in one portion. After 45 seconds an aliquot (0.5 mL) was removed and quenched with MeOH (3 mL), followed 15 seconds later by the addition of 4 (0.025 mmol) in 0.5 mL toluene, this was allowed stir for an additional 30
seconds, at which point a subsequent aliquot was removed and quenched, and another equivalent of 4 (0.025 mmol in 0.5 mL toluene) was added. This was repeated twice more, such that time points were taken at 45, 90, 135, and 180 seconds. All other living polymerization experiments of 4 and 5 were carried out in the same way.
**Initiator 3-14 NMR Data:**

a)

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<th>Internal standard</th>
<th>H_A</th>
<th>H_B</th>
<th>H_C</th>
<th>H_B/H_C</th>
<th>H_B+H_C</th>
<th>Still bound -NRR'</th>
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</table>

b)

**Figure 1 - 9:** Aromatic region in the $^1$H NMR of a titration of 3 with 14 in tol-d8. A stock solution of a 1:1 ratio of 1:internal standard was divided into 6 portions and increasing equivalents of 3 was added to each. a) Table of integration values comparing free amine to coordinated anilide. (1,3,5-Trimethoxybenzene aromatic proton is integrated to 3.) b) The aromatic region with aromatic protons of free aniline and bound anilide indicated.
Figure 1 - 10: Time resolved GPC analysis of aliquots taken from a polymerization of 28 with 34 at –78°C. Loading: 4:1:ArOH = 5:1:3.

Figure 1 - 11 Time resolved GPC analysis of aliquots taken from a polymerization of 28 with 14 at –78°C. Loading: 4:1:ArOH = 5:1:3.
Figure 1 - 12 Time resolved GPC analysis of aliquots taken from a polymerization of 28 with 35 at –78°C. Loading: 28:3:35 = 5:1:3.

Figure 1 - 13 Time resolved GPC analysis of aliquots taken from a polymerization of 28 with 36 at –78°C. Loading: 28:3:36 = 5:1:3.
Figure 1 - 14 Time resolved GPC analysis of aliquots taken from a polymerization of 28 with 37 at −78°C. Loading: 28:3:37 = 5:1:3.

Figure 1 - 15: GPC analysis of aliquots taken from living polymerization experiment of 28 with 14 at −78°C. Initial loading: 28:3:14 = 5:1:3. An additional 2.5 equivalents of 5 was added at 60, 105, and 150 seconds. Time points taken at 45, 90, 135, and 180 seconds.
Figure 1 - 16: GPC analysis of aliquots taken from living polymerization experiment of 28 with 34 at –78 °C. Initial loading: 28:3:34 = 5:1:3. An additional 2.5 equivalents of 5 was added at 60, 105, and 150 seconds. Time points taken at 45, 90, 135, and 180 seconds.

Figure 1 - 17. Time resolved GPC analysis of aliquots taken from a polymerization of 38 with 14 at –78 °C. Loading: 38:3:14 = 5:1:3 = 28:3:34 = 5:1:3.
Figure 1 - 18. Time resolved GPC analysis of aliquots taken from a polymerization of 38 with 34 at −78°C. Loading: 38:3:34 = 5:1:3.

Figure 1 - 19. Time resolved GPC analysis of aliquots taken from a polymerization of 38 with 35 at −78°C. Loading: 38:3:35 = 5:1:3.
Figure 1 - 20. Time resolved GPC analysis of aliquots taken from a polymerization of 38 with 36 at –78°C. Loading: 38:3:36 = 5:1:3

Figure 1 - 21. Time resolved GPC analysis of aliquots taken from a polymerization of 38 with 37 at –78°C. Loading: 38:3:37 = 5:1:3
Figure 1 - 22: GPC analysis of aliquots taken from living polymerization experiment of 38 with 14 at $-78\,^\circ\text{C}$. Initial loading: $38:3:14 = 5:1:3$. An additional 2.5 equivalents of 38 was added at 60, 105, and 150 seconds. Time points taken at 45, 90, 135, and 180 seconds.

Figure 1 - 23. GPC traces of aliquots taken from a polymerization of 28 with 14 at $-78\,^\circ\text{C}$. Loading: $28:3:14 = 5:1:3$. 
Figure 1 - 24. GPC traces of aliquots taken from a polymerization of 28 with 14 at RT. Loading: 28:3:14 = 5:1:3.

Figure 1 - 25. GPC traces of aliquots taken from a polymerization of 28 with 34 at –78°C. Loading: 28:3:34 = 5:1:3.
Figure 1 - 26: GPC traces of aliquots taken from a polymerization of 28 with 34 at RT. Loading: 28:3:34 = 5:1:3.
Polymer NMR and Mass Data:

a)

Figure 1 - 27 NMR analysis of aliquots taken from living polymerization experiment of 4 with 3 at –78°C. a) NMR signals of polymerization reactions taken at 45, 90, 135 and 180 seconds; b) Comparison of integrations of the NMR peaks corresponding to the protons on the ethyl bridge and the CH₂ group of the newly formed aryl butyne.

<table>
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<th>Time (s)</th>
<th>( H_{A1} + H_{A2} )</th>
<th>( H_{A1} )</th>
<th>( H_{A2} )</th>
<th>( H_B )</th>
<th>Ratio ((H_B/H_A))</th>
<th>( M_n )</th>
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</thead>
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Figure 1 - 28: MALDI MS of an aliquot taken after 15 s from a polymerization of 28 with 3-14 at –78°C. Loading: 5:1. Fragmentation peaks have been deleted for clarity. Some common fragments are shown.
Figure 1 - 29: $^1$H NMR of a polymerization of 38 with 3-14 carried out in tol-$D_8$, and quenched with MeOD after 30 seconds.
Figure 1 - 30: $^1$H NMR of a polymerization of 28 with 3-14 carried out in tol-$D_8$, and quenched with MeOD after 30 seconds. CDCl$_3$ was added in order to ensure solubility of polymer.
1.9 References:


(28) Jin, Y.; Yu, C.; Denman, R. J.; Zhang, W. Recent advances in dynamic covalent chemistry. Chemical Society Reviews 2013.


1.10 NMR Spectra

The following pages contain NMR spectra of the compounds discussed in the previous chapter.
Chapter 2. Ring-Opening Alkyne Metathesis via a Tungstenatetrahedrane Intermediate

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2.1 Introduction

----

As discussed in the previous chapter, the overall mechanism of alkyne metathesis is well accepted. The alkyne and metal-carbyne* bind to form a metallacyclobutadiene (MCB) intermediate, which fragments to again yield an alkyne and alkylidyne.

\[
\begin{array}{c}
\text{R}_1 \quad \text{M} \quad \text{R}_2 \\
\text{R}_1' \quad \text{M} \quad \text{R}_2'
\end{array}
\xrightarrow{\text{Degenerate}}
\begin{array}{c}
\text{R}_1 \quad \text{M} \\
\text{R}_2 \\
\text{R}_1' \quad \text{M} \\
\text{R}_2'
\end{array}
\xrightarrow{\text{Productive}}
\begin{array}{c}
\text{R}_1 \\
\text{R}_2 \\
\text{R}_1' \\
\text{R}_2'
\end{array}
\]

Scheme 2 - 1: The alkylidyne/metallacyclobutadiene mechanism for acetylene metathesis.

The steric and electronic properties of the incoming acetylene, the metal-carbyne, and the metal ligand framework each play a role in the system’s metathesis activity and productivity. Their interplay has been shown to have a dramatic effect on the reaction mechanism (associative vs. dissociative), the system’s propensity for alkyne polymerization, the stability of metallacyclobutadiene intermediates (A, Figure 2-1), and the formation of other organometallic species such as metallatetrahedranes (B, from here referred to as MTH), dimetallatetrahedranes (C), and metal-cyclopentadienyl complexes (D).1-21

* There is some debate in the field as to whether metal-carbyne is the appropriate term when referring the carbon triply bonded to the metal. This is because the bonding is these systems is essentially covalent, while the use carbyne implies an ionic bond to the metal with a C^3^- ligand. For lack of a better term, we choose to use metal-carbyne to describe generally both benzyl- and alkylidyynes.
MTHs (B), are the structural cousins of MCBs (A); the other MC$_3$R$_3$ fragment that can result from the bonding of a metal-carbyne and an alkyne. They are often also interchangeably referred to as metal-cyclopropenyl complexes to reflect C$_3$R$_3$ bound to M(IV) as opposed to C$_3$R$_3$ and M(VI). Unlike the ring in metal-cyclopentadienyl complexes (D), however, there is a sizeable barrier to rotation of the three-membered ring on metals with oxidation states higher than IV.$^{22,23}$ Therefore, all such complexes will be referred to as metallatetrahedranes (MTHs).

The focus of this chapter will be on the reactivity of a tungstenatetrahedrane intermediate in the ring opening reaction of 1 using Schrock’s tris(tertbutoxy) tungsten(VI) neopentyldyne (2) alkyne metathesis catalyst (Scheme 2 - 2). This reaction is significant on two fronts. First, no metallacyclic complex of Schrock’s catalyst and an alkyne has ever been reported—metallacyclobutadienes are only a presumed intermediate in the alkyne metathesis reaction.
Second, the metallatetrahedrane’s role in alkyne metathesis as anything other than an inconvenient side-product has not been widely considered. This is despite the fact that in the early days of alkyne metathesis research, there were nearly as many reports of metallatetrahedranes produced by the reaction of Mo and W carbynes and acetylenes as there were of metallacyclobutadienes.\textsuperscript{3,9,12,13,18-21,24} It was found that the formation of MTHs could be biased by the addition of Lewis basic ligands to metallacyclobutadiene complexes, or by the use of electron donating carboxylate ligands.\textsuperscript{3,9,19,21} In one noteworthy study that hints at the productivity of MTH’s in alkyne metathesis, the exchange of the carboxylate ligands on a tungstenatetrahedrane by addition of a \textit{tert}-butoxide salt caused it to decompose to an alkyne and a \textit{tert}-butoxide substituted alkylidyne. High-valent metallatetrahedranes have also have been treated theoretically alongside metallacyclobutadienes.\textsuperscript{25-27} A deeper understanding of the reactivity of these intermediates could help to explain why the development of alkyne metathesis has been far more difficult than that of olefin metathesis, and it could provide new design criteria for alkyne metathesis catalysts.

----

2.2 Polymerization Attempts

----

Scheme 2 - 3: The proposed polymerization reaction of 3.
This study began with an investigation of the ROAMP reactivity of dibenzocyclooctadiyne, 3a (Scheme 2 - 3), which was synthesized in our lab by Felix Fisher. We screened three preliminary ROAMP initiators (Table 2-1), but never observed characterizable polymer. In all cases, we observed a color change upon addition of the alkylidyne, but virtually no monomer was consumed by the reaction. Addition of one equivalent of Schrock’s tris(tertbutoxy) tungsten(VI) neopentylidyne (2) to one equivalent of 3a in deuterated toluene yields an uncharacterizable mix of products that turns into a red, paramagnetic paste upon addition of methanol. A likely explanation is that 3a reacts with 2 at a rate that is less than or equal to that of the linear alkyne generated from its ring-opening. Therefore, as soon as a fraction of 3a is ring-opened, it will in turn react with excess 2 in solution. We attempted to lower the concentration of 2 and 3a, but an identical product mix was obtained. We therefore decided to investigate other potential ROAMP monomers.

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<th>Substrate</th>
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<td>2</td>
</tr>
<tr>
<td>4</td>
<td>3b</td>
<td>2</td>
</tr>
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</table>

Table 2 - 1: Initiators screened for the polymerization of 3.

Because related dibenzocyclooctynes containing an ethyl or ethenyl bridge instead of the second alkyne are active in ROAMP\textsuperscript{28–31}, we believed that masking one of the alkynes in 3
would promote reactivity. Fortuitously, the synthesis of 1a was recently reported for use as a fluorogenic probe.\textsuperscript{32} We believed that a monomer such as 1 would readily undergo ROAMP, and that carbon monoxide could then be photolytically cleaved after the polymerization to yield the desired orthophenylyne polymer (Scheme 2 – 4). We set out to synthesize our targeted monomer by modifying Boons’s synthesis to replace the methoxy groups on the aryl rings with ethylhexyloxy groups (1b) to increase this potential new monomer’s solubility.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Scheme2-4.png}
\caption{The proposed polymerization reaction of 1b, followed by the photolytic cleavage of CO.}
\end{figure}

We screened a series of alkyne metathesis catalysts, including the initiators described in the Chapter 1, as well as the tri-dentate molybdenum propylidyne developed in our lab,\textsuperscript{31} Fürstner’s triphenylsiloxide benzylidyne,\textsuperscript{33,34} and Schrock’s catalyst (2). Once again, the reaction did not result in the synthesis of characterizable polymer. However, the addition of a carbyne to excess 1b did result in an immediate color change of the solution from yellow to a deep red or dark brown. When methanol was added to quench the reaction, the color disappeared and the only products recovered aside from unreacted 1b were not separable from one another or characterizable. It was clear that an organometallic complex was forming between 1b and these various carbynes, if only to decompose after exposure to air, water, and methanol. We wondered if coordinating solvents could promote the reactivity of this complex, however the reaction of 1b with 2 in THF proved to be virtually identical to that in toluene.
2.3 The Ring-Opening Reaction of 1

We chose to study the reaction between monomer 1a and catalyst 2 by NMR in order to characterize this complex, and to explain why the ROAMP reaction does not proceed as expected. When one equivalent of 1 is mixed with one equivalent of 2, a single, 1:1 complex of 1 and 2 forms immediately upon mixing (Scheme 2 - 5). This complex, 4, is red in solution at room temperature and forms a deep violet solid upon solvent evaporation. Based on the following collective NMR data†, we believe that 4 is likely a tungstenatetrahedrane. We assign its structure from the following evidence: The two aryl rings are equivalent by $^1$H and $^{13}$C NMR. The three tert-butoxy ligands are equivalent on the NMR time scale, and shift ~0.4 ppm up-field in the $^1$H NMR with respect to their position in 2. The formation of complex 4 also signaled by a large down-field shift of the aromatic protons and a large up-field shift of both the former alkylidyne and the former acetylene carbons in the $^{13}$C NMR. In 4a (R = Me), the alkylidyne

---


† Because this complex is the first of its kind, direct comparison to previously reported complexes is not possible. However, the large up-field shift of the carbons coordinated to tungsten is observed in many similar compounds when compared with those of alkylidyne and metallacyclobutadienes.
shifts from 270.6 ppm to 122.8 ppm ($J_{W.C} = 110$ Hz) and the acetylene from 106.8 ppm to 73.7 ppm ($J_{W.C} = 55$ Hz).

In solution, MTH 4 thermally decomposes to 5, the ring-opened benzylidyne that is expected from the metathesis reaction of 1 and 2 (cf. Scheme 2 - 2). Its structure is confirmed by X-ray crystallography (Figure 2 - 2). In the solid state, 5a is a formally 14-electron, approximately trigonal bipyramidal complex in which the carbonyl oxygen occupies a fifth coordination site on tungsten. In order to accommodate this coordination, the carbon-carbon-tungsten bond of the benzylidyne is slightly bent ($\phi = 167.8^\circ$).

![Figure 2 - 2: X-ray crystal structure of benzylidyne 5a. (R$^2 = 0.05$). Two different views are shown. W-C1A: 1.74 Å, W-O5: 2.32 Å, WCC<: 167.8°. Thermal ellipsoids represent 50% probability.](image)

This ring-opening reaction takes several days at room temperature, but can be dramatically accelerated at temperatures above 60 °C. We followed the decomposition of 4a in the presence of excess 2‡ by $^1$H NMR in order elucidate its mechanism. The reaction proceeds in greater than 90% yield based the total integration of the methoxy signal after completion of the reaction.

‡ 1a is only sparingly soluble in most organic solvents. Its complexation to 2 pulls it into solution. We therefore have not been able to isolate pure 4a. However, we see no evidence that 1a is coming out of reaction throughout the course of the reaction, as indicated by stability of the total integration of the methoxy signal.
Figure 2 - 3: Reaction progress over time in the conversion of 4a to 5a. (a) Integrations of the t-Bu peaks; (b) $^1$H NMR traces of the first 7.5 hours. Reaction was run in deuterated toluene at 65 °C and monitored by $^1$H NMR (500 MHz).

Figure 2-3 shows the integration values of the tert-butyl functionality over the course of the reaction (a) as well as $^1$H NMR spectra taken over the course of the reaction showing the change
in the aromatic region (b). Peaks corresponding to the proton para to the organometallic functionality are indicated. Immediately upon heating two new species appear in solution. One of these species is 5a, which grows in throughout the course of the reaction. (The para protons overlap at higher temperatures, but separate upon cooling, see experimental for details). The other, 6a, grows in initially and then disappears as the reaction proceeds. At first glance 6a would appear to be an intermediate in the transformation of 4a to 5a, however we have determined that this is not the case.

![Figure 2 - 4: Proposed Structure of 6.](image)

We speculate that 6 is also a tungstenatetrahedrane (Figure 2 - 4) based on the following evidence: (i) 6a is found to contain two equivalents of 1a with respect to tungsten one of which is symmetric, one of which is not. (ii) The $^{13}$C NMR shifts of the benzyldyne and acetylene carbons in 6a also shift up-field (for 6a: from 265.4 and 106.8 to 81.9 and 80.4). These peaks are both quite broad, as is the proton ortho to the organometallic functionality in the symmetrical unit of 1a. (iii) The appearance and disappearance of 6a is accompanied by that of 2, whose concentration increases linearly with that of 6a. And, (iv) 6a can also be obtained by the addition of one equivalent of 1 to purified 5a.
When the reaction is run with an excess of Schrock’s catalyst (2) as is the case in Figure 2 - 3, only 2 and 4a are visible in solution at the beginning of the reaction. Therefore, the only source of 1a in solution must come from the dissociation of 4a to 1a and 2, likely through a rapid equilibrium. As soon as the ring-opened 5a is formed it enters a competition with 2 for complexation with 1a. We see no evidence by NMR of any other intermediates.

Scheme 2 - 6: Partial mechanism for the transformation of 4 to 5.

The same reaction sequence takes place cleanly for 1b, however we chose to study 1a more thoroughly because the ethylhexyl groups obscure the tert-butyl and tert-butoxy peaks in all species. In both cases and unlike 4, 6 does not undergo a ring-opening reaction, even after prolonged heating at temperatures up to 80 °C, and in the presence of excess 1. At higher temperatures, 6 decomposes slowly to unidentifiable paramagnetic material. If excess 1 is not present, all 6 is eventually converted to 4. Scheme 2 - 6 shows the partial mechanism for the
formation of 5. It is not yet clear whether 4 is transformed directly to 5, or whether 1 and 2 react to give 5. Our efforts to distinguish these two possibilities are described in section 2.4 below.

![Scheme 2 - 7: Photoreaction of 4a to yield 7.](image)

Photolysis of 5a gives rise to one major product, which we presume to be 7a (Scheme 2 - 7), formed through the expulsion of carbon monoxide. 7a is relatively stable at lower temperatures, but reacts slowly (presumably with itself) at temperatures above 0 °C. When additional 1a is added, the solution turns bright red, and two new products appear in solution. Over time one of these products disappears and the other grows in, however during that time the reaction mixture becomes very complex, especially in the aliphatic region. We note that by 1H NMR the major reaction product appears to contain only two inequivalent aryl rings. The product of the ring-opening reaction should contain four inequivalent aryl rings. Full characterization of 7 and its reaction products with 1 are in progress.

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2.4 Kinetic Analysis of the tungstenatetrahedrane’s decomposition

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For ring opening to occur, 4 must either: (i) rearrange to another species (for example, a metallacyclobutadiene) which is rapidly converted into 5; (ii) rearrange directly to 5; or, (iii)
dissociate to 1 and 2 which in turn react rapidly to yield 5, again potentially through a metallacyclobutadiene (cf. Scheme 2 - 6). It is worth noting that because we do not directly observe the metallacyclobutadiene, it is not possible to distinguish between (i) and (ii). However we hoped that kinetic modeling and variable temperature analysis would allow us to confirm or exclude (iii), and thus clarify the tungstenatetrahedrane’s role in alkyne metathesis.

Figure 2 - 5: Decrease in concentration of 4a (mol/L) over time at (a) 50 °C, (b) 60 °C, and (c) 70 °C.

The decomposition rate of 4 increases significantly with increased temperature. At 70 °C, 4a reaches one tenth of it’s initial value in less than an hour, while the same decrease in
concentration takes over 2.5 hours at 60 °C and over 10 hours at 50 °C. Figure 2 - 5 shows concentration change in \( \textit{4a} \) versus time at these three temperatures. At all three temperatures, the reaction fits well to a biexponential decay \( (R^2 > 0.999) \).

Qualitatively, we can think of the overall decomposition of \( \textit{4} \) as the result of two to concurrent reactions. One of these leads to the ring opened product, the other is the dissociation of \( \textit{4} \) to \( \textit{1} \) and \( \textit{2} \). However, because the benzylidyne formed in the ring-opening step \( (\textit{5}) \) binds competitively to \( \textit{1} \), determining the decomposition rate of \( \textit{4} \) becomes immensely complicated. This in turn makes it difficult to isolate the transformation of \( \textit{4} \) to \( \textit{5} \), and, therefore, to determine its mechanism. In order to learn what we could about the reaction, we monitored the decomposition reaction of \( \textit{4a} \) at various temperatures. We used the kinetic modeling program, Kintecus\(^\text{©} \),\(^{35} \) to fit the rate constants for each step in the reaction (equations 1 – 5).

\[
\begin{align*}
(1) & \quad \textit{1} + \textit{2} \xrightarrow{k_1} \textit{4} \\
(2) & \quad \textit{4} \xrightarrow{k_{-1}} \textit{1} + \textit{2} \\
(3) & \quad \textit{4} \xrightarrow{k_2} \textit{5} \\
(4) & \quad \textit{5} + \textit{1} \xrightarrow{k_3} \textit{6} \\
(5) & \quad \textit{6} \xrightarrow{k_{-3}} \textit{5} + \textit{1}
\end{align*}
\]

Kintecus\(^\text{©} \) can fit the rate constants to the experimental data well (see experimental section for plots of theoretical vs. experimental concentrations). However, with the exception of \( k_2 \) in Eq. 3, all other rate constants varied widely over several orders of magnitude based on the initial guess for their value, and regardless of the fit program selected. In contrast, at all temperatures studied \( (50 – 70 \; ^\circ\text{C}) \), and for a wide range of initial guesses, \( k_2 \) converges to the same value. When we replaced Eq. 3 with Eq. 6, all five rate constants, including \( k_2^* \) varied with initial guess.
We speculate that this in part because no 1a is observed in solution, and so Kintecus cannot fit rates of reactions directly involving 1a. Ongoing studies using an excess of 1b or an excess of 2 are in progress to clarify the results discussed below. However it is important to note that addition of excess 1 will likely obscure the presence of 2 and 5 in solution. Preliminary results show that even if less than 0.5 equivalents excess 1 is present in solution, we do not observe 5. If five equivalents excess 1 is present, we do not observe 2. Also, if an excess of 2 is not present, the conversion of 6 to 5 will not go to completion. On the other hand, at large enough excess of 2, the formation of 6 should be largely diminished, allowing us to isolate the transformation of 4 to 5.

![](image)

**Table 2 - 2: Rate constants fit for the conversion of 4a to 5a.**

<table>
<thead>
<tr>
<th>#</th>
<th>T (K)</th>
<th>(k_2 \times 10^4) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>323</td>
<td>1.4 ± 0.0097</td>
</tr>
<tr>
<td>2</td>
<td>333</td>
<td>4.2 ± 0.11</td>
</tr>
<tr>
<td>3</td>
<td>343</td>
<td>12 ± 0.78</td>
</tr>
</tbody>
</table>

The values for \(k_2\) in equation 3 at the three temperatures studied (as modeled by Kintecus) are given in Table 2 - 2. We used these values determine the activation parameters for transformation of 4 to 5, using a non-linear, least squares regression of \(k_2\) versus Temperature. The linear Arrhenius and Eyring plots are shown for clarity (Figure 2 - 6). The pre-exponential factor (A), Arrhenius activation energy (Ea), activation enthalpy (\(\Delta H^\dagger\)), and activation entropy (\(\Delta S^\dagger\)) determined from this analysis are listed in Table 2 - 3.36
Figure 2 - 6: (a) Arrhenius and (b) Eyring Plots of modeled $k_2$ in the conversion of 4a to 5a.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ln(A, \text{s}^{-1})$</td>
<td>28 ± 26</td>
</tr>
<tr>
<td>$E_a, \text{kcal/mol}$</td>
<td>24 ± 0.087</td>
</tr>
<tr>
<td>$\Delta H^\ddagger, \text{kcal/mol}$</td>
<td>23 ± 0.083</td>
</tr>
<tr>
<td>$\Delta S^\ddagger, \text{eu}$</td>
<td>−4.8 ± 0.24</td>
</tr>
</tbody>
</table>

Table 2 - 3. Activation parameters for the conversion of 4a to 5a.

The data fit well to both the Arrhenius equation and the Eyring-Polanyi equation (see experimental section for details). The activation enthalpy ($\Delta H^\ddagger$) is on the order of those found for other slow alkyne metathesis reactions, and the $E_a$ is reasonable with respect to $\Delta H^\ddagger$ within the expected error of the experiment. All of this suggests that $k_2$ is a reasonable, first-order rate constant. The small negative activation entropy $\Delta S^\ddagger$ is also consistent with a unimolecular transformation. Because we would expect the ring opening reaction to have a positive $\Delta S^\ddagger$, we this is consistent with a rearrangement to a metallacyclobutadiene, followed by a rapid ring-opening. We note that this activation entropy is several times smaller than that expected from a bi-molecular reaction, even accounting for significant error in the experiment.
2.5 Discussion

Because of the rate constants and activation parameters extracted from the model, we conclude that 4 is likely converted to 5 via a metallacyclobutadiene intermediate. 4’s utility in this ring-opening reaction is unique to the alkyne metathesis literature. 4 is also the first example of a MTH whose formation is completely controlled by the alkyne substrate, as well as the first from an active alkyne metathesis catalyst. While metallatetrahedranes of tungsten and molybdenum are known in the literature, they have not been shown before to be active in alkyne metathesis. As far as we can tell, it is the only known metallacycle from a complex with Schrock’s catalyst, despite the latter’s presence in the literature for more than thirty years.

Scheme 2 - 8: Partial mechanism for the transformation of 4 to 5.
One of the more stunning features of this reaction is that while 4 will yield the ring-opened benzylidyne under relatively mild conditions, 6 will not. This explains why it has not been possible to polymerize 1 using ROAMP. 6 does appear to be far more stable in solution, as evidenced by its much longer lifetime, even at elevated temperatures. There are several possible reasons for this that are consistent with a necessary transformation to the metallacyclobutadiene. (i) The cyclopropenone from the ring-opened benzylidyne could stabilize the MTH, preventing it from rearranging. (ii) The aryl substituent itself could stabilize the MTH and again, raise the barrier to rearrangement. (iii) If a second equivalent of alkyne is required to drive the decomposition of 6 (see reference 6 for similar behavior of a MCB), then the cyclopropenone could prevent this complexation. We favor one of the first two options (i or ii), as the cyclopropenone would then also be expected to aid in the decomposition described in the latter, (iii). The first, (i), is especially appealing given the previously demonstrated ability of Lewis bases to aid in metallatetrahedrane formation, as well as promote the reactivity of electron deficient metallacyclobutadienes.\textsuperscript{6,9–11,19,21} 

This mechanism is also consistent previous computational work which suggests that the direct formation of a metallatetrahedrane from an alkylidyne and an alkyne is symmetry forbidden and has a sizable barrier when compared with the formation of the thermodynamically less stable metallacyclobutadiene.\textsuperscript{27} We therefore speculate that the metallacyclobutadiene forms and then is rapidly converted to 4, and that 4 in turn converts to a metallacyclobutadiene that leads to the ring-opened 5. While this conversion has in part been treated computationally for low-valent metallatetrahedranes,\textsuperscript{37} it has not been looked at in detail for the high-valent systems known to undergo alkyne metathesis. Nevertheless, our data suggests an expansion of the well-accepted mechanism for alkyne metathesis (Figure 2 - 7).
Figure 2 - 7: Potential reaction energy diagram for an alkyne metathesis reaction involving a metallatetrahedrane intermediate.

The presence of a metallatetrahedrane intermediate on the reaction pathway helps to explain the sensitivity of active metathesis systems to the ligand system. In order to effectively metathesize acetylenes, the metal center must be able to accommodate the formation and subsequent transformation of three structurally distinct intermediates. Therefore, the differences in the height of the energy barrier to each intermediate should play an important role determining metathesis activity. For example, ligands that stabilize the metallacyclobutadiene could prevent it from rearranging to the metallatetrahedrane or vice versa. If the rate of insertion of a second equivalent of alkyne is faster than the rearrangement to the MTH, alkyne polymerization will predominate. This provides an explanation for the difficulty in designing alkyne metathesis catalysts, and of the slow development of the field of alkyne metathesis when compared with olefin metathesis.

2.6 Conclusion
We have elucidated a partial mechanism for the ring-opening metathesis reaction between a
cyclopropenone substituted dibenzocyclooctyne (1) and Schrock’s tris(tert-butoxy)tungsten(VI)
neopentylidyne (2). The reaction proceeds via a tungstenatetrahedrane intermediate (4) whose
formation is reversible. The ring-opened product (5) enters a competition for complexion of 1 to
yield a second tungstenatetrahedrane (6) that is also formed reversibly, but which does not
undergo the ring-opening reaction. No metallacyclobutadiene is observed in solution. Based on
preliminary variable temperature experiments, we believe that the metallatetrahedrane is a
productive intermediate on the alkyne metathesis pathway. A deeper understanding of the role of
MTHs in alkyne metathesis will provide significant insight into catalyst design requirements, and
aid chemists in the development of this understudied field.

I am grateful to the following people for their assistance on this project. Professor Roger
Lalancette of Rutgers University in Newark solved the crystal structure of 5a. Professor Felix
Fisher, currently of the University of California Berkeley, synthesized 3a during his postdoctoral
research in the Nuckolls lab. Professor Jack Norton and Deven Estes provided helpful
discussions about the kinetic data, as well as training on Kintecus. Daniel Paley provided many
helpful discussions and suggestions, as well as all of the organometallic complexes screened in
sections 2.2 and 2.3, with the exception of 2, and assisted in drying solvents.

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2.7 Experimental Section

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Materials and General Methods:
All chemicals were purchased from Sigma-Aldrich, Fisher Scientific, or Strem Chemicals and were used without further purification. When necessary, solvents were dried by passing through a column of activated alumina under an atmosphere of Ar, distilled from sodium and benzophenone, or dried over 4 Å molecular sieves. All reactions were performed in oven dried or flame dried glassware under an atmosphere of Ar. Flash chromatography was performed on a Teledyne ISCO CombiFlashRf using RediSepRf silica gel columns. $^1$H (300, 400, or 500 MHz) and 13C (75, 100, or 125 MHz) nuclear magnetic resonance spectra were recorded at 300 K (unless otherwise noted) on Bruker FT NMR spectrometers. Spectra are referenced to the solvent residual peak (CDCl₃, $\delta = 7.26$ [1H] and $\delta = 77.26$[13C], tol-d₈, $\delta = 2.09$[1H]). Resonance peaks are categorized as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), and multiplet (m). Coupling constants (J) are given in Hz. All NMR experiments with 1 were set up inside an argon Glove box and performed in Wilmad® quick pressure valve NMR tubes purchased from Sigma-Aldrich. 1a was prepared as described in reference 32. Felix Fischer provided 3a. Kintecus Windows version 4.50 kinetic modeling software was used to model the reaction rates versus the experimental data. Prism version 5 for Mac OSX was used to fit Activation parameters and to create plots. The X-ray crystal structure of 5a was solved using an Oxford Diffraction Xcalibur-2 CCD diffractometer with graphite monochromatized MoKα radiation. The crystal was mounted in a cryoloop under Paratone-N oil and cooled to 100K with an Oxford Diffraction Cryojet system. The collected frames were analyzed using the Crysalis program package, and integrated intensities were corrected for absorption using the Gaussian integration method.

_Synthesis of 1b and 3b:_
Scheme 2 - 9: Synthesis of 1b. (a) EtHexBr, KI, K₂CO₃, DMF, 2 days 90 °C (56%); (b) i: TMS-acetylene, PdPPh₃, CuI, piperidine, PhMe; ii: K₂CO₃, 1:1 MeOH/THF (95%); (c) 9, PdPPh₃, CuI, piperidine, PhMe (95%); (d) Lindlar’s catalyst (20% w/w), quinolone, hexanes, H₂ (90%); (e) tetrachlorocyclopropene, AlCl₃, CH₂Cl₂, −78 °C (93%); (f) Br₂, CH₂Cl₂, 0 °C (53%); (g) KOH, EtOH (34%)

1-((2-ethylhexyl)oxy)-3-iodobenzene (9): Dimethylformamide (700 mL) was added under argon to a mixture of 3-iodophenol (8) (25.0 g, 113 mmol), 2-ethylhexylbromide (50.5 mL, 284 mmol), potassium carbonate (47.1 g, 341 mmol), and potassium iodide (94.3 g, 568 mmol). The mixture was heated to 90 °C and stirred at that temperature for two days. The reaction was cooled to room temperature, water was added, and the solution was extracted 3x with ether. The organic layer was concentrated, and the residue was purified by column chromatography (100% hexanes)
to yield 9 (21.2 g, 63.8 mmol, 56% yield) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 7.26$ (dp, $J = 4.2, 1.4$ Hz, 2H), 6.98 (t, $J = 8.2$ Hz, 1H), 6.86 (ddd, $J = 8.5, 2.5, 1.1$ Hz, 1H), 3.81 (d, $J = 5.7$ Hz, 2H), 1.71 (hept, $J = 6.0$ Hz, 1H), 1.62 – 1.17 (m, 10H), 0.92 (td, $J = 7.1, 4.3$ Hz, 6H).

1-((2-ethylhexyl)oxy)-3-ethynylbenzene (10) To a flame-dried, three-necked, round-bottomed flask under argon was added 8 (5.00 g, 15.1 mmol), palladium(0) (tetrakis)triphenylphosphine (870 mg, 0.753 mmol), toluene (120 mL), and piperidine (25 mL). Argon was bubbled through the solution for ten minutes, then copper(I) iodide (248 mg, 1.31 mmol) was added. Argon was bubbled for an additional 10 minutes, then trimethylsilylacetylene (6.4 mL, 45 mmol) was added to the solution. The amine salt forms within five minutes, and the reaction was stirred for 3 hours at room temperature. The solution was filtered through a pad of celite, which was washed several times with toluene. The solvent was evaporated on a rotary evaporator, and the residue was purified via silica gel chromatography (100% hexanes). The combined fractions containing TMS-protected 9 were concentrated in a rotary evaporator. The resulting colorless oil was immediately re-dissolved into 25 mL of a solution of 2:1 MeOH/THF. Excess potassium carbonate was added, and the reaction was allowed to stir overnight. 1 M HCl was added to the reaction until the solution was neutral. The resulting solution was then extracted 3x with ether, and the combined organic fractions were washed with 1x with brine. The organic layer was dried over magnesium sulfate, and the solvent was removed to yield 9 as a colorless oil (3.32 g, 14.4 mmol, 95% yield) $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.21$ (t, $J = 7.9$ Hz, 1H), 7.11 – 6.98 (m, 2H),
6.90 (ddd, $J = 8.4, 2.7, 1.1$ Hz, 1H), 3.83 (d, $J = 5.7$ Hz, 2H), 3.04 (s, 1H), 1.72 (hept, $J = 6.0$ Hz, 1H), 1.58 – 1.19 (m, 10H), 1.01 – 0.80 (m, 6H); $^{13}$C NMR, (100 MHz, CDCl$_3$):

$$\text{EtHexO}$$

1,2-bis(3-((2-ethylhexyl)oxy)phenyl)ethyne (11) To a flame-dried, three-necked, round-bottomed flask under argon was added 8 (4.35 g, 13.1 mmol), palladium(0) (tetrakis)triphenylphosphine (757 mg, 0.665 mmol), toluene (120 mL), and piperidine (25 mL). Argon was bubbled through the solution for ten minutes, then copper(I) iodide (287 mg, 1.51 mmol) was added. Argon was bubbled for an additional 10 minutes, then 10 in 25 mL of toluene (3.32 g, 14.4 mmol) was added to the solution. The amine salt forms within five minutes, and the reaction was stirred for 3 hours at room temperature. The solution was filtered through a pad of celite, which was washed several times with toluene. The solvent was evaporated on a rotary evaporator, and the residue was purified via silica gel chromatography (100% hexanes). The combined fractions were concentrated to yield 10 (5.44 g, 12.5 mmol, 95% yield.) $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.22$ (d, $J = 8.0$ Hz, 2H), 7.13 – 7.04 (m, 4H), 6.89 (ddd, $J = 8.4, 2.7, 1.1$ Hz, 2H), 3.86 (d, $J = 5.7$ Hz, 2H), 1.72 (sept, $J = 6.0$ Hz, 2H), 1.58 – 1.16 (m, 22H), 0.92 (m, 12H); $^{13}$C NMR, (75 MHz, CDCl$_3$): 159.21, 129.30, 124.18, 123.90, 117.11, 115.50, 89.14, 77.44, 77.02, 76.59, 70.58, 39.42, 30.57, 29.11, 23.92, 23.06, 14.08, 11.12.

$$\text{EtHexO}$$
(Z)-1,2-bis(3-((2-ethylhexyl)oxy)phenyl)ethylene (12): 10 (1.23 g), quinolone (0.72 mL), and lindlar's catalyst (135 mg, 20% by weight) were dissolved in hexanes. The reaction was flushed with hydrogen, and stirred under a hydrogen atmosphere for 2.5 hours, until the starting material disappeared (reaction monitored by TLC). The solution was filtered through a pad of celite, the filtrate was rinsed several times with hexanes, the solvent was evaporated, and the resulting yellow residue was chromatographed on silica gel (0→10% CH$_2$Cl$_2$ in Hexanes) to a colorless oil, 11 (1.10 g, 2.53 mmol, 90% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.15 (t, J = 7.9 Hz, 2H), 6.88 – 6.81 (m, 4H), 6.76 (dd, J = 8.4 Hz, 2H), 6.59 (s, 2H), 3.69 (d, J = 5.8 Hz, 2H), 1.67 (sept, J = 6.0 Hz, 2H), 1.57 – 1.23 (m, 16H), 0.92 (m, 12H); $^{13}$C NMR, (100 MHz, CDCl$_3$): 59.24, 138.55, 130.36, 129.07, 121.21, 114.46, 114.01, 70.43, 39.31, 30.52, 29.05, 23.86, 23.06, 14.08, 11.05

(Z)-4,9-di-(2-ethylhexyl)oxy-1H-dibenzo[a,e]cyclopropa[c][8]annulen-1-one (12): Aluminum chloride (1.25 g, 9.42 mmol) and tetrachlorocyclopropene (0.54 mL, 4.7 mmol) were dissolved in 20 mL CH$_2$Cl$_2$ under argon and stirred at room temperature for 45 minutes, until the solution had turned dark red-brown. Another 80 mL of CH$_2$Cl$_2$ was added, and the reaction was cooled to -78 °C. 11 (1.37 g, 3.14 mmol) in 20 mL CH$_2$Cl$_2$ was added dropwise. The reaction was stirred for five hours, and was allowed to warm slightly over that period, but not above -30 °C to prevent deprotection of the ethylhexyloxy. Upon the reaction’s completion, water (100 mL) was added to the cooled solution. The reaction was allowed to warm to room temperature and then was extracted 3x with CH$_2$Cl$_2$. The organic layer was dried over magnesium sulfate,
concentrated. The residue was purified by column chromatography (0→1% MeOH in CH₂Cl₂, yeah I know, really polar). After concentration of the solvent there remained 12 (1.42 g, 2.91 mmol, 93% yield—this is the highest. Yields vary widely, from 40 – 93%. The major side-products are the mono and di-deprotected phenol, which can be re-proctected to yield 12) NMR spectra are consistent with those reported for the corresponding dimethyl reported analog in reference 32. ¹H NMR (300 MHz, CDCl₃): δ = 7.42 (d, J = 8.4 Hz, 1H), 6.68 (dd, J = 8.4, 2.5 Hz, 1H), 6.59 (d, J = 2.5 Hz, 2H), 5.97 (s, 2H), 3.85 (d, J = 5.7 Hz, 2H), 1.70 (q, J = 6.0 Hz, 2H), 1.55 – 1.11 (m, 20H), 0.98 – 0.75 (m, 12H); ¹³C NMR, (75 MHz, CDCl₃): 163.32, 152.36, 146.85, 139.87, 136.08, 131.63, 122.20, 114.64, 113.85, 70.83, 39.24, 30.41, 29.01, 23.78, 22.98, 14.03, 11.05.

6,7-dibromo-4,9-di-(2-ethyhexyl)oxy-6,7-dihydro-1H-dibenzo[a,e]cyclopropa[c][8]annulen-1-one (13): A solution under Argon of 12 (1.42 g, 2.91 mmol) in CH₂Cl₂ (60 mL) was cooled to 0 °C in an ice bath. A solution of Br₂ (0.18 mL, 3.49 mmol) in CH₂Cl₂ (2 mL), was added dropwise. The reaction was stirred 1 hour in the ice bath, then excess Na₂S₂O₃ was added. The mixture was extracted 3x with CH₂Cl₂. The organic layer was dried over magnesium sulfate, and concentrated. The residue was purified by column chromatography (0→0.5% MeOH in CH₂Cl₂) to yield 13 (1.00 g, 1.55 mmol, 53% yield). NMR spectra are consistent with those reported for the corresponding dimethyl reported analog in reference 32. ¹H NMR (300 MHz, CDCl₃): δ = 8.04 (d, J = 8.4 Hz, 2H), 7.05 (dd, J = 8.5, 2.4 Hz, 2H), 6.97 (d, J = 2.5 Hz, 2H), 5.75 (s, 2H), 3.95 (d, J = 5.7 Hz, 4H), 1.86 – 1.28 (m, 22H), 0.94 (m, 12H); ¹³C NMR, (75 MHz, CDCl₃):
4,9-di-(2-ethyhexyl)oxy-6,7-didehydro-1H-dibenzo[a,e]cyclopropa[c][8]annulen-1-one (1b): 13 (1.00 g, 1.55 mmol) was dissolved in 40 mL of absolute ethanol under argon. Potassium hydroxide (866 mg, 15.5 mmol) was dissolved in absolute ethanol and added to the solution, which was then stirred overnight. After 14 hours 1 M HCl was added until the solution was neutral, the layers were separated, and the aqueous layer was extracted 3x with CH₂Cl₂. After evaporation of the solvent the residue was purified by column chromatography (0 → 1.5% MeOH in CH₂Cl₂ OR 20 → 40% EtOAc in Hexanes). This yielded 1b (255 mg, 0.53 mmol, 34% yield) as a bright orange, waxy solid. NMR spectra are consistent with those reported for 1a in reference 32. ¹H NMR (400 MHz, PhMe-D): δ = 7.28 (d, J = 8.4 Hz, 2H), 6.28 (d, J = 2.6 Hz, 2H), 6.23 (dd, J = 8.5, 2.6 Hz, 2H), 3.40 (d, J = 5.6 Hz, 2H), 1.59 – 1.12 (m, 22H), 0.95 (t, J = 7.1 Hz, 6H), 0.85 (t, J = 7.5 Hz, 6H); ¹³C NMR, (100 MHz, PhMe): 162.50, 147.15, 136.25, 126.40, 125.71, 114.44, 113.94, 106.93, 70.34, 39.17, 30.39, 29.04, 23.68, 23.05, 13.90, 10.84.

5,6-dehydro-11,12-dehydro-2,9-di-(2-ethyhexyl)oxy-dibenzo[a,e][8]annulene (3b): 1b (24.2 mg, 0.0050 mmol) was dissolved in a 1:1 mixture of MeOH/THF (4 mL) under Argon balloon.
The solution was irradiated (medium pressure Hg lamp) for 1.5 hours at room temperature. The solvent was concentrated, and the residue was purified by silica gel preparatory TLC (100% Hexanes) to yield 3b (15.7 mg, 3.5 mmol 69%) as a bright yellow oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 6.65$ (d, $J = 8.4$ Hz, 1H), 6.43 (dd, $J = 8.4$, 2.6 Hz, 1H), 6.39 (d, $J = 2.6$ Hz, 1H), 3.76 (dd, $J = 5.7$, 1.7 Hz, 2H), 1.68 (p, $J = 6.1$ Hz, 1H), 1.63 – 1.14 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR, (125 MHz, CDCl$_3$): $\delta = 159.53$, 133.66, 127.20, 124.66, 115.53, 113.17, 109.11, 108.09, 70.63, 39.21, 30.42, 29.03, 23.76, 23.03, 14.09, 11.08.

NMR studies of organometallic complexes:

4a used for characterization (not isolated): In an argon glove-box 1a (8.6 mg, 0.030 mmol) and 2 (14.3 mg, 0.030 mmol) were mixed in toluene-D8 that was degassed and dried over 4 Å molecular sieves. The solution was allowed to stand until most of the 1a was dissolved in solution. The solution was filtered through PFTE syringe filter (0.2 m) into a Wilmad® quick pressure valve NMR tube. There remains approximately 33% 2 in solution and some 5 is visible after $^{13}$C is taken. $^1$H NMR (500 MHz, Tol): $\delta = 8.15$ (d, $J = 8.6$ Hz, 2H), 7.12 (d, $J = 2.6$ Hz, 2H), 6.36 (dd, $J = 8.6$, 2.6 Hz, 2H), 3.40 (s, 6H), [1.50 (s, 13H) t-BuO from xs 2], 1.42 (s, 9H), [1.39 (s, 4H) t-Bu from xs 2], 1.13 (s, 27H). $^{13}$C NMR (126 MHz, Tol): $\delta = 159.09$, 153.71, 149.97, 139.91, 139.41, 133.95, 122.80 ($J_{W-C} = 110$ Hz), 120.05, 119.13, 112.88, 80.12, 73.69 ($J_{W-C} = 55$ Hz), 54.34, , 31.28, 30.89; 28.43 [270.99 (CCH$_3$ from xs 2), 78.58 (OC(CH$_3$)$_3$ from xs
from 5) 33.86 (C(CH₃)₃ from xs 2), 32.23 OC(CH₃)₃ from xs 2)]. IR: C=O stretch (sharp) at 1847 cm⁻¹, C-C stretch (broad) at 2053 cm⁻¹. See NMR spectra section for HSQC and HMBC.

4a used for the study in Figure 2-3 and IR measurements: In an argon glove-box 1a (14.1 mg, 0.049 mmol) and 2 (23.2 mg, 0.049 mmol) were mixed in THF (1 mL) distilled from sodium and benzophenone. The mixture was allowed to stand until most of the 1a was dissolved in solution. The solution was filtered through PFTE syringe filter (0.2 m) and the filtrand was concentrated by evaporation. The solid is redissolved in ether (also distilled) placed in a freezer at −29 C. A purple solid precipitates which is rapidly filtered through vacuum filtration, the filtrate is washed with cold ether and dried. This yields 4a (7.2 mg, ~10% 2 impurity by NMR). This was redissolved in toluene-D8.

5a typical procedure: A solution of 4a in toluene-D8 and prepared as described above was heated to 80 C for 2 hours in a Wilmad® quick pressure valve NMR tube, until all 4a and 6a had been consumed. The solution was transferred to vial in an Argon glove-box and the solvent was evaporated slowly over 2-3 days. This grew large, bright orange crystals. These were either rinsed several times with <0.2 mL of toluene, and used for crystallographic analysis. Alternatively, <0.2 mL of toluene was added, and the mixture was filtered by vacuum filtration. This yielded up to 11 mg (0.014 mmol, 29%) at a time of 5a. ¹H NMR (500 MHz, Tol) δ 7.48 (dd, J = 8.6, 4.9 Hz, 2H), 6.95 (d, J = 2.6 Hz, 1H), 6.51 (d, J = 2.5 Hz, 1H), 3.31 (s, 5H), 3.17 (s,
3H), 1.63 (s, 27H), 1.55 (s, 9H), [1.50 (d, J = 2.4 Hz, 22H), 1.39 (s, 6H) xs 2]. $^1$H NMR (126 MHz, Tol): δ = 265.37, 164.24, 162.43, 162.01, 154.82, 146.05, 135.91, 132.95, 131.60, 130.03, 119.80, 118.35, 117.08, 114.79, 111.72, 111.47, 106.36, 78.12, 76.99, 54.50, 54.24, 32.54, 30.60, 30.21, 28.43. IR:

$^{13}$C NMR (126 MHz, Tol): δ = 265.37, 164.24, 162.43, 162.01, 154.82, 146.05, 135.91, 132.95, 131.60, 130.03, 119.80, 118.35, 117.08, 114.79, 111.72, 111.47, 106.36, 78.12, 76.99, 54.50, 54.24, 32.54, 30.60, 30.21, 28.43. IR:

6a: Crystalline 5a (3 mg) and an excess of 1a were mixed in 1 mL toluene-D8 in a Wilmad® quick pressure valve NMR tube for NMR analysis The mixture was heated to 80°C to promote dissolution of 1a. It was filtered via a PTFE syringe filter and the solution was again added to a Wilmad® quick pressure valve NMR tube for NMR analysis. This solution was then transferred to a vial. $^1$H NMR (500 MHz, Tol) δ = 8.12 (d, J = 8.5 Hz, 2H), 7.99 (d, J = 8.6 Hz, 1H), 7.63 (d, J = 8.6 Hz, 1H), 6.80 (d, J = 2.5 Hz, 1H), 6.69 (d, J = 2.9 Hz, 2H), 6.63 (dd, J = 8.7, 2.5 Hz, 1H), 6.58 (dd, J = 8.6, 2.6 Hz, 1H), 6.38 (dd, J = 8.6, 2.6 Hz, 2H), 3.35 (s, 6H), 3.18 (s, 3H), 3.02 (s, 3H), 1.35 (s, 9H), 1.30 (d, J = 10.4 Hz, 27H). $^{13}$C NMR (101 MHz, Tol) δ = 164.37, 162.50, 160.63, 159.13, 155.13, 153.60, 145.51, 140.50, 139.05, 134.93, 133.60, 133.02, 133.00, 119.68, 118.72, 118.37, 117.21, 115.23, 115.13, 114.86, 113.79, 113.25, 106.52, 86.38, 81.90, 81.67, 80.42, 80.03, 77.47, 54.57, 54.26, 31.66, 31.59, 30.79, 30.57, 30.21, 28.27, 22.72, 20.60, 20.49, 20.41, 20.30, 20.22, 20.10, 20.02, 19.83, 19.64. IR: C=O, 1847, CC, 1847 (broad), CC, 2214
for characterization (not isolated): In an argon glove-box 1b (14.5 mg, 0.030 mmol) and 2 (14.3 mg, 0.030 mmol) were mixed in toluene-D8 that was degassed and dried over 4 Å molecular sieves. The solution immediately turns from yellow to a dark blood-red. The solution was filtered through PFTE syringe filter (0.2 m) into a Wilmad® quick pressure valve NMR tube. \(^1\)H NMR (500 MHz, Tol): \(\delta = 8.19\) (d, \(J = 8.6\) Hz, 2H), 7.21 (d, \(J = 2.5\) Hz, 2H), 6.45 (dd, \(J = 8.6, 2.5\) Hz, 2H), 3.86 – 3.76 (m, 4H), 1.68 – 1.58 (m, 2H), [1.50 (s, 6H) t-BuO from xs 2], 1.46 – 1.34 (m, 16H) (incl: 1.44 (s) 9H), 1.34 – 1.21 (m, 11H), 1.16 (s, 27H), 0.99 – 0.84 (m, 12H). \(^{13}\)C NMR (125 MHz, Tol) \(\delta = 158.89, 153.73, 139.90, 139.32, 133.99, 123.08, 120.86, 120.83, 119.07, 113.36, 80.11, 73.93, 70.18, 39.32, 39.29, 36.50, 31.33, 30.97, 30.94, 30.60, 30.51, 29.10, 29.07, 23.83, 23.77, 23.05, 20.48, 20.33, 20.18, 20.03, 19.87, 19.72, 19.57, 13.90, 10.88, 10.84.
5b was not isolated separately from 6b. The tetrahedrane shifts carbon in 6b were found by analyzing the 13C NMR of the combined mixture and comparing it to that of 6a. See NMR section.

7: In an argon glove-box, 5a (3 mg) was dissolved in CD$_2$Cl$_2$ that was dried over molecular sieves and degassed. The solution was transferred to a low-pressure, J. Young tube. This was placed in an ice bath and irradiated (medium pressure mercury lamp) over a two hour period, while maintaining the temperature at 0 °C. NMR spectra were taken periodically to monitor the reaction. This yields 7 as the major product, which was not isolated from solution.

*Variable temperature measurements and Kinetic modeling:*

Preparation of the solution of 4a used for variable temperature NMR (not isolated): In an argon glove-box 1a (15.1 mg, 0.052 mmol) and 2 (23.6 mg, 0.050 mmol) were mixed in toluene-D8
(2.6 mL) that was degassed and dried over 4 Å molecular sieves. The solution was allowed to stand until most of the 1a was dissolved in solution (~30 minutes). The solution was filtered through PFTE syringe filter (0.2 m), and hexamethyldicyclotrisiloxane (5.9 mg, 0.027 mmol) was added to 2.4 mL of this solution. This was divided into 4 (3 were used in variable temperature studies) Wilmad® quick pressure valve NMR tube (0.05 mL each).

Variable temperature experiments were run at 60 C, 70 C and 50 C respectively. Other NMR samples were kept at -78 C prior to the experiment to prevent the reaction of 4a. For each data set, the instrument was heated to the desired temperature using a blank. Once the temperature had equilibrated, this was switched out for a sample tube. The temperature was allowed to stabilize (~3 – 5 minutes) before locking and shimming the sample, and then the experiment was started. Because of this the initial concentrations for each of the three experiments vary with temperature. Spectra were taken at a variable intervals, every 80 and 225 seconds. The integration values of each of the peaks was taken with respect to the IS, and this data was entered into Kintecus using the Powell algorithm and least squares regression (~FIT:2:2) along with statistical bootstrapping to obtain the standard deviations in k.
Plots of experimental vs theoretical concentrations:

Figure 2 - 8: Modeled (gray) versus experimental (black) concentrations at 323 K.

Figure 2 - 9: Modeled (gray) versus experimental (black) concentrations at 333 K.
Figure 2 - 10: Modeled (gray) versus experimental (black) concentrations at 343 K.

Calculations of activation parameters:

Figure 2 - 11: Plot of $k_2$ versus Temperature. Blue line: Fit to the Arrhenius equation (Eq. 7). Red line: Fit to the Eyring-Polanyi equation (Eq. 8)

\[
(7) \quad k_2 = A \cdot e^{\left(\frac{E_{\text{ad}}}{RT}\right)}
\]
\[ k_2 = \frac{k_B T}{h} \cdot e^{\frac{\Delta S^\sigma}{R}} \cdot e^{\frac{\Delta H^\sigma}{RT}} \]

2.8 References:


(23) Ditchfield, R.; Hughes, R. P.; Tucker, D. S.; Bierwagen, E. P.; Robbins, J.; Robinson, D. J.; Zakutansky, J. A. Synthesis and dynamic NMR studies of .eta.3-triphenyl- and .eta.3-trimethylcyclopropenyl complexes of ruthenium, [Ru(.eta.5-C5R5),(.eta.3-C3R’3)X2] (R = H, Me; R’ = Me, Ph; X = Cl, Br, I). Extended Hueckel molecular orbital study of barriers to rotation of. Organometallics 1993, 12, 2258–2267.

(24) Hughes, R. P.; Reisch, J. W.; Rheingold, A. L. Oxidative addition of cyclopropenyl cations to zerovalent molybdenum and tungsten centers. Synthesis of .eta.3-cyclopropenyl and .eta.3-oxocyclobutenyl complexes of molybdenum(II) and tungsten(II). Crystal and molecular structures of [Mo(.eta.5-C5H5),(.eta.3-C3H3)Cl]. Organometallics 1985, 4, 1754–1761.


2.9 NMR Spectra

The following pages contain NMR spectra of the compounds discussed in the previous chapter.
Chapter 3. Functionalization of Diphenyloligoenes

3.1 Introduction

Polyacetylene is the quintessential conjugated polymer. The discovery of its remarkable electronic properties catalyzed an exponential growth in the study of organic materials for electronics. It bridged the gap between condensed matter physicists, who were interested in the metallic and insulating properties of solids, and polymer chemists, who were interested in synthesizing ever more complex and functional macromolecular architectures. These materials have revolutionized the electronics industry. Polymer solar cells have reached an efficiency of 10%. Organic-light emitting diodes are regularly used in electronic displays of superior color quality and resolution. These materials are so appealing because they can (or have the potential to) be solution processed and printed on a large-scale, which could drastically reduce the costs and energy consumption in electronics manufacturing.

The majority of research conducted in this field (including that discussed in the previous chapters) revolves around the improvement in the variety and performance of polymeric materials. Although great strides have been made in our understanding of conducting polymers since the discovery of polyacetylene, because they are inherently disordered systems, their extrinsic properties and performance cannot be decoupled from their intrinsic electronic properties dictated by their chemical composition. This complicates the design of new materials for specific applications. Conjugated small-molecules can serve as ideal model system for

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\textsuperscript{1}\textit{The work described in this chapter has been published. It is reprinted here with the permission of the Royal Society of Chemistry, which allows inclusion of journal articles in dissertations.}
studying the origin of a material’s electronic properties.\textsuperscript{8} By comparison, their solid-state structure can be more easily modulated through design to pinpoint idealized intra- and intermolecular interactions. However, despite decades of research into polyacetylene, oligomeric model systems for it have failed to live up to this purpose, either largely because of their instability, their synthetic inaccessibility, or because their poly-olefin backbones have large deviations from planarity.\textsuperscript{9–13}

![Figure 3 - 1: The structure of α,ω-diphenyl-μ,ν-dicyano-oligoenes (DPDCn).](image)

With the goal of resolving these issues, Dr. Jeffrey Meisner, a former graduate student in the Nuckolls lab, synthesized a series of α,ω-diphenyl-μ,ν-dicyano-oligoenes (DPDCn) (Figure 3 – 2).\textsuperscript{1} These molecules serve as a discreet length model system for polyacetylene. The odd-numbered series can be synthesized up to thirteen olefin units in length (DPDCn, \(n = 3 – 13\))—a significant feat. The two nitriles appended to the oligoene backbone are integral to their functional capabilities, both as a model system and as functional organic material in their own right. They are installed through a double Knoevenagel condensation of 1,4-dicyanobutene with a series of derivatives of cinnamaldehyde where the conjugated \(\pi\)-system was extended through iterative Wittig homologations. This synthesis can be applied to a variety of substituted analogs whose electronic structure covers a large range.
Crystals were obtained of all six DPDC\textsubscript{n} molecules, including DPDC\textsubscript{13}, the longest discreet oligomer of polyacetylene synthesized to date. They align in herringbone patterned stacks with eight nearest neighbor. The stacks are slightly off-set, and there is a slight curvature in the oligoene back-bone for DPDC\textsubscript{n} where \( n > 5 \), because of the presence of a single solvent molecule for every oligoene.

**Figure 3 - 3: Electronic structure of the DPDC\textsubscript{n} series.** (a) Extinction coefficient versus absorption wavelength in the UV-vis absorption spectra of the DPDC\textsubscript{n} in CH\textsubscript{2}Cl\textsubscript{2}; (b) Redox gap of the DPOn series (grey), polyacetylene (blue), and the DPDC\textsubscript{n} series as determined by cyclic voltammetry (CV); (c) \( \lambda_{\text{max}} \), the optical band gap (E\textsubscript{DG}) and the redox band gap (E\textsubscript{CV}) for the DPDC\textsubscript{n} series versus 1/L\textsuperscript{2}. 

Figure 3 - 2: X-ray crystal Structure of DPDC\textsubscript{13} showing three views. Thermal ellipsoids represent 50% probability.
As electron-withdrawing substituents the cyano-functionalization acts as a ‘protecting group’ for the poly-olefin chain, shielding it from oxidative decomposition. It does not impose A-1,3 strain on the backbone as evidenced in the crystal structure, unlike the stabilizing methyl groups on the naturally oligoenes, carotenoids, and thus the conjugation length is not perturbed. This is reflected in the UV-Visible spectroscopy, where the $\lambda_{\text{max}}$ increases progressively over a range of 350 nm from DPDC3 to DPDC13 (left to right: $\lambda_{\text{max}} = 363, 418, 459, 499, 513$ and 536 nm, respectively, Figure 3 - 3a). Cyclic Voltammetry studies also show that HOMO-LUMO gap decreases with each successive addition of an olefin unit, and that the nitriles play a significant role in lowering the energy of the frontier orbitals when compared with unsubstituted $\alpha,\omega$-diphenyloigoenes (DPOn). Finally, the $\lambda_{\text{max}}$, optical band gap ($E_{\text{OG}}$), and redox band gap ($E_{\text{CV}}$) can be plotted versus a particle in a box model ($E$ vs. $1/L^2$). The linear fit for $E_{\text{OG}}$ and $E_{\text{CV}}$ can be extrapolated to those of polyacetylene.

3.2 DPDC’s Designed for Post-Synthetic Modification

Figure 3 - 4: Bromine and carboxylic acid substituted DPDCs.
We were interested in synthesizing a new series of DPDCs that were further functionalized on the aryl ring. We focused first on the synthesis of the dibromo- and dicarboxylic acid series, **DPDCn-Br** and **DPDCn-CO₂H** (Figure 3 - 4). These contained functionality that could be modified in order to tune the electronics of the molecules or to integrate them into electronic devices. A proof of concept using **DPDC3-CO₂H** is illustrated in Section 3.3 below. **DPDCn-Br** were synthesized in the same manner as the **DPDCn** series. Scheme 3 - 1 briefly outlines this synthesis. Starting with 4-bromobenzaldehyde (1, y = 0), iterative Wittig homologations with the ylide of ((1,3-dioxolan-2-yl)methyl)triphenylphosphonium bromide followed by deprotection of the dioxolane during acid work-up gave aldehydes 2 – 4 (y = 1 – 3) in good yield (74 – 92%). 1 through 4 were each condensed with 1,4-dicyanobutene using DBU as a catalyst to yield **DPDCn-Br** (n = 3 – 9) in 7.6 to 37% yield.

![Scheme 3 - 1: Synthesis of the DPDCn-Br series (n = 3 – 9).](image)

In the synthesis of 2 – 4 the deprotection of the dioxolane after the homologation can be avoided by simply quenching with water. This yields the E and Z protected aldehydes, which can be easily separated by column chromatography to give 4-bromophenylidi- and trienes 5 and 6 (a
= E or b = Z, combined yields 85 – 90%). (They can also be carried forward as a mixture in the following step.) 5 and 6 were used to synthesize 4-carboxyphenyldi- and trieneals (8 and 9) via a lithium halogen exchange that was trapped by dry carbon dioxide. These can be easily purified via an acid-base extraction to yield pure 8 and 9 in 89 – 90% yield. Along with 4-carboxybenzaldehyde (7) these were carried forward in a modified Knoevenagel where excess sodium methoxide is used as a base to give DPDCn-CO₂H. The yield of the DPDCn-CO₂H series is significantly decreased when compared to other series. This is likely a result of the deactivation of the aldehyde by the electron-withdrawing carboxylate. In order to synthesize characterizable amounts of DPDC7-CO₂H excess 1,4-dicyanobutene must be added throughout the reaction run over 24 hours because it decomposes faster than the rate of the condensation.

**Scheme 3 - 2: Synthesis of DPDCn-CO₂H.**

**DPDC5-CO₂H** can be crystalized from dimethylformamide (figure 3 - 5). It crystalizes in the P₁ space group (R² = 0.0503). The crystals contain two molecules of DMF for every one DPDC5-CO₂H. The packing structure of these molecules is remarkably different from the DPDCn series. Structures show that the hydrogen donor/acceptor, a carboxylic acid, groups
guides the assembly into π-stacked sheets of oligoenes. They are oriented by a single hydrogen bonding interaction to DMF at each carboxylic acid. No solvent packs in between the π-stacked sheets of oligoene,

Figure 3 - 5: X-ray crystal structure of DPDC5-CO2H. (a) DPDC5-CO2H hydrogen bonding to DMF (thermal ellipsoids represent 50% probability), (b) side view showing the slipped stacks, (c) edge view showing the close packed π stacks.
thus reinforcing a planar geometry. This allows a very close intermolecular distance between the oligoenes in a stack to decrease to 3.38 Å, approaching the distances found in graphite of 3.35 Å. They are oriented in a hexagonal pattern when viewed down the length of the molecule, with six nearest neighbors. These stacks are off-set from one another by approximately the length of the aryl ring, which sits over the nitrile group in neighboring molecules.

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3.3 Coordination of DPDC3-CO₂H to iron oxide nanoparticles

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Figure 3 - 6: Scanning electron micrographs (SEM) of 10-nm Fe₃O₄ nanoparticle SAMs made using DPDC3-CO₂H. Monolayers made using (a) 1.5 mM and (b) 3.0 mM solution of DPDC3-CO₂H. Monolayer coverage occurs at low concentrations and the presence of multilayers can be detected at higher concentration. Scale bars are set to 500 nm, while insert scale bar is set to 50 nm. (c) Schematic of oligoene-Fe₃O₄ composite monolayer.

Figure 3 - 6 shows scanning electron micrographs (SEM) of monolayers of iron oxide (Fe₃O₄) nanoparticles that were assembled using DPDC3-CO₂H to connect them to the substrate. We found that when a solution of Fe₃O₄ nanoparticles capped with oleate ligands¹ and dispersed
in DMF is treated with a solution of DPDC3-CO2H in DMF, rapid precipitation of the nanoparticles occurs, indicating a fast ligand exchange. We sought to utilize this exchange to direct the formation of nanoparticle monolayers atop GaAs substrates. It has been shown previously that carboxylic acids bind to GaAs and Fe3O4 through known ligand exchange procedures. Before application of oligoenes the native oxide layer of the substrates was removed through submersion in aqueous ammonium hydroxide. After rinsing with ethanol they were submerged in a 1.5 mM solution of oligoene (DPDC3-CO2H) in DMSO. They were then removed from solution, again rinsed with ethanol, and submerged for 1 hour in a solution of 10-nm Fe3O4 nanoparticles in DMF. Scanning electron microscopy (SEM) analysis of these films shows clear formation of nanoparticle monolayers as shown in Figure 6. Nanoparticle coverage was found to be dependent upon the concentration (1.5 mM, 3.0 mM, or 6.0 mM) of the oligoene solution. At the higher concentrations (3.0 and 6.0 mM) the appearance of multilayers in addition to monolayers was observed (Figure 6b; Figure SI12). No monolayer formation was observed when only DMSO without oligoene was used or upon the direct submersion of the GaAs substrate into the nanoparticle solution (see experimental section).

3.6 Conclusion

We have synthesized a series of DPDCn molecules that have functionality for post synthetic modification and integration into electronic devices. The DPDCn-CO2H series can be used to assemble monolayers of colloidal nanoparticles. Qishui Chen, a current graduate student in the Nuckolls group, is continuing research on the DPDCn-Br series. She is also synthesizing functionalized DPDCn’s for use in ultra-fast microscopy in order to understand their carrier
dynamics and probe their potential as materials for singlet fission.\textsuperscript{15} The DPDCn-CO2H series described in this chapter are also tempting candidates for these studies because they are well aligned in the solid state, and because the slip-slacked alignment predicted to be ideal for singlet fission.

Meisner went on to further study DPDCn’s and related stilbenes and paraphenylenes in quantum conductance measurements.\textsuperscript{16–18} He demonstrated their remarkably high conductance when compared with other organic systems, and elucidated several key features about electronic coupling in these molecules.

I am grateful to the following people for their assistance on this project. Dr. Jeffery Meisner assisted with UV-Vis spectroscopy. Dr. Aaron Sattler in Professor Ged Parkin’s group solved the crystal structure of DPDC5-CO2H. Professor Christopher Murray and Jun Chen provided soluble Fe3O4 nanoparticles. Hasti Amiri and Hanfei Wang assisted in taking SEM images.

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3.7 Experimental Section

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\textit{General Materials and Methods:}

All chemicals were purchased from Sigma-Aldrich, Fisher Scientific, TCI America, or Strem Chemicals and were used without further purification. When necessary, solvents were dried by passing through a column of activated alumina under an atmosphere of Ar or distilled from sodium and benzophenone. All reactions were performed in oven dried or flame dried glassware under an atmosphere of Ar. Flash chromatography was performed on a Teledyne ISCO CombiFlashRf using RediSepRf silica gel columns. \textsuperscript{1}H (400 or 500 MHz) and \textsuperscript{13}C (100 or 125
MHz) nuclear magnetic resonance spectra were recorded at 300 K (unless otherwise noted) on 
**Bruker** 400 and 500 FT NMR spectrometers. Spectra are referenced to the solvent residual peak 
(CDCl₃, δ = 7.26 [¹H] and δ = 77.26[¹³C], tol-d₈, δ = 2.09[¹H]). Resonance peaks are 
categorized as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (b). Coupling constants 
(J) are given in Hz. Gallium Arsenide (100) single crystalline wafer was purchased from Sigma-
Aldrich. Ammonium Hydroxide, 30% in water (NH₄OH) and Ethanol, 200 proof (EtOH) were 
purchased from Fischer Scientific. Dimethyl Sulfoxide (DMSO) 99% anhydrous was purchased 
from Sigma-Aldrich. EtOH and DMSO were degassed over several (three or greater) freeze 
pump thaw cycles before use. Monolayer formation was observed using a Hitachi S-4700 FE-
SEM.

**General Procedure for Wittig Homologation of Aldehydes:**

Lithium methoxide (2.6 eq.) in dry THF solution was added via syringe to a stirring solution of 
(1,3-dioxolan-2-yl)methyl-triphenylphosphonium bromide (2.5 eq.) in dry tetrahydrofuran 
(THF). The suspension was heated to reflux stirred for 30 minutes, changing color from off-
white to light orange/pink. The aldehyde (1 eq.) in dry THF solution was added dropwise over 
30-60 min. The suspension was refluxed for 24 h. The reaction suspension was then cooled to 
room temperature at which point 10% aqueous hydrochloric acid was added. Stirring was 
continued for 1 hour in order to hydrolyze the intermediate acetal and equilibrate the aldehyde to 
the thermodynamically preferred all-trans configuration. The organic layer was extracted with 
CH₂Cl₂ (x3) and the combined fractions were washed with water, sat. aqueous sodium 
bicarbonate solution and brine and dried over MgSO₄. Solvent was removed by rotary
evaporation and the product was purified via column chromatography using an eluent gradient from 0% to 10% ethyl acetate in hexanes over 25 column volumes.

**General Procedure for Double Knoevenagel Condensation:**

Aldehyde (150 mg) and 1,4-dicyano-2-butene (0.6 eq.) were dissolved in methanol in a 100-mL round-bottomed flask. The flask was sealed with a rubber septum and purged with nitrogen for 10 minutes. 3.0 eq. of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were added via syringe and the solution was left stirring for 16 hours. Upon completion of the reaction, the crude product was filtered off and washed with methanol and then purified by recrystallization from dichloromethane/methanol solutions or flash column chromatography using dichloromethane/hexanes as eluent.

![Cinnamaldehyde](image)

4-Bromocinnamaldehyde (2): General Wittig Homologation Procedure. The product was isolated by column chromatograph (15% ethyl acetate in hexanes) as a white solid in 91.5% yield. 1H NMR (400 MHz, CDCl3): δ 9.69 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.4 Hz, 2H), 7.43–7.38 (m, 3H), 6.69 (dd, J = 7.6 Hz, 16.0 Hz, 1H). 13C NMR (300 MHz, CDCl3): δ 193.4, 151.2, 133.1, 132.5, 129.9, 129.2, 125.8.
(2E,4E)-5-(4-bromophenyl)penta-2,4-dienal (3): General Wittig Homologation Procedure. The product was isolated by column chromatography (15% ethyl acetate in hexanes) as a yellow solid in 85.6% yield. 1H NMR (400 MHz, CDCl3): δ 9.62 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.27-7.21 (dd, J = 9.6 Hz, 15 Hz, 1H), 7.02-6.91 (m, 2H), 6.31-6.25 (dd, J = 8.0 Hz, 15.0 Hz, 1H). 13C NMR (400 MHz, CDCl3): δ 193.5, 151.5, 140.9, 134.5, 132.1, 132.0, 128.9, 126.8, 123.8.

(2E,4E,6E)-7-(4-bromophenyl)hepta-2,4,6-trienal (4): General Wittig Homologation Procedure. The product was isolated by column chromatograph (15% ethyl acetate in hexanes) as a orange-yellow solid in 73.7% yield. 1H NMR (400 MHz, CDCl3): δ 9.60 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.18 (dd, J = 11.0 Hz, 15.0 Hz, 1H), 6.92-6.72 (m, 3H), 6.58 (dd, J = 11.0 Hz, 14.0 Hz, 1H), 6.21, (dd, J = 7.6 Hz, 15.0 Hz, 1H). 13C NMR (400 MHz, CDCl3): δ 193.4, 151.3, 142.1, 136.8 135.3, 132.0, 131.4, 130.6, 128.3(4), 128.3(2), 122.7.

(2Z,3E,5Z)-2,5-bis(4-bromobenzylidene)hex-3-enedinitrile (DPDC3-Br): General Double Knoevenagel Condensation Procedure. The product was isolated as a yellow solid in 35.6% yield. 1H NMR (400 MHz, C2D2Cl4): δ 7.72 (d, J = 8.4 Hz, 4H), 7.62 (d, J = 8.4 Hz, 4H), 7.19 (s, 2H), 6.86 (s, 2H); (400 MHz, DMSO-d6): 7.81 (d, J = 8.0 Hz, 4H), 7.76 (s, 2H), 7.74 (d, J =
8.4 Hz, 4H), 6.97 (s, 2H). 13C NMR (400 MHz, DMSO-$d_6$): \(\delta\) 145.7, 133.2, 132.6, 131.4, 130.6, 124.8, 116.1, 110.2.

(2Z,3E,5Z)-2,5-bis((E)-3-(4-bromophenyl)allylidene)hex-3-enedinitrile (DPDC5-Br): General Double Knoevenagel Condensation Procedure. The product was isolated as a peach-orange solid in 33.4% yield. 1H NMR (400 MHz, C$_2$D$_2$Cl$_4$): \(\delta\) 7.54 (d, J = 8.4 Hz, 4H), 7.42 (d, J = 8.4 Hz, 4H), 7.24 (dd, J = 12 Hz, 15 Hz, 2H), 7.02 (d, J = 12 Hz, 2 H), 6.93 (d, J = 15 Hz, 2H), 6.71 (s, 2H). 13C NMR (500 MHz, C$_2$D$_2$Cl$_4$): \(\delta\) 146.2, 142.0, 136.2, 133.6, 130.8, 130.3, 126.8, 125.4, 116.2, 114.0.

(2Z,3E,5Z)-2,5-bis((2E,4E)-5-(4-bromophenyl)penta-2,4-dienylidene)hex-3-enedinitrile (DPDC7-Br): General Double Knoevenagel Condensation Procedure. The product was isolated as a red solid in 15.5% yield. 1H NMR (500 MHz, C$_2$D$_2$Cl$_4$): \(\delta\) 7.54 (d, J = 8.5 Hz, 4H), 7.36 (d, J = 8.5 Hz, 4H), 6.98-6.64 (m, 12H). 13C NMR (500 MHz, C$_2$D$_2$Cl$_4$): \(\delta\) 145.8, 143.5, 143.1, 138.6, 138.3, 133.5, 130.7, 130.2, 129.8, 124.2, 116.3, 113.4.
4-((1E,3E,5E,7Z,9E,11Z,13E,15E,17E)-18-(4-bromophenyl)-8,11-dicyanooctadeca-1,3,5,7,9,11,13,15,17-nonaenyl)benzoic acid (DPDC9-Br): General Double Knoevenagel Condensation Procedure. The product was isolated as a red-purple solid in 7.6% yield. 1H NMR (500 MHz, C2D2Cl4): δ 7.52 (d, J = 8.4 Hz, 4H), 7.33 (d, J = 8.4 Hz, 4H), 6.99 - 6.55 (m, 16H). Limited solubility prevented acquisition of 13C NMR.

(E)-2-(4-bromostyryl)-1,3-dioxolane (5a): General Wittig Homologation Procedure. Acetals were synthesized using the General Wittig Homologation Procedure without acidic hydrolysis. Water was added to quench the reaction solution and the product was isolated by column chromatography (15% ethyl acetate in hexanes) as a white solid in 36.3% yield (both stereoisomers in overall 80.5% yield). 1H NMR (400 MHz, CDCl3): δ 7.44 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.8 Hz, 2H), 6.73 (d, J = 16.0 Hz, 1H), 6.15 (dd, J = 6.0 Hz, 16.0 Hz, 1H), 5.41 (d, J = 6.0 Hz, 1H), 4.09-3.19 (m, 4H). 13C NMR (400 MHz, CDCl3): δ 134.8, 133.5, 131.7, 128.4, 125.9, 122.3, 103.6, 65.1.
(Z)-2-(4-bromostyryl)-1,3-dioxolane (5b): Acetals were synthesized using the General Wittig Homologation Procedure without acidic hydrolysis. The product was isolated by column chromatography (15% ethyl acetate in hexanes) as a colorless oil in 44.2% yield (both stereoisomers in overall 80.5% yield). $^1$H NMR (300 MHz, CDCl3): δ 7.45 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 11.7 Hz, 1H), 5.73 (dd, J = 7.5 Hz, 11.7 Hz, 1H), 5.44 (d, J = 7.5 Hz, 1H), 4.09-3.84 (m, 4H). $^{13}$C NMR (300 MHz, CDCl3): δ 135.0, 134.7, 131.8, 131.0, 129.0, 122.4, 99.9, 65.6.

2-((1$E,3E$)-4-(4-bromophenyl)buta-1,3-dienyl)-1,3-dioxolane (6a): Acetals were synthesized using the General Wittig Homologation Procedure without acidic hydrolysis. The product was isolated by column chromatography (15% ethyl acetate in hexanes) as a pale yellow solid in 36.4% yield (both stereoisomers in overall 93.5% yield). 1H NMR (400 MHz, CDCl3): δ 7.44 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 6.77 (dd, J = 10.8 Hz, 15.6 Hz, 1H), 6.54 (m, 2H), 5.78 (dd, J = 6.0 Hz, 15.2 Hz, 1H), 5.35 (d, J = 6.0 Hz, 1H); $^{13}$C NMR (400 MHz, CDCl3): δ 135.7, 134.5, 133.4, 131.7, 129.3, 128.0, 121.7, 103.4, 65.0.

2-((1$E,3Z$)-4-(4-bromophenyl)buta-1,3-dienyl)-1,3-dioxolane (6b): Acetals were synthesized using the General Wittig Homologation Procedure without acidic hydrolysis. The product was
isolated by column chromatography (15% ethyl acetate in hexanes) as a pale yellow solid in 93.5% yield (both stereoisomers in overall 80.5% yield). 1H NMR (400 MHz, CDCl3): δ 7.44 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.14 (dd, J = 11.2 Hz, 15.2 Hz, 1H), 6.55 (d, J = 15.0 Hz, 1H), 6.40 (t, J = 11.0 Hz, 1H), 5.78 (d, J = 6.4 Hz, 1H), 5.54 (dd, J = 4.4 Hz, 11.0 Hz, 1H), 4.10-3.91 (m, 4 H). 13C NMR (400 MHz, CDCl3): δ 135.8, 134.6, 134.1, 131.8, 128.2, 127.2, 124.0, 121.9, 99.5, 65.1.

\[ \text{HO}_2\text{C} \]
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\( (E)-4-(3\text{-oxoprop-1-etyl})\text{benzoic acid (8)}: \) A three-neck round-bottomed flask was charged with acetal protected aldehyde (either \( E \) or \( Z \), 1.0 eq.) in dry THF and cooled to -78° C. n-butyl lithium (1.6 M in hexanes, 1.1 eq.) was added dropwise and the yellow solution was stirred for 15 minutes. Carbon dioxide gas (CO\(_2\) tank, Matheson Tri-Gas; Product Grade) was bubbled into the solution until the yellow color disappeared, and then the reaction was left to warm to room temperature. The solution was diluted with diethyl ether, and then extracted (3x) with water. 1 M aq. hydrochloric acid was added to the aqueous layer and stirred for 1 h during which time a precipitate formed. This was collected by vacuum filtration to yield pure product \((\text{C}_{10}\text{O}_2\text{H}_8)\).

[Note: When the \( Z \)-alkene is used, acetal hydrolysis is remains incomplete. In that event, the precipitate is dissolved in tetrahydrofuran before adding 1 M aq. hydrochloric acid. After stirring for 1 h, the solution was diluted with water and extracted (3x) with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate, and concentrated to yield the all-trans product (89.4%) as a white solid. It is important to note that both the \( E \) and \( Z \) starting acetals yield the same all-trans product. Therefore an \( E/Z \) mixture can be used as the starting
4-((1E,3E)-5-oxopenta-1,3-dienyl)benzoic acid (n = 2): A three-neck round-bottomed flask was charged with acetal protected aldehyde (1.0 eq.) in dry THF and cooled to -78° C. n-butyl lithium (1.6 M in hexanes, 1.1 eq.) was added dropwise and the yellow solution was stirred for 15 minutes. Carbon dioxide gas (CO₂ tank, Matheson Tri-Gas; Product Grade) was bubbled into the solution until the yellow color disappeared, and then the reaction was left to warm to room temperature. The solution was diluted with diethyl ether, and then extracted (3x) with water. To the water layer was added 1 M aq. hydrochloric acid and this was stirred for one hour during which time a precipitate formed. This was collected by vacuum filtration to yield pure product (C₁₂O₂H₁₀). [Note: When the Z-alkene is used, acetal hydrolysis is remains incomplete. In that event, the precipitate is dissolved in tetrahydrofuran before adding 1 M aq. hydrochloric acid. After stirring for 1 h, the solution was diluted with water and extracted (3x) with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate, and concentrated to yield the all-trans product (90.7%) as a pale yellow solid.

1H NMR (400 MHz, Acetone-d₆): δ 11.39 (bs, 1H), 9.68 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.51 (dd, J = 10.8 Hz, 14.8 Hz, 1H), 7.43-7.36 (m, 1H), 7.26 (d, J = 15.6 Hz, 1H), 6.35 (dd, J = 8.0 Hz, 15.2 Hz, 1H). 13C NMR (400 MHz, Acetone-d₆): δ 193.0, 166.3, 151.2, 137.3, 132.8, 130.8, 130.1, 129.0, 127.4, 125.2.
4,4’-((1Z,3E,5Z)-2,5-dicyanohexa-1,3,5-triene-1,6-diyl)dibenzoic acid (DPDC3-CO$_2$H): A round-bottomed flask is charged with the corresponding enal-benzoic acid (1.0 eq.) and trans-1,4-dicyano-2-butene (1.0 eq.) in methanol under a nitrogen atmosphere. Sodium metal (>6.0 eq.) is dissolved in methanol and this is added directly to reaction solution. The reaction is stirred for 12 hours during which time a colored precipitate forms. The precipitate is collected by vacuum filtration, then suspended in methanol, and excess 1 M aq. hydrochloric acid is added. The reaction mixture is left to sit for one hour while the solid settles and is again collected by vacuum filtration. The yellow solid is pure product; 19.8% yield. 1H NMR (400 MHz, DMSO-$d_6$): $\delta$ 13.22 (bs, 2H), 8.05 (d, $J = 8.4$ Hz, 4H), 7.94 (m, 6H), 7.04 (s, 2H). 13C NMR (400 MHz, DMSO-$d_6$): $\delta$ 167.0, 146.2, 137.8, 132.9, 131.1, 130.4, 129.7, 116.1, 111.2.

4,4’-((1E,3Z,5E,7Z,9E)-4,7-dicyanodeca-1,3,5,7,9-pentaene-1,10-diyl)dibenzoic acid (DPDC5-CO$_2$H): A round-bottomed flask is charged with corresponding enal-benzoic acid (1.0 eq.) and trans-1,4-dicyano-2-butene (1.0 eq.) in methanol under a nitrogen atmosphere. Sodium metal (>6.0 eq.) is dissolved in methanol and this is added directly to reaction solution. The reaction is stirred for 12 hours during which time a colored precipitate forms. The precipitate is collected by
vacuum filtration, then suspended in methanol, and excess 1 M aq. hydrochloric acid is added. The reaction mixture is left to sit for one hour while the solid settles and is again collected by vacuum filtration. The dark orange solid is pure product; 14.4% yield. 1H NMR (400 MHz, DMSO-\textit{d}_{6}):

\[ \delta \quad 13.00 \text{ (bs, 2H)} \quad 7.95 \text{ (d, J = 8.0 Hz, 4H)} \quad 7.75 \text{ (d, J = 8.0 Hz, 4H)} \quad 7.61 \text{ (d, J = 10.4 Hz, 2H)} \quad 7.33-7.21 \text{ (m, 4H)} \quad 6.86 \text{ (s, 2H)} \]

13C NMR (400 MHz, DMSO-\textit{d}_{6}):

\[ \delta \quad 167.3, \quad 146.7, \quad 141.5, \quad 139.9, \quad 131.8, \quad 130.4, \quad 129.8, \quad 128.2, \quad 127.0, \quad 115.2, \quad 112.7. \]

4,4'-(\(1E,3E,5Z,7E,9Z,11E,13E\))-6,9-dicyanotetradeca-1,3,5,7,9,11,13-heptaene-1,14-diyl)dibenzoic acid (\textit{DPDC7-CO}_{2}\textit{H}): A round-bottomed flask is charged with 4-formyl benzoic acid (1.0 eq.) and \textit{trans}-1,4-dicyano-2-butene (1.0 eq.) in methanol under a nitrogen atmosphere. Sodium metal (>6.0 eq.) is dissolved in methanol and this is added directly to reaction solution. The reaction is stirred for 12 hours during which time a colored precipitate forms. The precipitate is collected by vacuum filtration, then suspended in methanol, and excess 1 M aq. hydrochloric acid is added. The reaction mixture is left to sit for one hour while the solid settles and is again collected by vacuum filtration. The dark red solid is pure product; 18.1% yield. 1H NMR (400 MHz, DMSO-\textit{d}_{6}):

\[ \delta \quad 13.00 \text{ (bs, 2H)} \quad 7.91 \text{ (d, J = 8.4 Hz, 4H)} \quad 7.68 \text{ (d, J = 8.4 Hz, 4H)} \quad 7.51 \text{ (d, J = 11.6 Hz, 2H)} \quad 7.42 \text{ (dd, J = 11.0 Hz, 15.4 Hz, 2H)} \quad 7.04-7.00 \text{ (m, 4H)} \quad 6.87 \text{ (dd, J = 11.6 Hz, 14.8 Hz, 2H)} \quad 6.78 \text{ (s, 2H)} \]

Limited solubility prevented acquisition of 13C NMR.

\textit{Monolayer Formation Procedure:}
Gallium Arsenide crystal was cut into several 0.75-1.0 cm square wafers using a diamond scribe. The wafers were submerged in NH₄OH and allowed to stand covered for 10 minutes. Upon removal from the NH₄OH, a wafer is rinsed with ethanol, dried under an argon stream, rinsed and dried a second time, then immediately submerged in a 1.5 mM solution of DPDC₃-CO₂H in dimethyl sulfoxide (DMSO). The solution is transferred to a nitrogen glove box and allowed to stand for 16 hours. After removal from the glove box, the wafer is removed from the solution, rinsed thoroughly with ethanol and dried under an argon stream. It is immediately submerged into a solution of 10-nm iron oxide (Fe₃O₄) nanoparticles in dimethylformamide, and allowed to stand 1-2 hours. Upon removal from the nanoparticle solution, the wafer is again rinsed with ethanol and dried under an argon stream, at which point it is ready for microscopy (Figure S12a).

**Controls.** In order to probe the dependence of monolayer formation on oligoene concentration in DMSO, the above procedure was carried out using both 3.0 and 6.0 mM solutions. It was found that nanoparticle coverage increased with increasing concentration of DPDC₃-CO₂H (Figure S12b and S12c). In order to show that monolayer formation is initiated by the oligoene linker, two controls were carried out. First, to eliminate the possibility that DMSO was acting as a linker the above procedure was carried out using pure DMSO in place of the oligoene solution. Second, in order to eliminate the possibility that submersion in the nanoparticle solution was sufficient to generate monolayers, a wafer was placed into the nanoparticle solution directly after cleaning. As seen in Figure S12g and S12h, no monolayer formation was observed in either case.
Figure 3 - 7: SEM images of monolayers of Fe3O4 nanoparticles formed after carrying out the above procedure using: (a) 1.5 mM DPDC3-CO2H at 500 nm resolution; (b) 1.5 mM DPDC3-CO2H at 300 nm resolution; (c) 3.0 mM DPDC3-CO2H at 1 µm resolution; (d) 3.0 mM DPDC3-CO2H at 300 nm resolution; (e) 6.0 mM DPDC3-CO2H at 100 nm resolution; (f) 6.0 mM DPDC3-CO2H at 300 nm resolution; (g) DMSO only; (h) DMF only.
3.8 References


(5) Fann, W.-S.; Benson, S.; Madey, J.; Etemad, S.; Baker, G.; Kajzar, F. Spectrum of $\chi^\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\prime\'


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3.9 NMR Spectra

The following pages contain NMR spectra of the compounds discussed in the previous chapter.