Discrete Polyene Oligomer Synthesis and Related Polymer Characterization
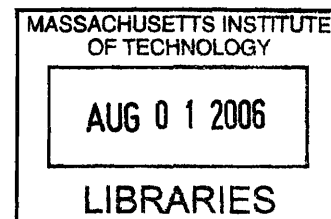(Appendix I: Reduced Tungsten Dimeric Compounds)

By

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B.S. in Chemistry Virginia Military Institute
May 2004

Submitted to the Department of Chemistry
In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE
At the
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
June 2006

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ABSTRACT

CHAPTER 1

Molybdenum complexes, $\{Mo(NAr')[OCMe(CF_3)_2]_2\}_2\{CH[5]'CH\}$ and $Mo(NAr')(CH[5]')(OCMe(CF_3)_2)_2$ ($CH[5]'CH$ = 3,4-divinyl-cyclopentene-1,1-dicarboxylic acid diisopropyl ester, Ar' = 2,6-dimethylphenyl, $[5']$ = 3-vinyl-4-dimethylvinyl-cyclopentene-1,1-dicarboxylic acid diisopropyl ester) were used to synthesize polyene oligomeric compounds with up to 15 conjugated double bonds by reaction with aldehyde compounds in a Wittig-like fashion. The optical properties of highly π-conjugated systems are investigated due to potential application in photooptical materials. To this end, discrete oligomers have been synthesized in order to study properties of the varying lengths and to what extent solvent and substitution patterns affect these properties. Trends have been established based on solvent polarity and steric bulk at the ester functionality. Extrapolation of the data here yields pertinent information to the polymer field since the oligomers mimic polymeric materials made by RCMP of 1,6-heptadiyne substrates that are fully five-membered ring containing structures with a disubstitution pattern of ester functionalities.

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LIST OF ABBREVIATIONS

Ad   Adamantyl
anal   Analysis
Ar   2,6-diisopropylphenyl
Ar'   2,6-dimethylphenyl
arom   aromatic
br   broad
t-Bu t-butyl, $-C(CH_3)_3$
calcd   calculated
Cp (C_5H_5)-
d   doublet
DEDPM   diethyl dipropargylmalonate, diethyl 2,2-di(prop-2-ynyl)malonate
D^{i}PrDPM   diisopropyl dipropargylmalonate, diisopropyl 2,2-di(prop-2-ynyl)malonate
DMDPM   dimethyl dipropargylmalonate, dimethyl 2,2-di(prop-2-ynyl)malonate
DEMDPME   diethylmethylene dipropargyl malonoether, 4,4-bis(ethoxymethyl) hepta-1,6-diyne
DEDPMA   diethyl dipropargyl malonoamide, N^1,N^1,N^3,N^3-tetraethyl-2,2-di(prop-2-ynyl)malonamide
equiv   equivalents(s)
EI   Electron Impact
ESI   Electron Spray Ionization
Et   ethyl
Fc   ferrocenyl
FMR   five-membered ring
GPC   Gel Permeation Chromatography
h   hour(s)
HPLC   High Pressure Liquid Chromatography
HRMS   High Resolution Mass Spectroscopy
J coupling constant in Hertz
k_i initiation rate constant for polymerization reactions
k_{obs} observed rate constant for polymerization reactions
k_p propagation rate constant for polymerization reactions
K   equilibrium constant
Li-HMDS   lithium bis(trimethylsilyl)amide
m   multiplet(s)
M_n number averaged molecular weight
M_w weight averaged molecular weight
MALDI   Matrix Assisted Laser-Desorption Ionization
Me   methyl
M_n(f/c) M_n(found)/M_n(calculated)
MS   mass spectroscopy
NMR   nuclear magnetic resonance
Np   Neopentyl, $-CH_2C(CH_3)_3$
PDI   Polydispersity Index
Ph   phenyl
ppm   parts per million
i-Pr iso-propyl, $-CHMe_2$
q   quartet
quat   quaternary

quin	quinuclidine
RBF	round bottom flask
RCMP	Ring Closing Metathesis Polymerization
ROMP	Ring Opening Metathesis Polymerization
R.T.	room temperature
s	singlet (NMR); strong (IR)
sept	septet
t	triplet
T	temperature
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
TOF	Time of Flight
w	weak
δ	chemical shift downfield from tetramethylsilane in ppm
[5]	diethyl 3-(2-methylprop-1-enyl)-4-vinylcyclopent-3-ene-1,1-dicarboxylate
[5]'	di-*iso*-propyl 3-(2-methylprop-1-enyl)-4-vinylcyclopent-3-ene-1,1-dicarboxylate

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General Introduction

Since the initial findings of the 1970's, a defined method has been sought for the ring closing metathesis polymerization (RCMP) of 1,6-heptadiynes.[1] The materials obtained by catalyst systems that utilized a mixture of components, such as MoCl$_5$, EtOH and (n-Bu)$_4$Sn, were polyacetylenes containing five- and six-membered rings along the backbone.[2] The ring systems of the polymer act to solubilize the material while retaining desirable photophysical properties similar to polyacetylene.[3] The mechanism and the nature of the propagating species are unknown for these binary and ternary transition metal systems, and polydispersities are relatively high (PDI ≤ 4.2).[2]

A living polymerization is defined as a process that yields materials with narrow polydispersity and molecular weights that are compared to the amount of monomer that is added. In order for this to be achieved, the rate of propagation relative to the rate of initiation as well as the observed molecular weight with respect to the theoretical molecular weight should be equal to or closely approach one. A propagating chain of a living system must still be active towards further polymerization even after all of the substrate is used.[4]

As recently as 1992, it was found that these highly conjugated polymers could be synthesized in a living manner using a well-defined Schrock-type molybdenum alkylidene initiator.[5] The desirable electronic and optical properties exhibited in these materials are elucidated through structural characterization and mechanistic investigation using ^{1}H and ^{13}C NMR, MALDI-TOF, and GPC. Greater control of polymerization based on this information could allow for use in applications such as photonics, optoelectronics and semiconductors.[6,7] Over the years, the system by which diethyldipropargyl malonate (DEDPM) is polymerized has been fine-tuned. The methods yield predictable molecular weights, narrow polydispersities and rates of initiation to approach a truly living process.[8,9,10]

Disubstituted 1,6-heptadiynes, such as DEDPM, are polymerized by alkylidene initiators to give the same conjugated backbone consisting of five- and six-membered rings as was found by classic RCMP conditions.[5] The well-defined initiator allowed for understanding of what conditions cause each ring type. Specific ring size is determined by the addition orientation of the first triple bond of the monomer to the molybdenum catalyst. By α-addition of a substrate, and subsequent intramolecular ring-closing metathesis, a five-membered ring is formed. Conversely, a six-membered ring is formed if β-addition occurs (**Scheme I**). A polymer chain containing a greater number of five-membered rings with alternating cis-/trans-configuration has

a higher λ_{max} value due to the greater length of double bonds in conjugation. This is in contrast to polymers containing six-membered rings where $A^{1,3}$ strain results in disturbed planarity and therefore a lower N_{eff}.

Scheme 1

Figure 1

(a)   (b)
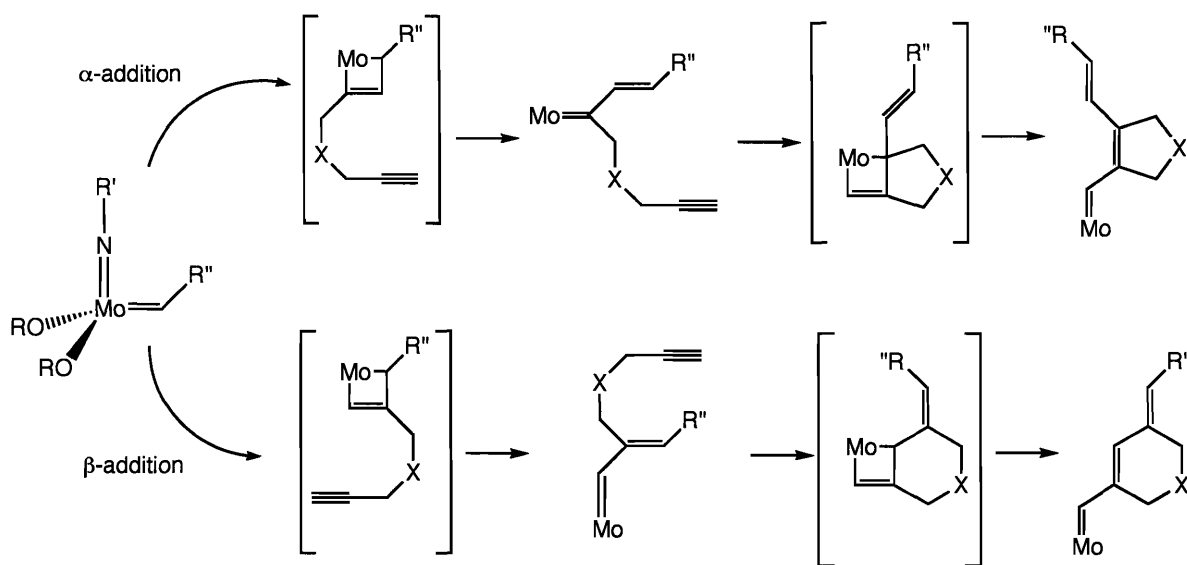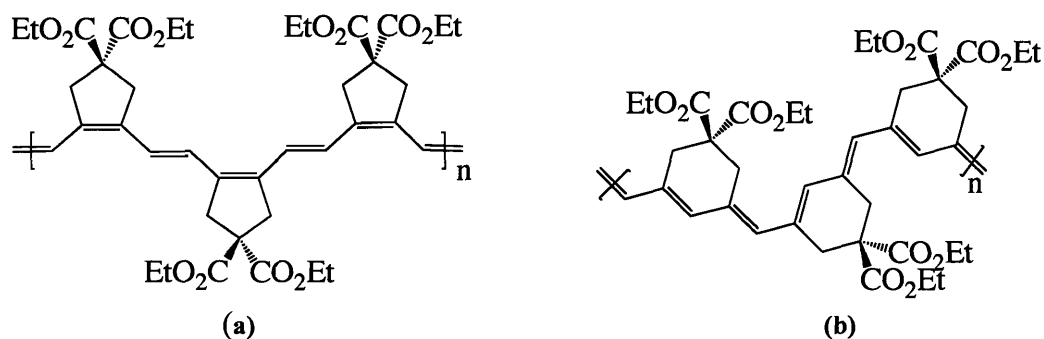
a) All five-membered ring polyene. **b)** All six-membered ring polyene.

Poly(DEDPM) comprised of a mixture of five- and six-membered rings synthesized using Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (Ar = 2,6-diisopropylphenyl) was characterized by a λ_{max} of 550 nm.[11] A polymer containing >99% six-membered rings, poly[1,3-(cyclohex-1-enylene)-methylidene], was found to have a maximum absorption band at 511 nm. The catalyst employed, Mo(NAr)(CHCMe$_3$)(O$_2$CCPh$_3$)$_2$, contained very bulky carboxylate ligands to encourage β-addition of DEDPM.[12] On the other hand, the same substrate has been used to form a polymer with almost 100% 1,2-(cyclopent-1-enylene)vinylene repeating units to yield a λ_{max} of

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591 nm. Here, the catalyst was a Grubbs-Hovyeda complex containing a highly polarized ruthenium-carbon double bond was used.[13] The Schrock catalyst, Mo(NAr)(CHCMe$_2$Ph) (O-t-Bu)$_2$(quin), has been employed to the same end by the production of a polymer containing >95% five-membered rings.[14] The latter included non-fluorinated alkoxide ligands to account for a faster syn/anti conversion rate,[15] and therefore encourages the α–addition of DEDPM.[14] Since during α-addition a less reactive disubstituted alkylidene is formed after the first alkyne of the substrate coordinates, the more active anti isomer of a catalyst allows for this alkylidene to propagate competitively with that formed by β-addition. Conversely, the less-reactive syn isomer is probably responsible for the greater occurrence of six-membered rings. Merely lowering the steric bulk at the CNO coordination site by decreasing the size of alkoxides is not sufficient for yielding an all five-membered ring polymer.[14a]

Chapter 1

Discrete Polyene Oligomer Synthesis and Related Polymer Characterization

Introduction

DEDPM polymerization was fine-tuned in the past years to allow for a highly selective and well-defined catalyst system.[8] Oligomers comprised of all five-membered rings were made in a living manner using the catalyst, $Mo(CH[5])(NAr)[OC(CH_3)_3]_2$ (Ar = 2,6-diisopropylphenyl, CH[5] = diethyl 3-(2-methylprop-1-enyl)-4-vinylcyclopent-3-ene-1,1-dicarboxylate).[8] The non-fluorinated alkoxide ligands in the catalyst allow for a greater ratio of 5- to 6-membered rings as evidenced by the comparison of $Mo(NAr)(CHMe_2Ph)(OR)_2$ and $Mo(NAr)(CHMe_2Ph)(OR_{F6})_2$ (where $R = C(Me)_3$ and $R_{F6} = CMe(CF_3)_2$).[11,14] With quinuclidine, employed to form a weakly bound adduct, the rate of propagation/rate of initiation (k_p/k_i) is lowered to significantly less than one.[8,16]

The symmetric five-membered ring trimer and tetramer were synthesized and isolated by the reaction of one equivalent of DEDPM with a stoichiometric amount of $Mo(NAr)(CH[5])[OC(CH_3)_3]_2(quin)$ in CD_2Cl_2 at -30 °C. After quenching the reaction with a five-membered ring aldehyde that mimicked the 1,2-(cyclopent-1-enylene)vinylene unit, chemical separation of oligomers was achieved by fractional precipitation and column chromatography. Clean separation of the five-, six-, and seven-mer, as evident by integration of the ^1H NMR spectrum, was not achieved by either thin layer or column chromatography. However, mixtures of oligomers with two to ten rings were separated by HPLC to yield E(0-0) and E(0-1) (λ_{max}) values for each oligomer length.[8]

The direct synthesis of pure oligomers with defined length is greatly desired. This would enable the study of structural and electronic properties intrinsic to each chain length. Here, the stoichiometric synthesis of pure oligomers is addressed. Feasible synthetic methods have been developed. In the organic realm, Constantin Czekelius has shown that McMurry coupling can aid in the synthesis of oligomers that have an even number of each monomer.[20] In order to deal with the synthesis of odd numbered chain lengths, a bimetallic molybdenum compound, $\{Mo(NAr')[OCMe(CF_3)_2]_2\}_2CH[5]'CH$ ([5]' = 3,4-divinyl-cyclopentene-1,1-dicarboxylic acid diisopropyl ester, Ar' = 2,6-dimethylphenyl) was utilized. Subsequent quenching with specifically tailored aldehyde compounds yielded isolable oligomeric products in good yield.

Although great steps have been made in understanding and controlling the mechanism of cyclopolymerization by RCMP, there are many questions still left unanswered. Towards this end, polymerizations of other substituted diyne substrates have been done to gain knowledge

concerning what other properties might govern the α–addition of a monomer. In this work, the system for RCMP of 1,6-heptadiynes yielded ambiguous results based on the monomers that were studied. Neither an increase nor decrease in steric bulk at the C4 position of the substrate proved to render information regarding orientation preference for the approach of each monomer to the catalyst, Mo(NAr)(*trans*-CHCHCHMe)(OCMe$_3$)$_2$(quin).

Results and Discussion

1.a. Synthesis of Bimetallic Compounds

Heptadiyne compounds have proven advantageous not only for RCMP to yield highly conjugated chain backbones but also for construction of a representative monomer of these materials. The reaction of DEDPM with one equivalent of $Mo(NAr)(CHCMe_3)(OCMe(CF_3)_2)_2$ under one atmosphere of ethylene yields a monomeric compound of a six-membered ring unit (**Figure 2**). Fox and coworkers prepared this molecule for reaction to form an initiator that would be representative of the growing polymer chain when reacted with a catalyst in a stoichiometric amount.[17]

Figure 2
(Six-membered ring triene)
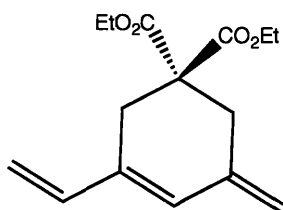
From previous research in the Trost group, a cationic Ruthenium catalyst was found to be very active for the cyclization of various diyne compounds to form a stable five-membered ring aldehyde (**Scheme II**).[18] Using this aldehyde, a Wittig reaction with an ylide yields a triene compound that is then reacted with a Mo-complex to form a successful initiator, such as the initiator that Adamchuck employed.[8]

Scheme II

R = Et,[19] iPr (6)   R = Et,[8] iPr (7), 80%   R = Et,[8] iPr, 64%
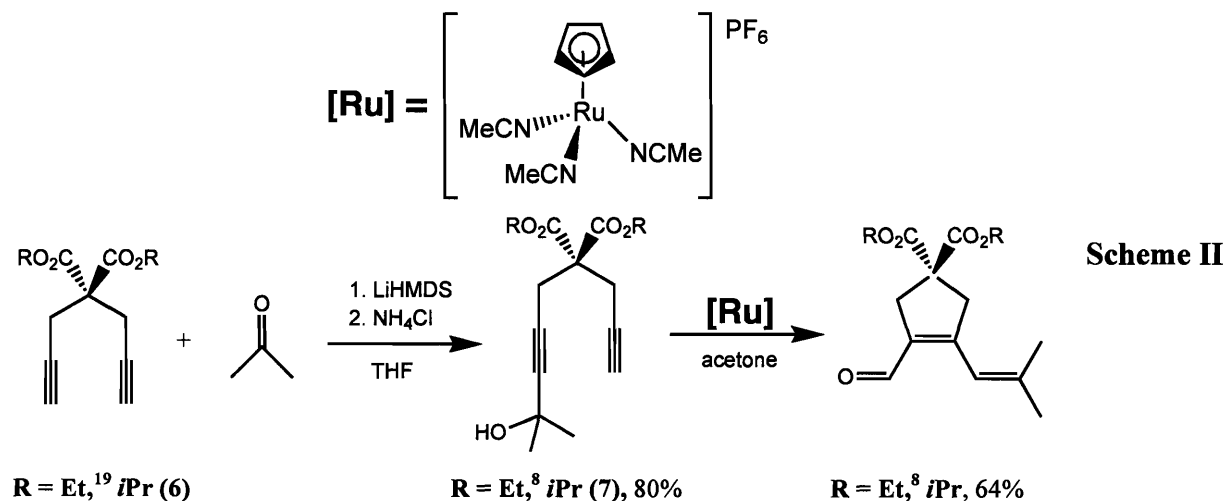
A primary alcohol will also react with the same ruthenium catalyst to form a five-membered ring aldehyde that lacks the two methyl groups on the vinyl carbon.[18] This reaction was first carried out with an alcohol that resembled DEDPM (**Scheme III**) to form 3,4-divinyl-cyclopentene-1,1-dicarboxylic acid diisopropyl ester (4a). It was found that the absence of steric protection by the two methyl groups on the vinyl carbon rendered a molecule that was quite unstable in solution while concentrating and especially on a silica gel column. The reaction yields for both the oily aldehyde and triene were extremely low, but clean compound could be isolated (**Figure 3**). When Scheme III was carried out at room temperature in DMF, a significant amount of uncharacterized byproduct containing phenyl rings was obtained.[20] Although the formation of this byproduct could be suppressed using a different procedure, significant decomposition of the desired product lowers the yield substantially. The ultimate downfall of this triene, however, is that the oily product cannot be stored for any amount of time.

Scheme III

R = Et (**2a**), iPr (**2b**)   R = Et (**3a**), iPr (**3b**)   R = Et (**4a**), iPr (**4b**)
41%   55%   73%
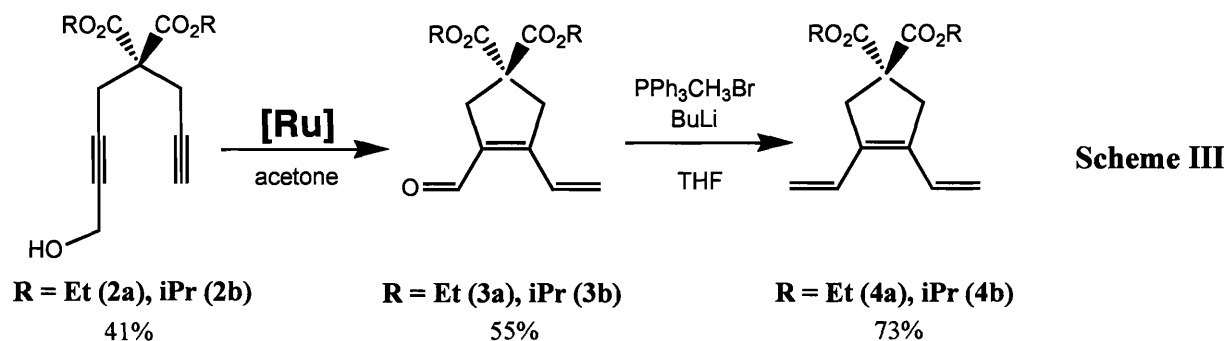
Attempts to increase the yield of (4a) further have failed. A smaller ylide was utilized in hopes of facilitating attack of the sterically encumbered aldehyde. Due to the expense and moisture-sensitivity of PMe_4Br, a Wittig-Horner reagent was chosen instead. Dimethyl methyl phosphinate $(P(O)(OMe)_2Me)$ deprotonated using NaH in THF and (3a) was added at -78 °C. The reaction did not yield isolable product, and the outcome was only the decomposition of (4a). Perhaps a different base such as LiO-*t*-Bu would serve better in this scenario to overcome potential solubility and reaction problems of NaH. Another methylene transfer agent that has been used in substitution for PPh_3MeBr was the Tebbe reagent, $Cp_2Ti(\mu\text{-}Cl)(\mu\text{-}CH_2)AlMe_2$, easily synthesized from $TiCp_2Cl_2$ and two equivalents of $AlMe_3$ in accordance with the published procedure. After one hour, the reaction had proceeded to yield one product by TLC with an R_f value in accordance with (4a). However, quenching of the active reagent was very exothermic and the separation of catalyst from product was difficult.

Figure 3

(^{1}H NMR of 3,4-divinyl-cyclopentene-1,1-dicarboxylic acid diisopropyl ester (4a))
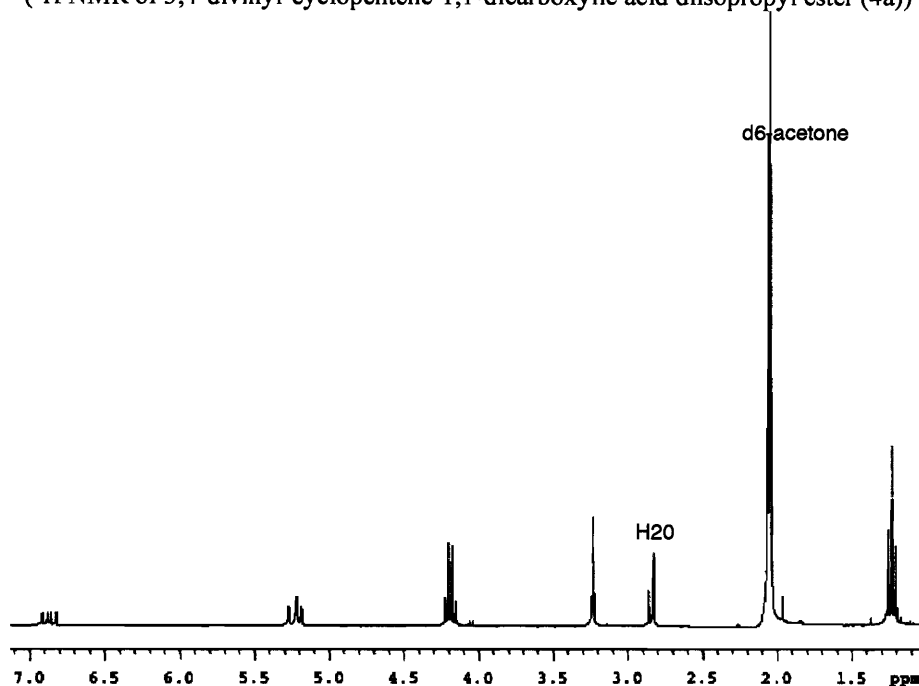
Reaction of (4a) with two equivalents of the trademark Schrock alkylidene catalyst, $Mo(CHCMe_3)(NAr)(OR_{F6})_2$, yields the bimetallic complex (5a) (**Scheme IV**). The compound is highly crystalline and soluble. X-ray quality crystals were formed from a concentrated solution of pentane. The solid-state structure portrays the same rotation of symmetry as seen by the proton and fluorine NMR of the compound in solution. By ^{1}H NMR, integration of the alkylidene, aryl, and alkoxide resonances versus those of the ethyl esters is indicative of a 2:1 ratio, respectively. In addition, the olefinic resonances of the triene are gone after reaction with the catalyst (**Figure 4**). Alkoxide, aryl, alkylidene and isopropyl resonances are all coincident to indicate C_{2v} symmetry of the molecule. Consequently, the ^{19}F NMR yields two broad/multiplet signals indicative of the inner and outer $-CF_3$ groups of the alkoxide ligand broadened by J_{CF} coupling values as expected. All of the solution structural information is corroborated by the x-ray crystal structure of $[Mo(NAr)(OR_{F6})]_2CH[5]CH$ (5a) (**Figure 5**). All parameters are as expected for such a molecule (See Appendix 2 for complete x-ray structural data). Note the slightly enlarged angle Mo(1)-C(1)-C(3) most likely due to steric interactions of the linker molecule ester groups with the isopropyl groups of the imido ligand. It should be noted that in a scale-up reaction of (5a), a great amount of homometathesis product, and consequently a mixture

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of starting material and product, is evident when carried out in pentane; even under very dilute conditions.

Scheme IV

+ 0.5 equiv.

E = CO$_2$Et

Pentane
3 h

62%
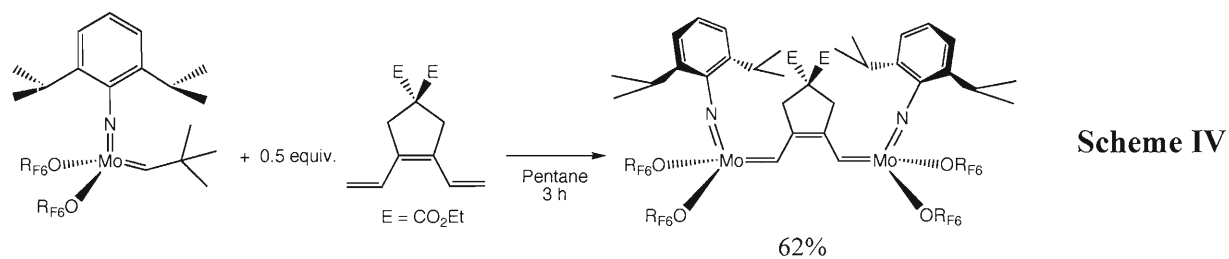
Figure 4
(^{1}H NMR of [Mo(NAr)(OR$_{F6}$)]$_2$CH[5]CH (5a))
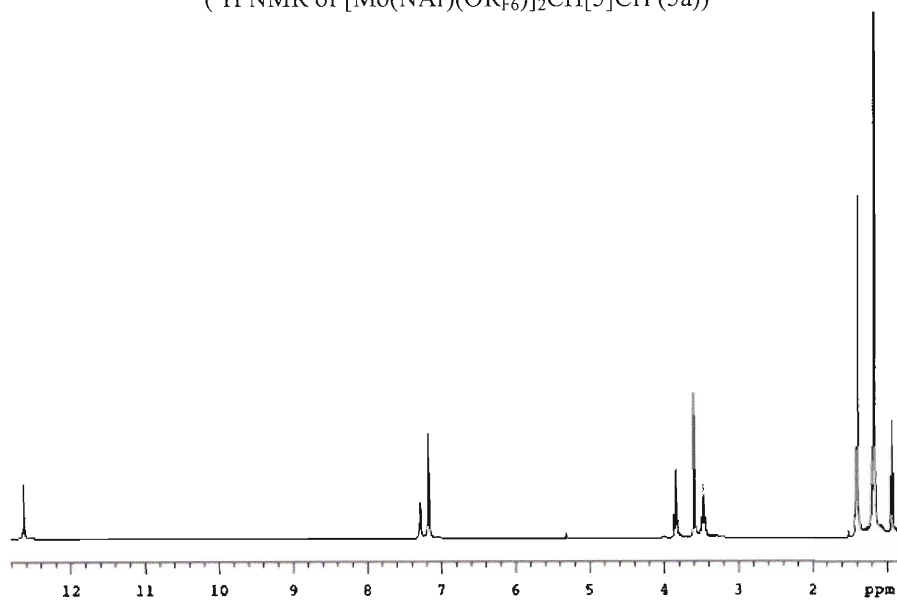
Figure 5
(Crystal structure of [Mo(NAr)(OR$_{F6}$)]$_2$CH[5]CH (5a))
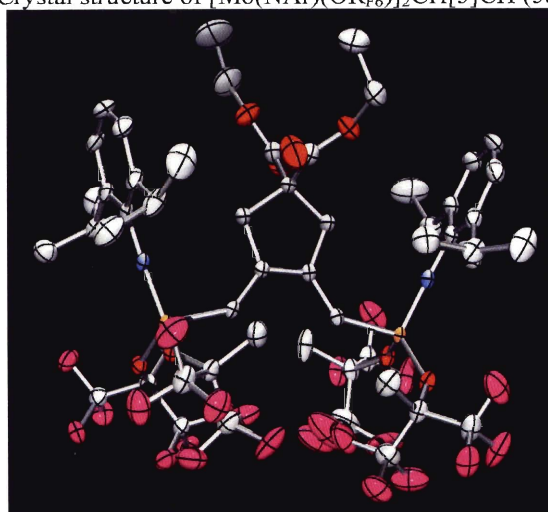
In an effort to increase the yield and shelf life of the five-membered ring triene, isopropyl ester functional groups were utilized. It had been found previously that diisopropyl dipropargyl malonate (DiPrDPM) was even more crystalline than DEDPM. Later, it will become more evident that the larger diethyl and diisopropyl ester groups have a stabilizing effect over dimethyl ester functionalities in analogous polymers. Work by Constantin Czekelius has also shown a trimeric five-membered ring aldehyde (**Figure 6**) to be stable if the ester functionality contains the isopropyl group versus ethyl. Consequently, Scheme III proved successful for the synthesis of (4b), although some decomposition occurred and a low yield was obtained. On the other hand, (4b) is a stable white solid when isolated in pure form. After storage for three weeks at low temperature, the proton NMR suggested that no significant decomposition had taken place (**Figure 7**). Furthermore, purification can be accomplished by recrystallization rather than column chromatography. By this method, the yield was elevated to 45% from the alcohol precursor.

Figure 6
(Trimer Aldehyde; E = CO_2iPr)
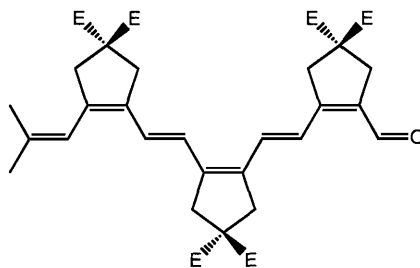
Figure 7
(^{1}H NMR of 3,4-divinyl-cyclopentene-1,1-dicarboxylic acid diisopropyl ester (4b))

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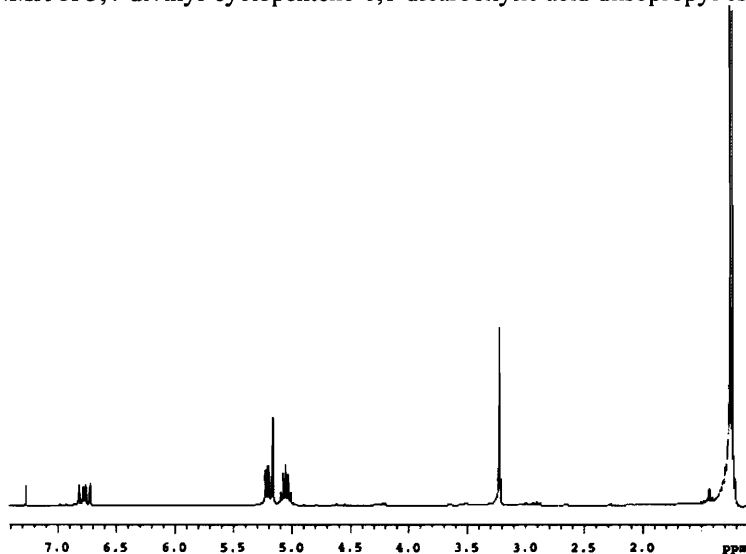
Reaction of (4b) with two equivalents of $Mo(NAr)(CHCMe_3)(OR_{F6})_2$ does not provide any isolable bimetallic complex. Instead, olefinic resonances in the ^1H NMR are still present. These most likely belong to the homometathesis dimeric product and also to the monometallic alkylidene complex once the triene reacts with one equivalent of catalyst. The monometallic product is probably unstable due to the highly reactive methylene group at the free end of the alkylidene ligand, and therefore accounts for the inability to isolate this product. The result of this reaction displayed that there is too much steric interaction between the isopropyl groups of the imido and alkylidene ligand. The crystal structure of (5a) is very crowded and it is vaguely surprising to find both metal centers capable of syn orientation. Therefore, catalysts with less sterically demanding imido groups were employed under various reaction conditions. $Mo(NAd)(CHCMe_3)(OR_{F6})_2$ and $Mo(NAr')(CHCMe_3)(OR_{F6})_2$ catalysts (Ar' = 2,6-dimethylphenyl) were tried in benzene and diethyl ether solvents (**Scheme V**). The bimetallic compound, $[Mo(NAr)(OR_{F6})]_2CH[5]'CH$ (5b), was formed by reaction of the triene (4b) with $Mo(NAr')(CHCMe_2Ph)(OR_{F6})_2$ in diethyl ether. The proton NMR corresponded entirely to that for $[Mo(NAr')(OR_{F6})]_2CH[5]CH$ (**Figure 8**). Each aryl, alkoxide, and alkylidene ligand resonance was coincident in a ratio of 2:1 versus the resonances of the linker five-membered ring triene (4b). It can be surmised that the coordination of diethyl ether slows the reaction enough to enable both equivalents of $Mo(NAr')(CHCMe_2Ph)(OR_{F6})_2$ to react and form the slightly soluble bimetallic compound in an 81% yield. In the case of $Mo(CHCMe_3)(NAd)(OR_{F6})_2$, the catalyst is too active and the formation of homometathesis products and subsequent reaction with another equivalent of catalyst is evident.

Scheme V

(5b) 81%

2 eq. [structure] + [structure] →(d₆-benzene)→ Very Messy; Multiple Alkylidene Peaks

2 eq. [structure] + [structure] →(Et₂O)→ Very Messy; Multiple Alkylidene Peaks
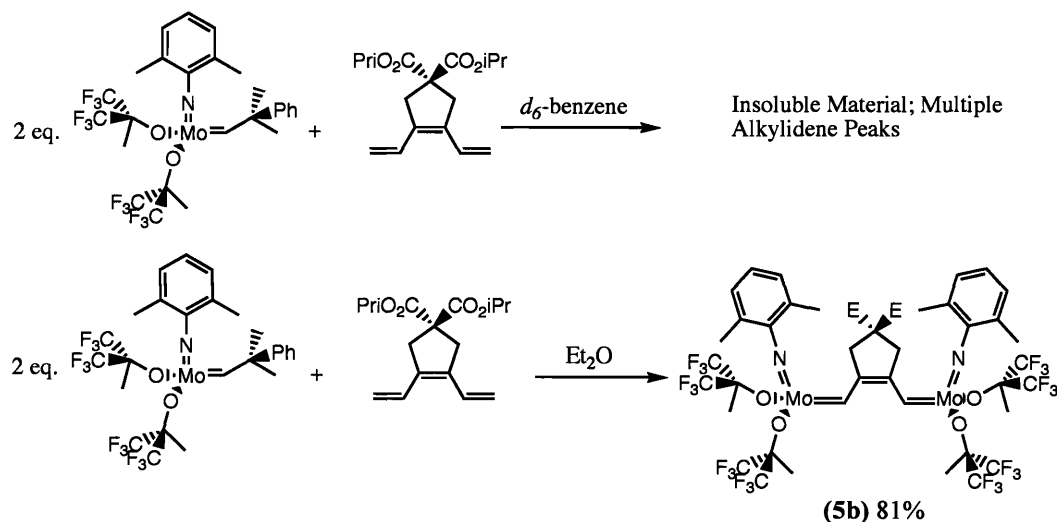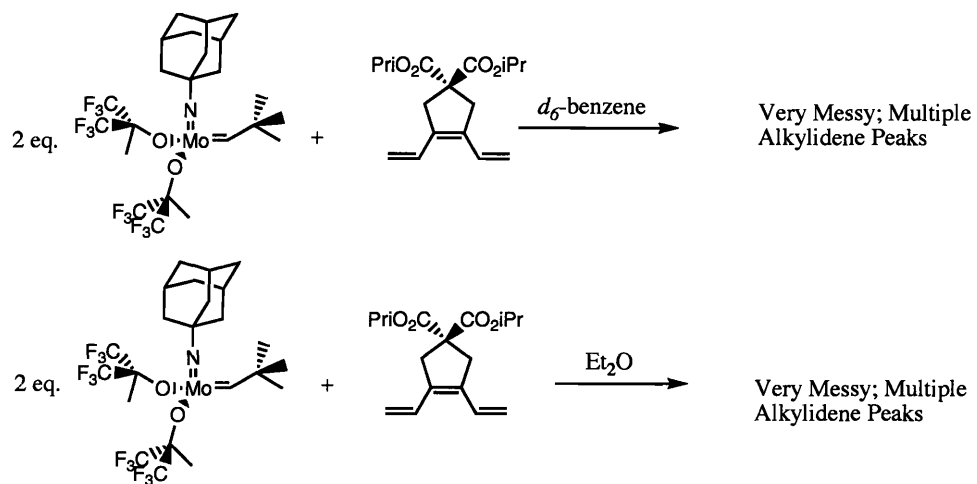
Scheme V
(cont.)

Figure 8
(^{1}H NMR of [Mo(NAr')(OR$_{F6}$)]$_2$CH[5]'CH (5b))
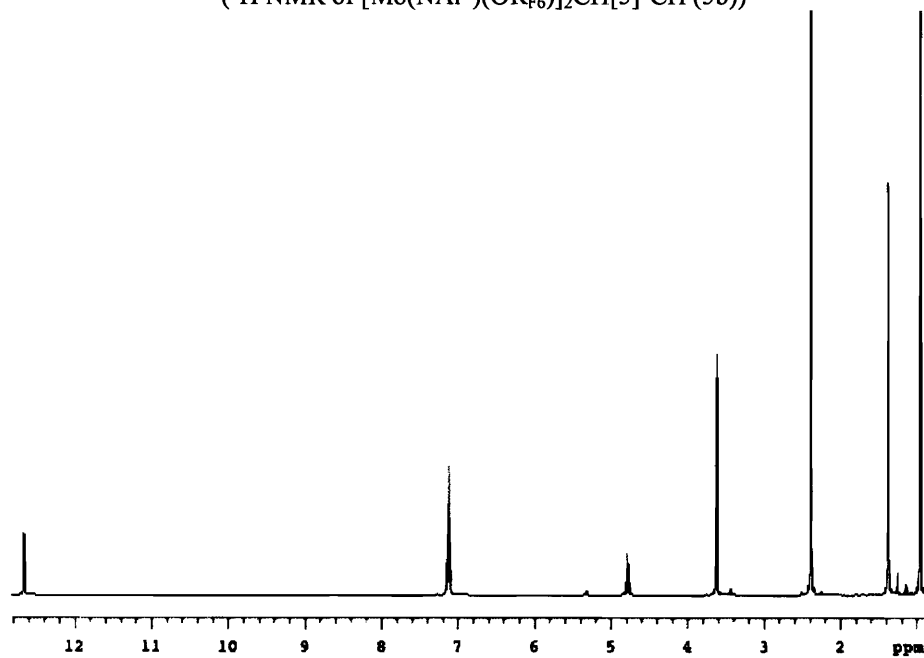
1.b. Polyene Oligomer Synthesis

Taking a look back at Scheme II, one of the compounds is a stable, α-methyl-substituted, five-membered ring aldehyde, which has been used to quench polymerization reactions in a Wittig-like fashion. As shown, the same route for aldehyde preparation works if the initial starting material is DiPrDPM or DEDPM, as used in the preparation of the successful initiator, Mo(NAr)(CH[5])[OC(CH$_3$)$_3$]$_2$(quin). [8] Each bimetallic complex, (5a) or (5b), was quenched using the corresponding alcohol, (4a) or (4b). The products, a trimeric oligomer representative of fully five-membered ring polymers (one containing ethyl ester groups and one containing isopropyl ester groups (9)), were formed via this route (**Scheme VI**). The first reaction shown here, utilizing [Mo(NAr)(OR$_{F6}$)]$_2$CH[5]CH was worked up outside of the drybox, and the trimer immediately started to decompose in air as noted by a color change from yellow to brown. Product was collected quickly enough to yield a relatively clean proton NMR. The molybdenum-oxo byproduct is most likely the secondary product that is evident by NMR. The UV-VIS spectrum exhibited a λ_{max}= 382 nm in ethyl acetate. Although this reaction yielded more decomposed than pure product, it showed that this method of making oligomeric compounds is successful and provides pure material in decent yield before workup. The bimetallic complex, [Mo(NAr)(OR$_{F6}$)]$_2$CH[5]'CH, was allowed to react with two equivalents of (8) in dichloromethane (due to limited solubility). Workup of the trimer (9) was done under a nitrogen atmosphere. Separation of the oligomer from the reaction mixture was facilitated through the use of a basic alumina plug. The reaction yielded 64% pure product with minimal workup. Both the proton and carbon NMR display resonance equivalency due to the C$_2$ axis of rotation in the highly symmetrical oligomer (**Figure 9**). Using (5b), the pentamer and heptamer were also made using aldehyde compounds provided by Constantin Czekelius (**Scheme VI**).[20]

Scheme VI

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Scheme VI (cont.)

x = 1-3
E = CO$_2$iPr

x = 1 **(8)**, x = 2 **(10)**, x = 3 **(12)**

(5b)

x = 1 **(9)**, x = 2 **(11)**, x = 3 **(13)**
64%, 82%, 79%
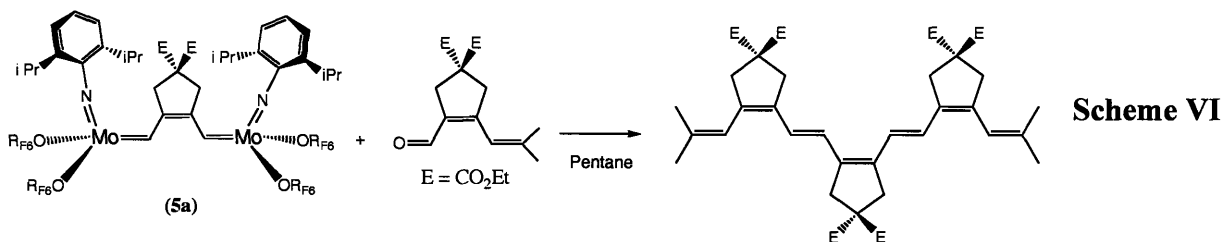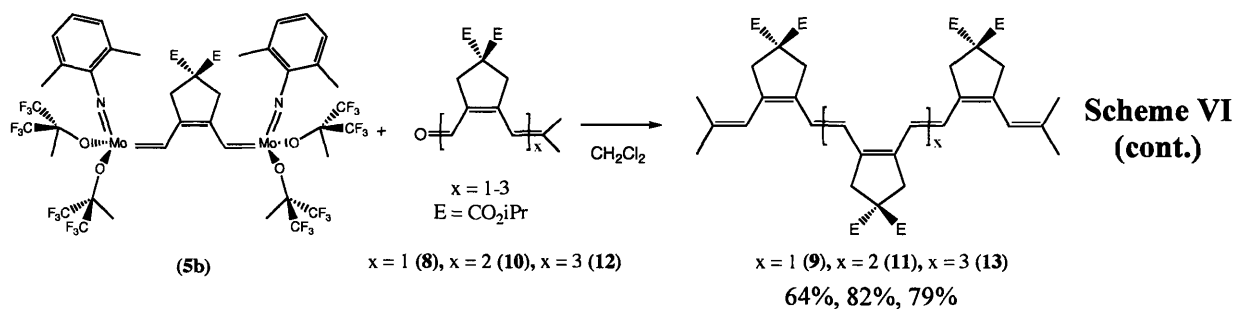
Figure 9
(^{1}H NMR of Isopropyl ester 5,5,5-membered ring trimer (9))
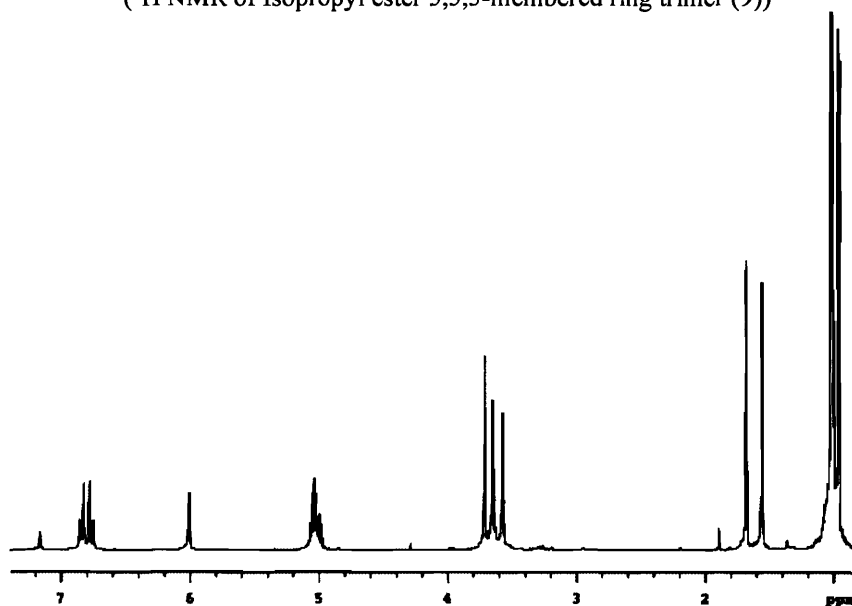
The even-numbered all five-membered ring oligomers, the dimer (18) and tetramer (20), were also made using the Wittig-like action of (8) and (12)[20] when allowed to react with a metal complex (**Scheme VII**). Here, Mo(NAr)(CH[5])[OCMe(CF$_3$)$_2$]$_2$[8] and a new compound, Mo(NAr)(CH[5]')[OCMe(CF$_3$)$_2$]$_2$, were employed. These reactions revealed yields comparable to the oligomers made using the bimetallic reactant.

Pentane

E = CO$_2$iPr

Scheme VII

(17) 71%
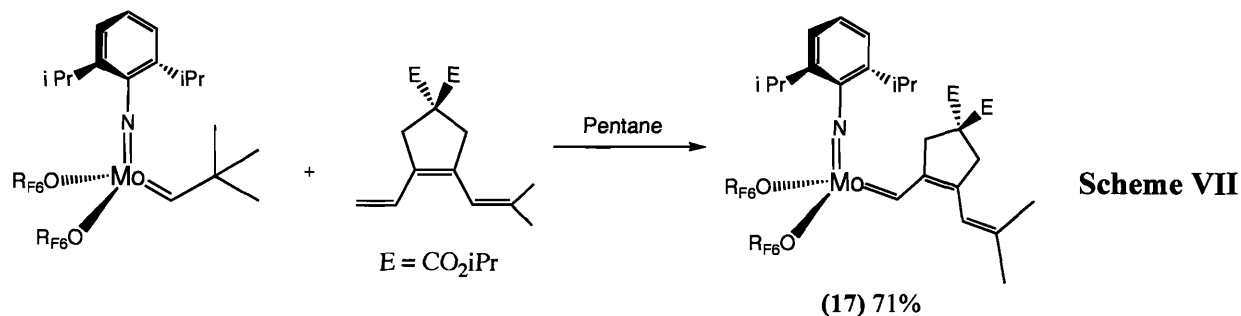
Figure 10
(Photo of trimer (9), tetramer (20), pentamer (11), heptamer (13), and 20-mer to show varying colors of resulting from increasing conjugation length)

1.c. Absorption Spectroscopy of Oligomers

Previous spectroscopic studies based on the living ring closing metathesis polymerization of DEDPM have yielded very interesting photochemical results for the conjugated polyene structure. Among the most important outcomes was the discovery by Christensen et al. of the energetically lower symmetry forbidden transition of $1^1Ag^- \rightarrow 2^1Ag^-$ relative to the strongly allowed HOMO-LUMO transition of $1^1Ag^- \rightarrow 1^1Bu^+$ symmetry.[21] The implication of the low-lying 21Ag- state is that it plays many roles in the spectroscopy and photochemistry of these molecules with respect to radiative lifetimes and nonradiative decay processes. In order to gain a better understanding of the value this information has in fields such as photobiology, it is necessary to study the specific energetics and dynamics with respect to π delocalization of the polyene system. The specific system that was studied here was based upon RCMP of DEDPM by $Mo(NAr)(CHCMe_3)(OCMe(CF_3)_2)_2$.[21] However, it is known that this catalyst, although considered living for polymerization of DEDPM with respect to PDI and M_w/M_n values, gives a mixture of five- and six membered rings within the polymer structure. Consequently, π delocalization is decreased and does not yield discrete values for each oligomer length even after separation by HPLC.

Other experiments have been done using catalysts that yield almost exclusively five-membered rings.[8,14a] After separation by prior workup to invoke solvent variances of six-membered ring containing oligomers and HPLC methods, the electronic spectrum of the shorter polyenes (2-mer through 10-mer) yielded results that could be used to further knowledge of the photochemical system.[8] Preliminary results displayed a previously described asymptotic value for the persistence of the effective conjugation length in longer polyenes where $1/N \approx 0$ (**Equation 1**) as portrayed when $1/N$ (N is the number of double bonds) is plotted against transition energy (λ_{max}).[22]

$$E = A + B/N \hspace{4cm} \textbf{Equation 1}$$

In the research done here, advantage is given due to the synthesis of each discrete oligomer length. Each pure compound is completely characterized by ^1H and ^{13}C NMR, IR, and HRMS. Of main concern in this section is the absorption spectroscopy of each length and the conclusions that can be made from this information. It should be noted that absorption values for the synthetically accessed oligomers containing isopropyl ester groups are numerically comparable to HPLC results of λ_{max} by direct UV-VIS analysis for the polymerization reaction of

26

DEDPM.[8] Using $Mo(CH[5]')(NAr)[OC(CH_3)_3]_2$ generated in situ from (17), this experiment can be repeated using DiPrDPM for direct comparison with pure oligomeric compounds.

Molar absorptivities (ε) of all oligomers synthesized here were determined in a benzene and also dichloromethane solution (**Table 1**). Due to low solubility, specifically in the even-numbered tetramer (19), approximately 0.4 mL $CDCl_3$ was used to solubilize the initial sample and diluted to approximate 0.1 μL $CDCl_3$ per 4 mL benzene. Less CH_2Cl_2 was used for the measurement of the pentamer (11). Although UV-VIS results were recorded in acetonitrile, limited solubility did not allow for the accurate measurement of absorptivity. Values for electronic transitions (**Figure 11**) were determined for all oligomers (**Table 2**) in acetonitrile (**Figure 12 and 13**), dichloromethane (**Figure 14 and 15**) and benzene (**Figure 16**). The series of UV-VIS absorptions for the oligomers synthesized by direct methods mimics the results that have been seen when a mixture of oligomers from the RCMP of DEDPM were separated by HPLC and immediately subjected to a UV-VIS detector for analysis.[8] Therefore, absorption intensities of separated oligomers from polymerization mixtures show epsilon dependence relative to each other. Here, the absorption intensities for each oligomer are not relative to each other but are of similar sample concentration.

Table 1

Values of λ_{max}, ε, and calculated conjugation length (Equation 2) for
oligomers in benzene, acetonitrile, and dichloromethane

Oligomer	Solvent	N' (π Elec-trons in Conjugation)	N (# of Double Bonds)	λ_{max} (nm) E_{0-1}	ε ($M^{-1}cm^{-1}$)	**Length (m)
Dimer (20)	C_6H_6	10	5	340	48,000	1.07×10^{-9}
Dimer (18)	C_6H_6	10	5	340	69,000	1.07×10^{-9}
Trimer (9)	C_6H_6	14	7	388	82,000	1.33×10^{-9}
Tetramer (19)	*$CHCl_3$/ C_6H_6	18	9	432	92,000	1.58×10^{-9}
Pentamer (11)	*CH_2Cl_2 /C_6H_6	22	11	458	100,000	1.79×10^{-9}
Heptamer (13)	C_6H_6	30	15	492	110,000	2.15×10^{-9}
Fc-Trimer-Fc (15)	C_6H_6	14	7	384	9,800	1.32×10^{-9}
Dimer (18)	CH_2Cl_2	10	5	356	N/A	1.09×10^{-9}
Trimer (9)	CH_2Cl_2	14	7	404	39,000	1.36×10^{-9}
Tetramer (19)	CH_2Cl_2	18	9	434	N/A	1.79×10^{-9}
Pentamer (11)	CH_2Cl_2	22	11	460	95,000	1.63×10^{-9}
Heptamer (13)	CH_2Cl_2	30	15	494	140,000	2.16×10^{-9}

Dimer (18)	CH$_3$CN	10	5	352	N/A	1.08 x 10^{-9}
Trimer (9)	CH$_3$CN	14	7	400	41,000	1.35 x 10^{-9}
Tetramer (19)	CH$_3$CN	18	9	428	N/A	1.57 x 10^{-9}
Pentamer (11)	CH$_3$CN	22	11	454	N/A	1.78 x 10^{-9}
Heptamer (13)	CH$_3$CN	30	15	486	N/A	2.14 x 10^{-9}

* Chlorinated solvent added to solubilize the compound
** Length determined by Equation 2

Figure 11

Excitation of ground state electrons into various vibrational excited states representative of the "three-finger" absorption pattern of polyene oligomers responsible for E(0-2), E(0-1) and E(0-0) transitions.
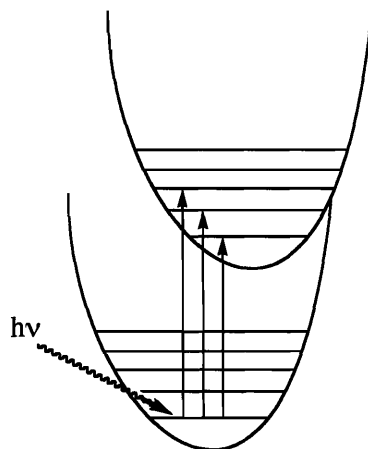
Table 2

Electronic transitions of oligomers and solvent effects

Oligomer	Solvent	E(0-2) (cm^{-1})	E(0-1) (cm^{-1})	E(0-0) (cm^{-1})
Dimer (18)	C$_6$H$_6$	29,411	29,412	N/A
Trimer (9)	C$_6$H$_6$	N/A	25,773	N/A
Tetramer (19)	*CHCl$_3$/C$_6$H$_6$	N/A	23,148	N/A
Pentamer (11)	*CH$_2$Cl$_2$/C$_6$H$_6$	N/A	21,834	20,661
Heptamer (13)	C$_6$H$_6$	21,551	20,325	19,011
Dimer (18)	CH$_2$Cl$_2$	29,411	28,090	26,810
Trimer (9)	CH$_2$Cl$_2$	25,773	24,752	23,640
Tetramer (19)	CH$_2$Cl$_2$	24,038	23,041	21,978
Pentamer (11)	CH$_2$Cl$_2$	23,041	21,739	20,661
Heptamer (13)	CH$_2$Cl$_2$	21,459	20,243	19,157
Dimer (18)	CH$_3$CN	29,762	28,409	27,100
Trimer (9)	CH$_3$CN	26,042	25,000	23,809
Tetramer (19)	CH$_3$CN	24,510	23,364	22,371
Pentamer (11)	CH$_3$CN	23,256	22,026	20,964
Heptamer (13)	CH$_3$CN	21,930	20,576	19,455

A more polar solvent shows a longer N_{eff} persistence when $1/N \approx 0$ is analyzed. Approximately parallel plots display a consistent bathochromic shift with respect to electronic transitions to various vibrational states as the length of the polymer increases. Constants, "A" and "B" of Equation 1 that are represented graphically in Figures 12 and 14 vary slightly from previously determined values for conjugated polyenes. The asymptotic value of λ_{max} for oligomers as $N \rightarrow \infty$ is seen even in this study where $N \leq 15$ (**Figure 16**).

Figure 12
Oligomer Absorbances in Acetonitrile
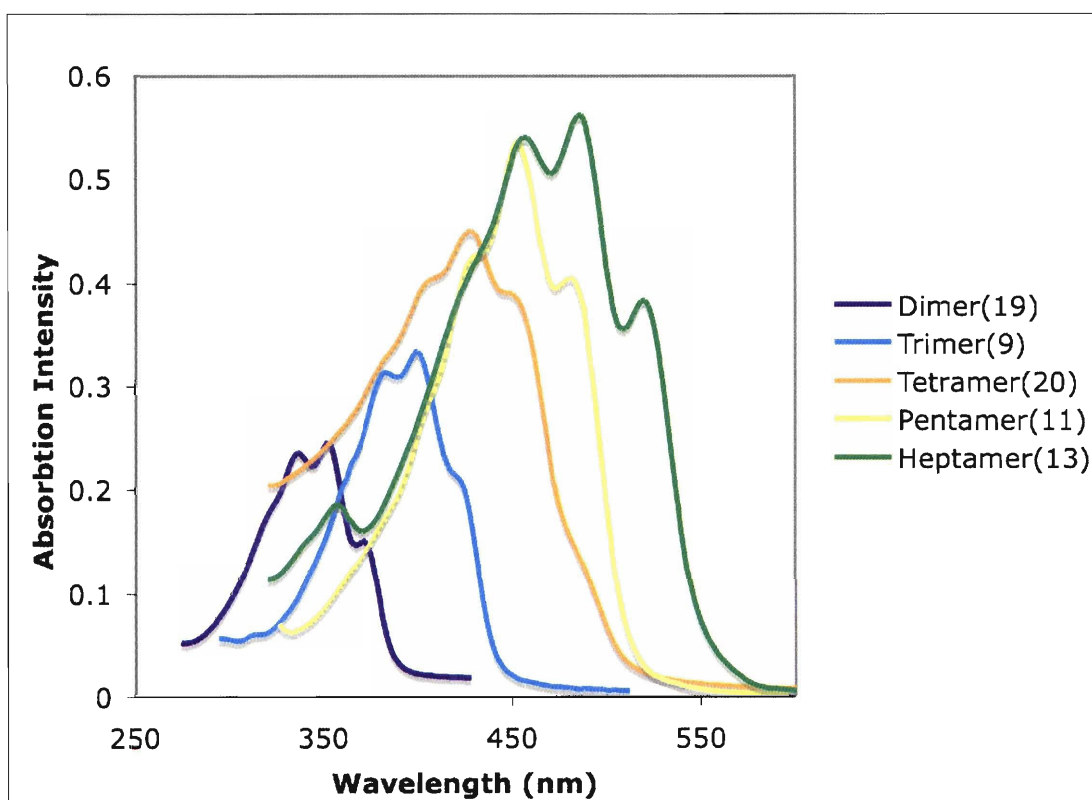
Figure 13

Electronic Transitions of Oligomers in Acetonitrile to approach 1/N = 0 (Equation 1)
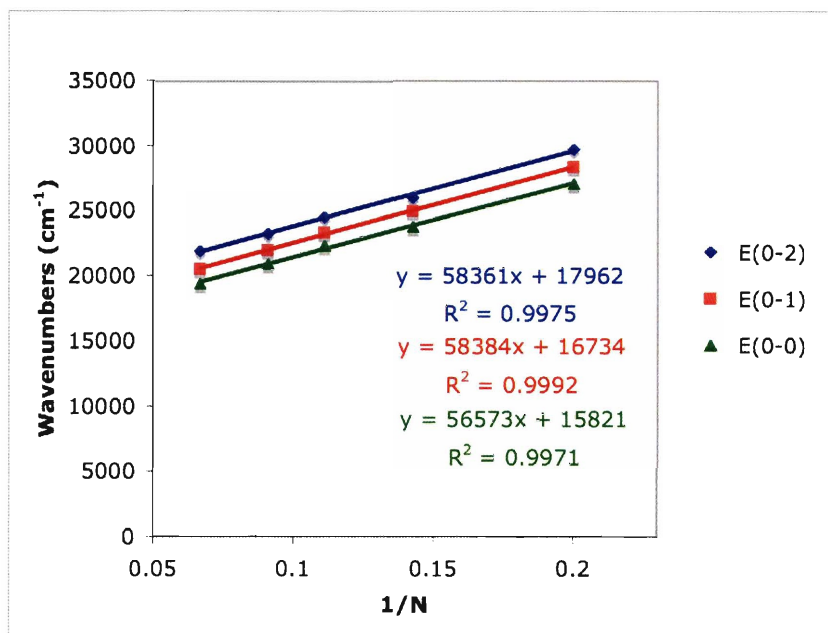
Figure 14

Oligomer Absorbances in Dichloromethane
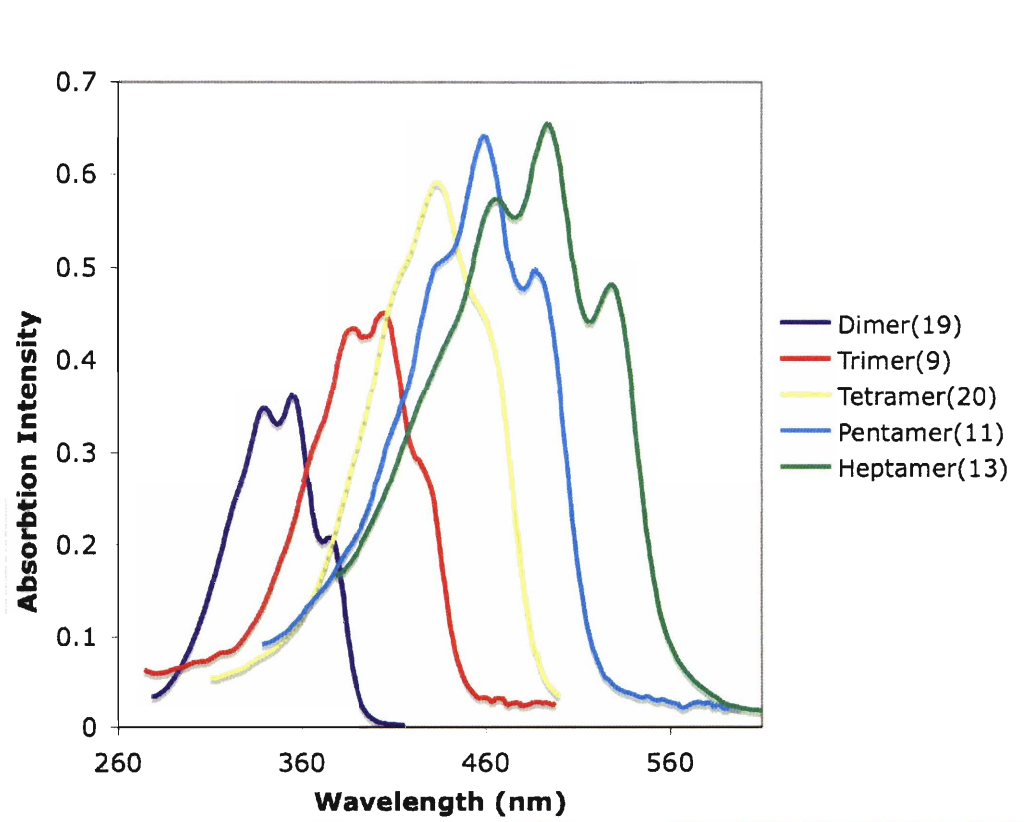
Figure 15

Electronic Transitions of Oligomers in Dichloromethane to approach $1/N = 0$ (Equation 1)
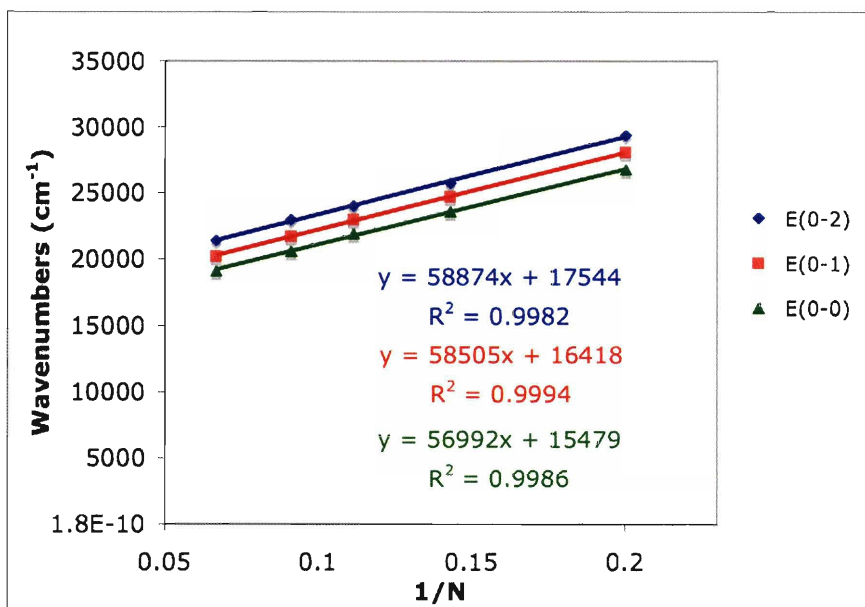
Figure 16

E(0-1) Transitions of Oligomers in Benzene to approach $1/N = 0$ (Equation 1)
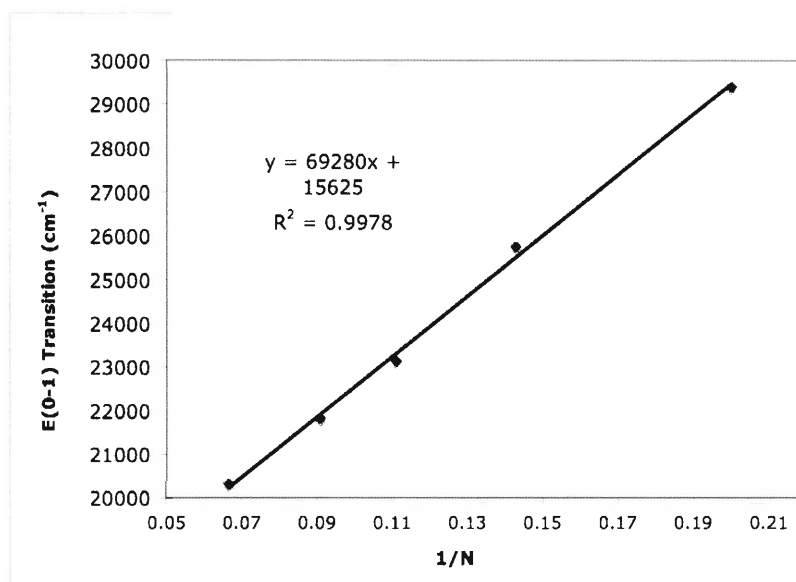
The presence of a conjugated aldehyde as in molecules (10) and (12) (**Table 3**) display bathochromic shift of λ_{max} as expected. However, molar absorptivity is lowered. The presence of ferrocene in (14) and (15) (**Table 1** and **3**) result in a blue shift of the spectrum only slightly

but a notable difference lies in the ε value, which is most likely due to two factors – a higher molecular weight per double bonds in conjugation and also the more electron rich nature of the molecule.

Table 3
Values of λ_{max}, ε, and calculated conjugation length
(Equation 2) for oligomeric aldehydes

Oligomer	Solvent	N' (π Electrons in Conjugation)	N (# of Double Bonds)	λ_{max} (nm) E_{0-1}	ε ($M^{-1}cm^{-1}$)	*Length (m)
Dimeraldehyde (10)	C_6H_6	8	3	358	32,000	1.09×10^{-9}
Timeraldehyde (12)	C_6H_6	12	5	416	42,000	1.38×10^{-9}
Fc-FMR-aldehyde (14)	C_6H_6	12	5	340	15,000	1.24×10^{-9}

The results of the UV-VIS data are represented by a linear relationship between the maximum absorption values for E(0-1) transitions versus the molar absorptivity (**Figure 17**) in two different solvents. The more polar the solvent, the steeper the slope of the line. Therefore, solvent polarity must affect the persistence as length increases. A plot of e versus N (**Figure 18**) displays the asymptotic nature of these polyene compounds.

Figure 17
Relationship between ε and λ_{max} Values for Oligomers
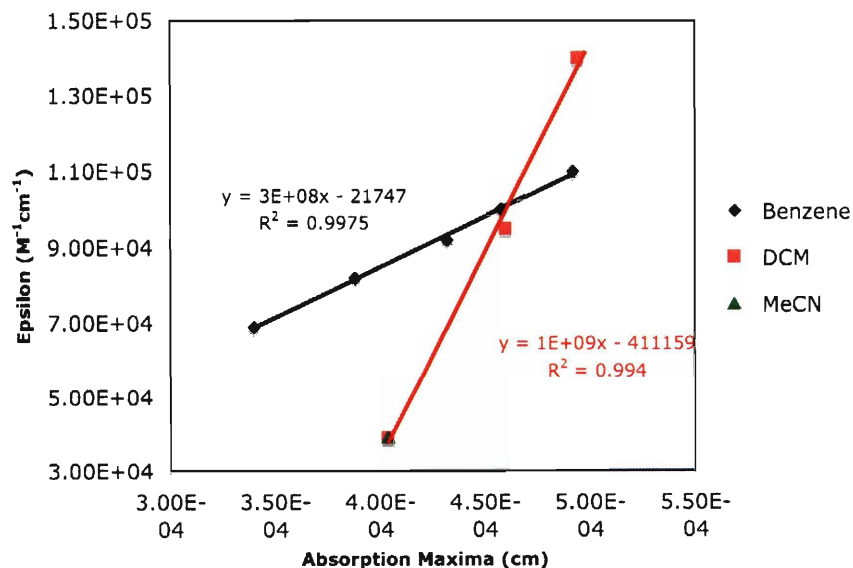
Figure 18

Relationship between Number of Double Bonds and Molar Absorptivity

$y = 37721Ln(x) + 8681.5$

$R^2 = 0.9982$
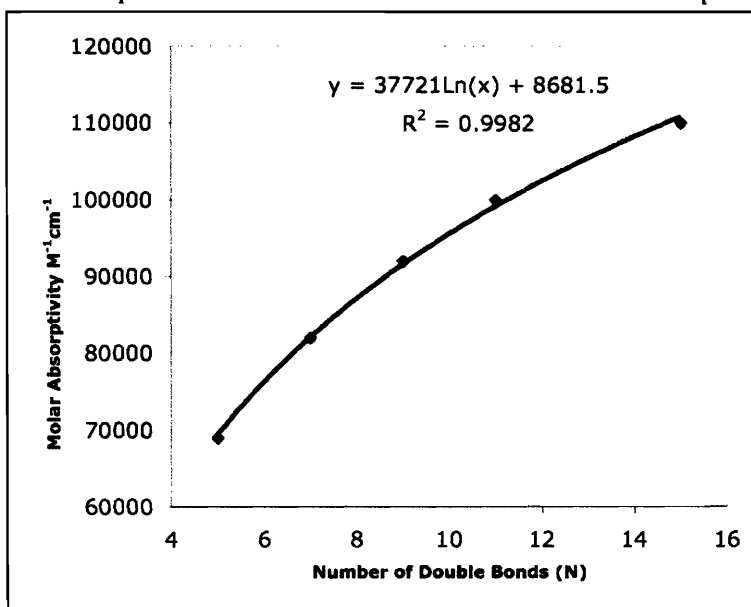
The particle in a box approximate for conjugated molecules (**Equation 2**) can be used to correlate the length and the absorption maxima (λ_{max}; E_{0-1}) where N is equal to the number of π electrons. Linear relationships are also evident for calculated conjugation length versus the number of conjugated double bonds (**Figure 19**) and epsilon values (**Figure 20**), although the latter linear relationship is a further stretch judging by the lower R^2 value.

$$L = \sqrt{\frac{\lambda h(N'+1)}{8mc}}$$

Equation 2

Figure 19

Relationship between Length and Number of Double Bonds

$y = 9E+09x - 5.1179$

$R^2 = 0.9919$
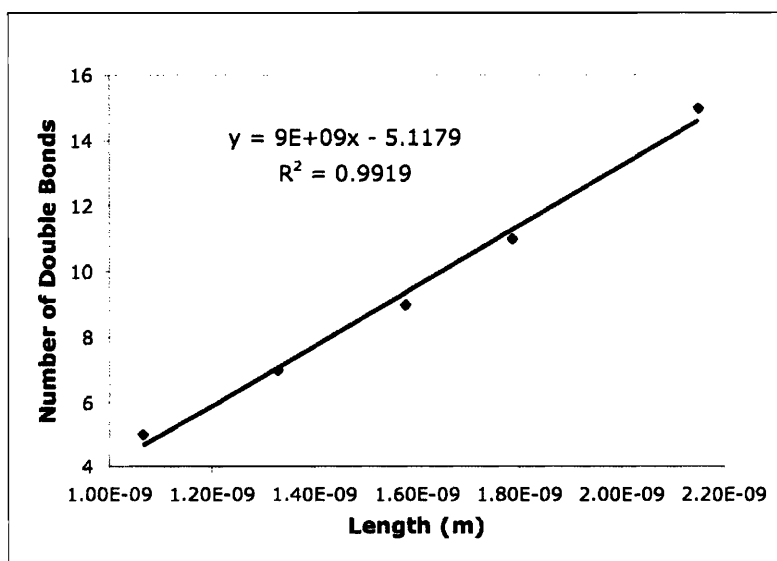
Figure 20
Relationship between Length and Epsilon value

y = 3E-12x - 8E-08
R^2 = 0.9854

Length (cm) vs ε (M^{-1}cm^{-1})
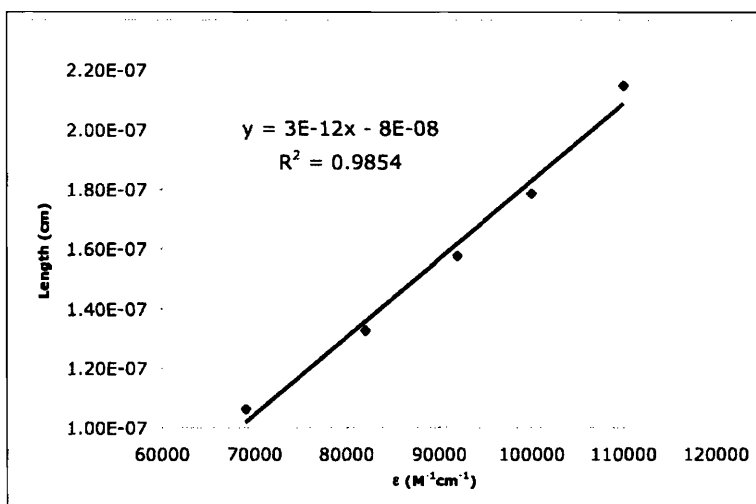
1.d. Novel Polyenes by RCM Polymerization

In an effort to determine the governing factors for the synthesis of a fully five-membered ring-containing polymer using a Schrock-type initiator, new substrates were investigated. As mentioned, DEDPM can be polymerized to yield greater than 95% five-membered ring-containing polymers using $Mo(CH[5])(NAr)[OC(CH_3)_3]_2$ or $Mo(trans-CHCHCHMe)(NAr)(OR)_2(quin)$ as the initiator.[8] In this work done by Jennifer Adamchuck as well as here, $Mo(trans-CHCHCHMe)(NAr)(OR)_2(quin)$ was used for all bulk polymerizations due to the ease of synthesis and purification.

Investigation began by modifying the steric bulk of the substrate. As a starting point, dimethyl dipropargyl malonate (DMDPM) and DiPrDPM were evaluated. It was found that poly(DiPrDPM) was comparable to poly(DEDPM). The M_n(observed)/M_n(expected), PDI, and λ_{max} values were very similar (1.25, 1.07 and 550 nm, respectively). As found by ^{13}C NMR with $Cr(acac)_3$ added as a relaxation agent,[23] the polymer contained 87% five-membered rings. These results were reproducible for a 20- and 50-mer. Poly(DMDPM), on the other hand, was almost completely insoluble. The trace amount that went into solution, which was not representative of the entire polymer, gave a multi-modal GPC trace characteristic of significant decomposition. The instability of the polymer is probably due to the loss of protection from the bulkier ester group (this same result will be seen later for an even smaller functional group at the C4 position). Due to solubility reasons, no ^{13}C NMR could be acquired, and therefore, the percentage of five-membered rings could not be accessed. The UV-VIS spectrum was indicative of the shorter chain solubility with a λ_{max} of 522 nm.

From these preliminary results, three conclusions can be drawn. By repeated experiments with $Cr(acac)_3$ as a relaxation agent, it can be determined that integration accuracy of carbon NMR is greatly increased for polyenes (**Table 4**). Secondly, as sterics substitution at the 4,4-position on the heptadiyne increase, the amount of six-membered rings increases as well. Unfortunately, as steric effects of the ester groups are decreased, solubility and protection of the polymer backbone is forfeited.

Table 4

Integration of the quaternary carbon versus carbonyl carbon of
poly(DiPrDPM) with and without $Cr(acac)_3$ as a relaxation agent

$Cr(acac)_3$?	% Quaternary Carbon	% Carbonyl Carbon	% Difference
Yes	87	92	5
No	72	89	17

In an effort to solve the steric/solubility dilemma, the ester functionality was altered. A new substrate was synthesized by the reduction of the esters to a primary alcohol functionalities and subsequent alkylation to yield 4,4-bis(ethoxymethyl)hepta-1,6-diyne (DEMDPME) (**Figure 21**).[20] Poly(DEMDPME)$_{20}$ was prepared in the drybox and workup was done under atmospheric conditions. Significant decomposition was seen by GPC analysis once again. UV-VIS analysis showed a fairly high λ_{max} of 554 nm, although this is lower than the known value for DEDPM of 591 nm.[13] This very soluble polymer yielded a clean ^{13}C NMR spectrum that seems representative of a remarkably high percentage of five-membered rings at first glance (**Figure 22**). Upon closer inspection, however, it is seen that most of the shifts, particularly that of the quaternary carbon, have a shoulder on the upfield side. These were tentatively assigned to shifts belonging to the six-membered rings along the polymer backbone. This hypothesis was confirmed when DEMDPME was reacted with Mo(NAr)(CHCMe$_3$)(OCMe(CF$_3$)$_2$), known to give a mixture of five- and six-membered rings for other 1,6-heptadiyne compounds.[5] The shifts for each ring structure are too close to integrate accurately. But it is clear that six-membered rings are present in significant quantity.

Figure 21
(4,4-Bis(ethoxymethyl)hepta-1,6-diyne (DEMDPME))
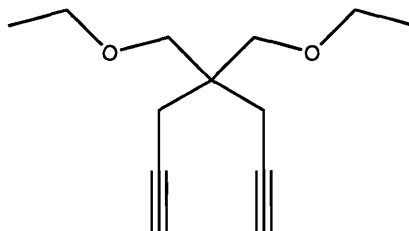
Figure 22
(^{13}C NMR spectrum of Poly(DEMDPME)$_{20}$ in CDCl$_3$)

45.2 ppm

140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
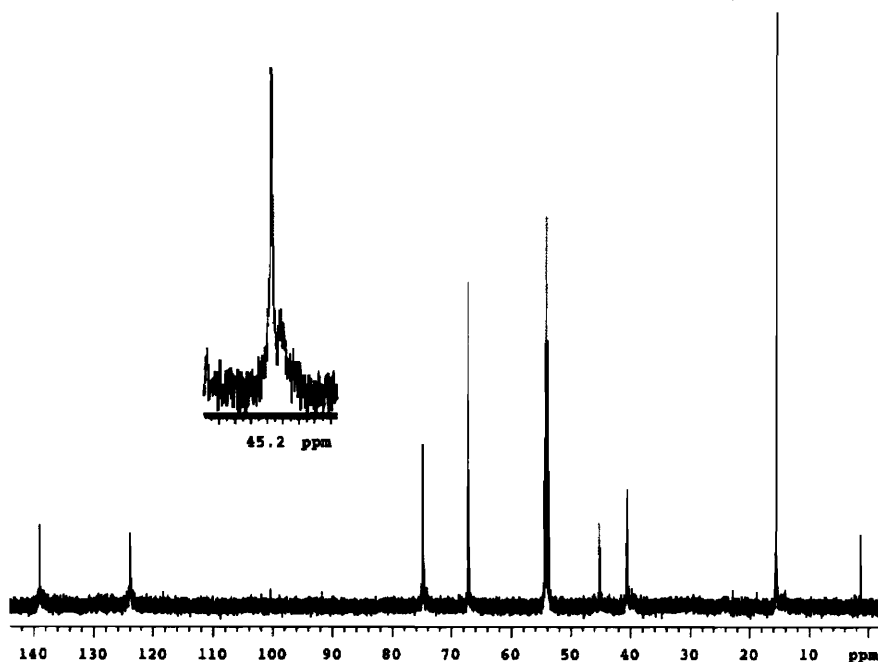
Another substrate was synthesized that would potentially give evidence to corroborate the theory stated above that the percentage of six-membered rings increases as the steric bulk of the monomer increases. The substrate made was N^1,N^1,N^3,N^3-tetraethyl-2,2-di(prop-2-ynyl)malonamide(DEDPMA) (**Figure 23**).[20] No bulk polymerization has been done using this substrate, but it is expected to proceed at a very slow pace judging from initiation studies that were done. The polymerization of 20 equivalents substrate was tracked by noting the depletion of the alkyne resonance. Up to 12 hours later, there still seemed to be active polymerization proceeding very slowly.

Figure 23
(N^1,N^1,N^3,N^3-tetraethyl-2,2-di(prop-2-ynyl)malonamide (DEDPMA))
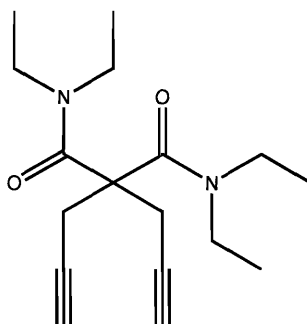
Conclusions

Odd and even chain length oligomers were made individually by a stoichiometric method. A bimetallic complex (5b) was allowed to react with two equivalents of specifically designed aldehydes[20] (8), (10), (12), and (14) to form oligomeric compounds containing an odd number of units by a Wittig-like reaction. The dimer and tetramer were made by reaction of (8) and (12), respectively, with the molybdenum complex (17). These highly conjugated polyene compounds were found to be slightly air-sensitive, but isolable in good yield when handled appropriately.

Analysis by UV-VIS gave much preliminary information concerning conjugated molecules with a fully five-membered ring containing backbone of varying lengths. Beginning with the shortest oligomers, dimers (18) and (20), the substitution at the C4 position of the five-membered ring unit was accessed. Although each compound had the same λ_{max} value, it was found that the larger ester functionality of (18) resulted in a higher ε value.. A plot of ε versus N reveals the non-asymptotic nature of molar absorptivity as N approaches infinity in the form of a logarithmic plot (however, the plot may change drastically when longer polyenes are studied; the plot will likely display an upper limit). This is in stark contrast to the limited value of λ_{max} as N approaches infinity. The fully five-membered ring oligomers with substitution by isopropyl ester groups that were assessed here, allowed for the finding of the asymptotic limit, which was found to be inversely proportional to the polarities and proportional to the increase in dielectric constants of the solvents (598 nm, 609 nm and 640 nm in acetonitrile, dichloromethane and benzene). Also, an unusual linear relationship between λ_{max} and ε is displayed by these conjugated structures, which the resulting effect is drastically changed by solvents with different dielectric constants. The trend is not fully investigated here due to limited solubility of the compounds, but it seems apparent that as the dielectric constant of the solvent increases, the ε value increases with respect to λ_{max} to give a linear plot with a steeper slope.

Although these findings may emphasize the fact that larger functional groups on the five-membered rings of analogous polymers may increase linearity and hence, optical properties, the larger groups were found to be more favorable for β-addition of the substrate and formation of six-membered rings. However, decreasing the steric bulk of the substrate does not necessarily increase the percentage of five-membered rings in a polymer since rates of polymerization and combined steric bulk also play important roles.

Experimental

General Comments. All moisture- and air-sensitive work was carried out in a Vacuum Atmosphere's glovebox or by the use of standard techniques on a dual-manifold Schlenck line (this includes all oligomer and metal complex synthesis). HPLC grade solvents (tetrahydrofuran, diethyl ether, toluene, pentane, and methylene chloride) were dried by passage through an activated alumina column under constant nitrogen flow. HPLC grade benzene was passed through Q-5 supported copper catalyst. Prior to use with sensitive metal compounds, all solvents, alcohols and organic compounds were stored over molecular sieves (4 Å). Deuterated d_6-benzene was dried over sodium and freeze-pump-thaw degassed before vacuum distillation. Deuterated d_2-methylene chloride was dried over CaH_2, freeze-pump-thaw degassed, vacuum distilled, and stored over molecular sieves for use with organometallic complexes.

Catalysts; $Mo(CHCMe_3)(NAr)(OR_{F6})_2$,[24] $Mo(CHCMe_2Ph)(NAr')(OR_{F6})$,[25] $Mo(CH[5])(NAr)(OR_{F6})_2$[8] and $RuCp(NCMe)_3PF_6$,[26] were prepared by previously reported methods (Ar = 2,6-diisopropylphenyl, Ar' = 2,6-dimethylphenyl, R_{F6} = $CMe(CF_3)_2$, CH[5] = diethyl 3-(2-methylprop-1-enyl)-4-vinylcyclopent-3-ene-1,1-dicarboxylate). The butenylidene initiator, $Mo(trans\text{-}CHCHCHMe)(NAr)(OR)_2(quin)$ (R = CMe_3) was prepared by Jennifer Adamchuck. Lithium alkoxides were prepared by the reaction of n-butyl lithium with the corresponding alcohol. Diisopropyl-3-formyl-4-(2-methylprop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate,[8] 2-(4-chloro-but-2-ynyloxy)-tetrahydro-pyran,[18] dimethyldipropargyl malonate[20] and diethyldipropargyl malonate[19] were prepared directly as described in the literature.

Unless otherwise stated, all ^{19}F NMR shifts are reported in parts per million referenced against fluorobenzene. In addition, ^1H and ^{13}C shifts are reported in parts per million referenced to residual resonances of deuterated solvents. All spectra were acquired near 22 °C. UV-VIS spectra were recorded using a Hewlett Packard 8452A Diode Array Spectrophotometer at approximately 22 °C.

Diethyl 2-(prop-2-ynyl)malonate (1a)[20]
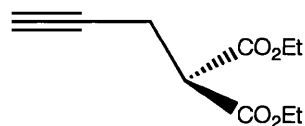
A round-bottom flask was charged with ethanol (600 mL) and NaH (60% in mineral oil, 6.32 g, 160 mmol) was stirred for 30 min until a clear solution was obtained. Neat diethyl malonate (22.8 mL, 150 mmol) was added via syringe to yield a thick slurry over 1 h. The reaction mixture was cooled to 0 °C and propargyl bromide (80% in toluene, 22.3 g, 150 mmol) was added dropwise over 80 min. After 3 h, the reaction was warmed to room temperature and allowed to stir for 18 h. Aqueous NH₄Cl was used to quench the reaction and ethanol was removed by rotary evaporation. The product was extracted with diethyl ether and dried over MgSO₄. The solvent was removed in vaccuo to yield a mixture of non-, mono-, and di-substituted diethyl malonate as quantified by ^{1}H NMR. Vacuum distillation (0.1 torr) was used to separate the three components to yield oily (1a) (13.8 g, 69.6 mmol, 47% yield).

R_f = 0.58 (6:1 hexanes/ethyl acetate). ^{1}H NMR (300 MHz, CDCl₃): δ = 3.91 (m, 4H, ^{Et}CH_2), 3.48 (t, 1H, J = 7.6 Hz, H₁), 2.77 (dd, 2H, J = 7.6, 2.7 Hz, CH_2), 1.70 (t, 1H, J = 2.7 Hz, ≡CH), 0.86 (t, 6H, J = 7.2, ^{Et}CH_3). The product was used without further purification.

Diisopropyl 2-(prop-2-ynyl)malonate (1b)
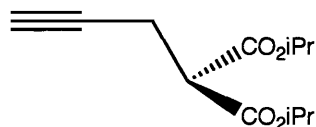
A round-bottom flask was charged with isopropanol (200 mL) and NaH (60% in mineral oil, 4.199 g, 105 mmol) and was stirred for 30 min until a clear solution was obtained. Neat diisopropyl malonate (18.99 mL, 100 mmol) was added via syringe to yield a thick slurry. The reaction mixture was cooled to 0 °C and propargyl bromide in toluene (80% in toluene, 11.14 mL, 100 mmol) was added dropwise over 45 min. After 3 h, the reaction was warmed to room temperature and allowed to stir for 12 h. Aqueous NH₄Cl was used to quench the reaction and isopropanol was removed by rotary evaporation. The product was extracted in diethyl ether and dried over MgSO₄. The solvent was removed in vaccuo to yield a mixture of non-, mono-, and di-substituted diisopropyl malonate as quantified by ^{1}H NMR. Crystalline diisopropyldipropargyl malonate was separated by vacuum filtration after standing at room temperature overnight. Vacuum distillation (0.1 torr) was used to separate the remaining two components to yield oily (1b) (9.59 g, 42.3 mmol, 42% yield).

R_f = 0.62 (6:1 hexanes/ethyl acetate). **^{1}H NMR** (300 MHz, CDCl$_3$): δ = 5.09 (septet, 2H, J = 6.3 Hz, ^{iPr}CH), 3.50 (t, 1H, J = 7.8 Hz, H$_1$), 2.76 (dd, 2H, J = 7.8, 2.7 Hz, CH_2), 2.01 (t, 1H, J = 2.7 Hz, ≡CH), 1.25 (m, 12H, ^{iPr}CH_3). The product was used without further purification.

2-(4-Hydroxy-but-2-ynyl)-2-prop-2-ynyl-malonic acid diethyl ester (2a)[20]
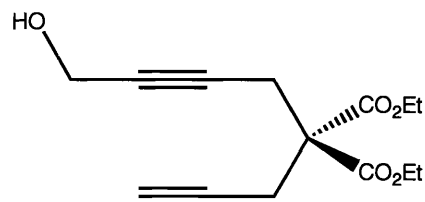
A 500 mL round-bottom flask was charged with freshly distilled (1a) (13.0 g, 65.5 mmol) and DMF (400 mL). While stirring, NaH (60% in mineral oil, 3.14 g, 78.6 mmol) was added slowly. After much effervescence, 2-(4-chloro-but-2-ynyloxy)-tetrahydro-pyran (12.4 g, 65.5 mmol) and NaI (0.98 g, 6.55 mmol) were added and the reaction was stirred for 40 h. The THP protecting group was removed with HCl (1.88 M, 600 mL) and stirred for 4 h. The organic product was extracted in diethyl ether and dried with MgSO$_4$. The solvent was removed by rotary evaporation. The product was obtained by column chromatography (silica gel, hexane/ethyl acetate, 20:1 to 5:1) (9.25 g, 34.7 mmol, 53%) as an oil.

^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 3.95 (q, 4H, J = 12 Hz, ^{Et}CH_2), 3.81 (t, 2H, J = 4 Hz, ^{OH}-CH_2), 3.37 (t, 2H, J = 4 Hz, CH_2), 3.31 (d, 2H, J = 4 Hz, CH_2), 1.70 (t, 1H, J = 4 Hz, ≡CH), 0.89 (t, 6H, J = 12 Hz, ^{Et}CH_3). **^{13}C NMR** (75 MHz, CDCl$_3$): δ = 168.8, 80.5, 79.5, 78.7, 71.9, 62.2, 56.5, 54.3, 25.5, 14.2. **IR** (cm^{-1}, CDCl$_3$) 3309, 2983, 2944, 2872 (w), 1721 (s), 1466, 1444, 1428, 1328, 1368, 1324, 1299, 1198 (s), 1159, 1118, 1076, 1055, 1027. The product was used without further purification.

2-(4-Hydroxy-but-2-ynyl)-2-prop-2-ynyl-malonic acid diisopropyl ester (2b)
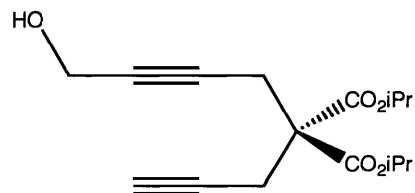
A 500 mL round-bottom flask was charged with freshly distilled (1b) (9.58 g, 42.3 mmol) and DMF (400 mL). While stirring, NaH (60% in mineral oil, 2.06 g, 51.5 mmol) was added slowly.

After much effervescence, 2-(4-chloro-but-2-ynyloxy)-tetrahydro-pyran (7.98 g, 42.3 mmol) and NaI (0.625 g, 4.23 mmol) were added and the reaction was stirred for 44 h. The THP protecting group was removed with HCl (1 M, 500 mL) and stirred for 2.5 h. The organic product was extracted in diethyl ether and dried with $MgSO_4$. The solvent was removed by rotary evaporation. The product was obtained by column chromatography (silica gel, hexane/ethyl acetate, 20:1 to 5:1) as an off-white solid (5.07 g, 17.2 mmol, 41%).

^{1}**H NMR** (500 MHz, C_6D_6): δ 5.04 (septet, 2H, J = 6 Hz, ^{iPr}CH), 4.18 (m, 2H, ^{OH}-CH_2), 3.89 (s, 2H, CH_2), 3.33 (d, 2H, J = 2.5 Hz, CH_2), 1.75 (t, 1H, J = 2.5 Hz, ≡CH) 1.00 (d, 12H, J = 6 Hz, $^{iPr}CH_3$). ^{13}**C NMR** (125 MHz, C_6D_6): δ 168.8, 83.3, 80.3, 79.4, 72.5, 69.8, 57.1, 51.2, 23.7, 23.4, 21.7. The product was used without any other purification.

3-Formyl-4-vinyl-cyclopentene-1,1-dicarboxylic acid diethyl ester (3a)[20] (Not isolated)
3,4-divinyl-cyclopentene-1,1-dicarboxylic acid diethyl ester (4a)[20]
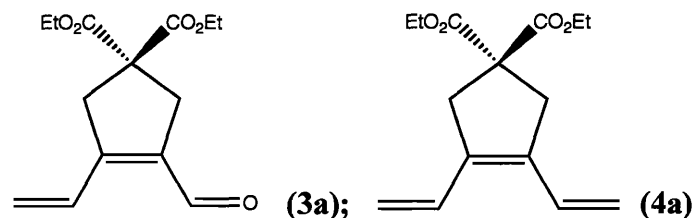
A test-tube type 50 mL teflon-stoppered Schlenck flask was charged with (2a) (1.63 g, 6.13 mmol) and dissolved in reagent-grade acetone (30 mL) and deionized water (3 mL). $RuCp(NCMe)_3PF_6$ (0.266 g, 0.606 mmol) was added. The atmosphere was charged with nitrogen, and the reaction heated to 60 °C for 1.5 h. Acetone was removed by rotary evaporation, minimal diethyl ether was added, and a NEt_3 charged silica plug was used to remove catalyst using diethyl ether as an eluent. The product was immediately used without further purification (79% crude yield).

Rf = 0.24 in 6:1 (hexane/ethyl acetate) ^{1}**H NMR** (500 MHz, C_6D_6): δ = 9.81(s, 1H, =C(O)H), 6.58 (dd, 1H, J = 10.8, 6.5 Hz, =CHR), 5.57 (m, 2H, =CH_2), 3.89 (m, 4H, $^{Et}CH_2$), 3.58 (s, 2H, CH_2), 3.37 (s, 2H, CH_2), 0.83 (t, 6H, J = 6.5 Hz). ^{13}**C NMR** (500 MHz, C_6D_6): δ = 186.1, 171.4, 152.4, 137.0, 128.7, 122.3, 61.1, 57.1, 42.2, 39.9, 14.2. **IR** (cm^{-1}, $CDCl_3$) 3904 (b, w), 2963 (b), 1729 (s), 1662 (s), 1367, 1262 (s), 1189, 1096, 1074, 1054, 1021.

A THF (45 mL) solution of triphenylphosphonium methylene bromide (0.48 g, 1.34 mmol) was cooled to -78 °C and deprotonated with n-BuLi (0.42 mL, 1.23 mmol). An immediate color

change to bright yellow persisted for the entire reaction. The yellow solution was warmed to room temperature before cooled to -78 °C and a THF (5 mL) solution of dry (3a) (0.297 g, 1.12 mmol) was added via cannula transfer. After 2 h, TLC revealed one product. Solvent was removed by rotary evaporation after the reaction was quenched with aqueous $NaHCO_3$, extracted into diethyl ether and dried with Na_2SO_4. Column chromatography (silica gel, hexane/ethyl acetate, 20:1) yielded the product (4a) (173 mg, 0.673 mmol, 14%).

Rf = .53 in 6:1 hexane/ethyl acetate. **^{1}H NMR** (500 MHz, C_6D_6): δ = 6.44 (dd, H, J = 18, 11 Hz, =CHR) 5.01 (m, 4H, =CH_2) 3.94 (m, 4H, ^{Et}CH_2), 3.47 (s, 4H, ^{ring}CH_2), 0.89 (t, 6H, J = 6.5 Hz, ^{Et}CH_3). **^{13}C NMR** (500 MHz, C_6D_6): δ = 172.1, 136.3, 132.0, 132.0, 130.0, 61.9, 57.6, 41.7, 14. **IR** (cm^{-1}) 3903 (b, w), 2984 (b, m), 2937 (b, m) 1719 (s), 1609 (w), 1375 (m), 1269 (s), 1194 (m), 1104 (m), 1068 (w). Due to product instability, further characterization was not done, and product was used directly.

3-Formyl-4-vinyl-cyclopentene-1,1-dicarboxylic acid diisopropyl ester (3b) (Not Isolated)
3,4-divinyl-cyclopentene-1,1-dicarboxylic acid diisopropyl ester (4b)
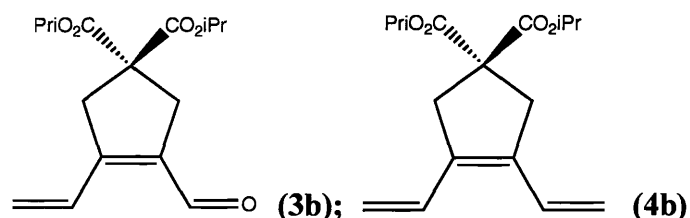
To a 100 mL Schlenck RBF was added (2b) (0.899 g, 3.04 mmol) and dissolved in reagent-grade acetone (60 mL) and deionized water (0.6 mL). RuCp(NCMe)$_3$PF$_6$ (0.162 g, 0.373 mmol) was added under nitrogen. The reaction was heated to 60 °C, and stirred for 1.5 h. Acetone was removed by rotary evaporation, minimal diethyl ether was added, and a NEt$_3$ charged silica plug was used to remove catalyst with diethyl ether as an eluent. The product was immediately used without further purification (55% crude yield).

R$_f$ = .46 (6:1 hexane/ethyl acetate). **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 10.12 (s, 1H, C(O)H), 7.18 (dd, 1H, J = 18, 11 Hz, =CHR), 5.60 (m, 2H, =CH_2), 5.03 (septet, 2H, J = 7 Hz, ^{iPr}CH), 3.39 (s, 2H, CH_2), 0.89 (t, 12H, J = 7 Hz, ^{iPr}CH_3). **^{13}C NMR** (500 MHz, C_6D_6): δ = 172.1, 136.3, 132.0, 132.0, 130.0, 61.9, 57.6, 41.7, 14.3. **IR** (cm^{-1}) 3903 (b, w), 2984 (b), 2937 (b) 1719 (s), 1609 (w), 1375, 1269 (s), 1194, 1104, 1068 (w).

A THF (150 mL) solution of triphenylphosphonium methylene iodide (0.756 g, 1.87 mmol) was cooled to -78 °C and deprotonated with *n*-BuLi (0.64 mL, 1.71 mmol). An immediate color change to bright yellow persisted for the entire reaction. The yellow solution was warmed to room temperature before cooled to -78 °C and a THF (7 mL) solution of dry (3b) (0.460 g, 1.56 mmol) was added via syringe. After 2 h, TLC revealed one product. Solvent was removed by rotary evaporation, extracted into diethyl ether, washed with water three times and dried over Na_2SO_4. Recrystallization from pentane at -40 °C yielded (4b) as a white solid (397 mg, 1.36 mmol, 73%).

R_f = 0.70 (6:1 hexane/ethyl acetate). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = 6.91 (m, 2H, =CHR), 5.32 (m, 4H, =CH_2), 5.14 (m, 2H, ^{iPr}CH), 3.31 (s, 4H, CH_2), 1.32 (d, 12H, J = 6 Hz, ^{iPr}CH_3). **^{13}C NMR** (500 MHz, CD_2Cl_2): δ = 171.8, 136.0, 129.8, 116.2, 69.6, 57.1, 41.2, 21.8. **IR** (cm^{-1}, $CDCl_3$) 3093 (b, w), 3062 (b, w), 2983 (b), 2940 (b) 1723 (s), 1608 (w), 1458, 1367, 1298, 1261 (s), 1188, 1073, 1022 (w).

[Mo(NAr)(OR$_{F6}$)]$_2$CH[5]CH (5a)

E = CO$_2$Et
R$_{F6}$ = CMe(CF$_3$)$_2$
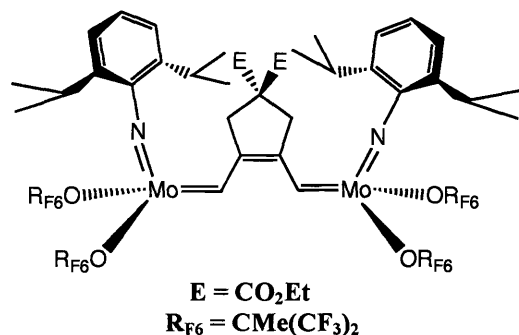
Triene (4a) (35 mg, 0.132 mmol) was dissolved in pentane (5 mL) and stored over molecular sieves (4Å) for 15 min. Pentane (5 mL) was then used to dissolve Mo(NAr)(CHCMe$_3$)(OR$_{F6}$)$_2$ (186 mg, 0.265 mmol). The triene solution was slowly added to the catalyst solution and stirred for 4 h. The solution was then concentrated and stored at -40 °C yielding x-ray quality crystalline material. Two crops of crystals were collected (124 mg, 0.082 mmol, 62%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 12.65 (s, 2H, J_{CH} = 125 Hz, Mo=CHR), 7.28 (t, 2H, J = 7.5 Hz, *p*-Ar), 7.17 (d, 4H, J = 7.5 Hz, *m*-Ar), 3.84 (q, 4H, J = 7 Hz, ^{Et}CH_2), 3.60 (s, 4H, ^{ring}CH_2), 3.47 (septet, 4H, J = 7 Hz, ^{iPr}CH), 1.39 (s, 12H, OR$_{F6}$) 1.17 (d, 24H, J = 7 Hz, ^{iPr}CH_3), 0.93 (t, 6H, J = 7 Hz, ^{Et}CH_3). **^{13}C NMR** (125 Hz, CD_2Cl_2). **^{19}F NMR** (282 MHz, C_6D_6): δ -78.19 (s, broad), -78.36 (s, broad).

[Mo(NAr')(OR$_{F6}$)]$_2$CH[5]'CH (5b)

E = CO$_2$iPr
R$_{F6}$ = CMe(CF$_3$)$_2$
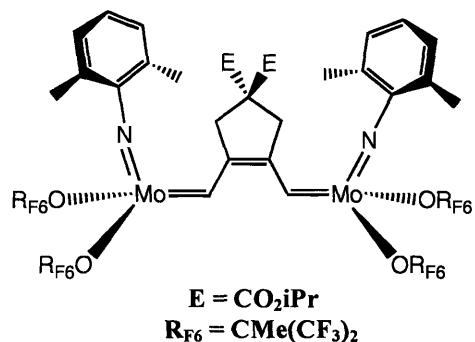
A 50 mL round-bottom flask was charged with Mo(NAr')(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ (609 mg, 0.858 mmol), which was subsequently dissolved in diethyl ether (12 mL). Triene (4b) (125 mg, 0.429 mmol) was dissolved in diethyl ether (8 mL) and stored over molecular sieves (4Å) for 30 min, after which it was slowly added to the catalyst solution and stirred for 18 h. Solvent was removed in vaccuo and redissolved in pentane/diethyl ether (15:0.7 mL). Storage at -40 °C yielded pure crystalline material (2 crops, 494 mg, 0.348 mmol, 81%).

^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 12.66 (s, 2H, J_{CH} = 128 Hz, Mo=CHR), 7.13 (m, 6H, Ar'), 4.78 (septet, 2H, J = 6.5 Hz, ^{iPr}CH), 3.62 (s, 4H, ^{ring}CH_2), 2.39 (s, 12H, $^{Ar'}$CH_3), 0.96 (d, 12H, J = 6.5 Hz, ^{iPr}CH_3). ^{13}C NMR (125 MHz, CD$_2$Cl$_2$): δ 170.9, 157.5, 138.1, 133.1, 129.8, 128.5, 124.2 (qd, J_{CF} = 286, 26.9 Hz), 81.9 (septet, J_{CF} = 26.9 Hz, 69.3, 56.7, 45.1, 30.2, 21.6, 19.4. ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): δ -78.06 (s, broad), -78.39 (s, broad). **Anal.** Calcd. for C$_{47}$H$_{50}$N$_2$F$_{24}$Mo$_2$O$_8$; C, 39.79; H, 3.55; N, 1.97. Found C, 39.72; H, 3.51, N, 1.96.

Diisopropyldipropargyl Malonate (6)[20]
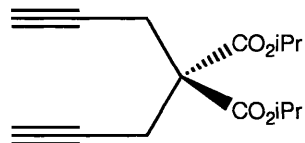
Provided by Constantin Czekelius.

Diisopropyl-2-(4-hydroxy-4-methylpen-2-enyl)-2-(prop-2-ynyl)malonate (7)

45
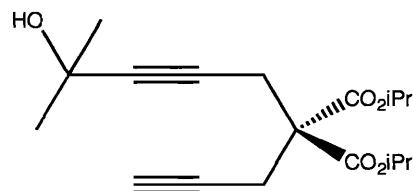
An oven-dried 3-neck 500 mL round-bottom flask equipped with an addition funnel, nitrogen inlet, and septum was cooled under vacuum, diisopropyldipropargyl malonate (11.83 g, 47.3 mmol) was added and dried for 30 min in vaccuo. Dry THF (200 mL) was cannula-transferred to the reaction flask and stirred until completely dissolve (6). The reaction was cooled to -78 °C. LiHMDS (1.0 M in THF, 47.3 mL, 47.3 mmol) was added dropwise to the reaction over 15 min (temperature rose to -60 °C). The reaction was allowed to stir for 1 h. Dry acetone (3.5 mL; stored over molecular sieves for two weeks) was transferred via syringe and stirred for another 2 h at -78 °C. The reaction was slowly warmed to room temperature, and quenched with aqueous NH_4Cl. THF was removed by rotary evaporation. The organic product was extracted with diethyl ether and dried over $MgSO_4$. The product was purified by silica gel column chromatography (silica gel, hexane/ethyl acetate, 6:1) to yield 3.515 g (6) and product (7) (8.18 g, 26.5 mmol, 80%).

*Characterized fully by Constantin Czekelius[20]

Diisopropyl-3-formyl-4-(2-methylprop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate (8)
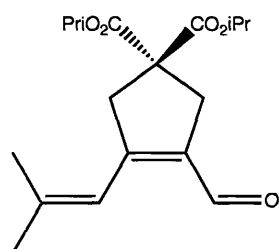
A test-tube type Teflon stoppered 250 mL Schlenck flask was charged with (7) (7.98 g, 25.9 mmol) and dissolved in acetone (200 mL). Deionized water (0.6 mL) was added via syringe. Subsequently, $RuCp(NCMe)_3PF_6$ (1.12 g, 2.58 mmol) was added and allowed to react for 2 h. Volatiles were removed by rotary evaporation, the residue dissolved in diethyl ether (5 mL) and a NEt_3 charged silica plug was used to remove catalyst using diethyl ether as an eluent. The solvent was removed and purification by silica gel column chromatography (hexane/ethyl acetate, 20:1) yielded (8) (5.10 g, 16.5 mmol, 64%).

^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.87 (s, 1H, C(O)H), 6.26 (s, 1H, =CHR), 5.05 (septet, 2H, J = 6.3 Hz, ^{iPr}CH), 3.38 (s, 2H, ^{ring}CH_2), 3.22 (s, 2H, ^{ring}CH_2), 1.92 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 1.24 (d, 12H, J = 6.3 Hz, ^{iPr}CH_3). Characterized fully by Constantin Czekelius.[20]

Di-1,2-[1-(*E*)-(2-Methyl-propenyl)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-enyl]-vinyl)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-ene (9)
(Trimer)

E = CO₂iPr
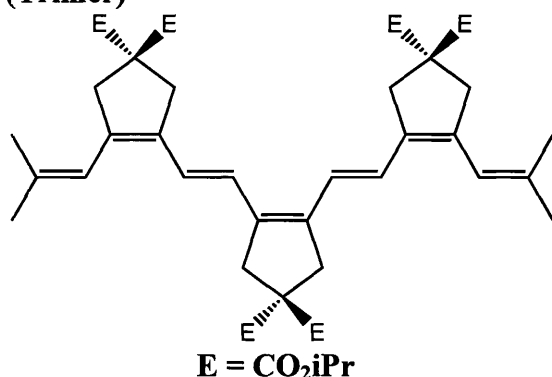
Recrystallized and dried (8) (35.4 mg, 0.115 mmol) was dissolved in dichloromethane (2 mL), stored over molecular sieves (4Å) for 30 min and added to a solution of (5b) (81.4 mg, 0.057 mmol) in dichloromethane (3 mL). The reaction was stirred vigorously for three hours to note an initial darkening in color to a brownish-yellow solution. The solvent was removed in vaccuo and the residue dissolved in diethyl ether for elution through an activated basic alumina plug. The product was obtained as a yellowish solid (32 mg, 0.037 mmol, 64%). The UV-VIS spectrum was taken using a 7.6 x 10^{-6} M solution in benzene and 7.6 x 10^{-6} M solution in dichloromethane. **¹H NMR** (500 MHz, C_6D_6): δ = 6.79 (dd, 4H, *J* = 38.5, 15.5 Hz, =C*H*), 6.00 (s, 2H, Me₂=C*H*R), 5.04 (septet, 4H, *J* = 6 Hz, ^{iPr}C*H*), 5.01 (septet, 2H, *J* = 6.5 Hz, ^{iPr}C*H*), 3.71 (s, 2H, C*H*₂), 3.65 (s, 2H, C*H*₂), 3.57 (s, 2H, C*H*₂), 1.68 (s, 6H, C*H*₃), 1.55 (s, 6H, C*H*₃), 1.01 (m, 24H, ^{iPr}C*H*₃), 0.97 (d, 12H, *J* = 6 Hz, ^{iPr}C*H*₃). **¹³C NMR** (125 MHz, C_6D_6): δ = 171.8, 171.7, 137.7, 137.4, 136.7, 134.6, 125.6, 122.9, 120.5, 69.3, 69.1, 58.7, 58.0, 45.8, 42.3, 40.9, 27.6, 21.8, 20.8 . **IR** (cm⁻¹, CDCl₃) 2983, 2936(w), 1722(s), 1467, 1376, 1262(s), 1196, 1104(s), 1068. **HRMS** (EI, [M]⁺). Calc'd for $C_{51}H_{72}O_{12}$: 876.5018: Found: 876.4996. λ_{max} = 388 nm, 404 nm; ε = 8.2 x 10^4 cm⁻¹M⁻¹, 4.4 x 10^4 cm⁻¹M⁻¹ in benzene and dichloromethane, respectively.

2-{(*E*)-2-[2-(2-Methyl-propenyl)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-enyl]-vinyl}-4,4- di-*iso*-propyl-carboxy -cyclopent-1-enecarbaldehyde (10)[20]
(Dimeraldehyde)

47
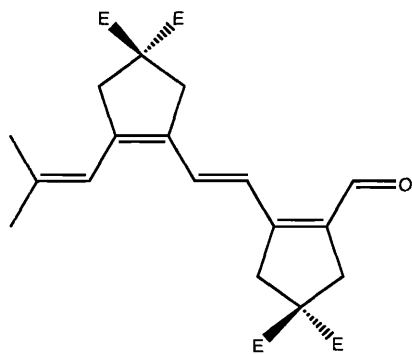
E = CO₂iPr

¹H NMR (500 MHz, C₆D₆): δ = 9.79 (s, 1H, =C(O)*H*), 6.76 (q, 2H, *J* = 15.5 Hz, RC*H* =C*H*R), 5.89 (s, 1H, =C*H*R), 5.05 (sept, 2H, *J* = 6 Hz, ^{iPr}C*H*), 4.93 (sept, 2H, *J* = 6 Hz, , ^{iPr}C*H*), 3.64 (s, 2H, ^{ring}C*H₂*), 3.60 (s, 2H, ^{ring}C*H₂*), 3.57 (s, 2H, ^{ring}C*H₂*), 3.48 (s, 2H, ^{ring}C*H₂*), 1.61 (s, 3H, C*H₃*), 1.51 (s, 3H, C*H₃*), 1.04 (m, 12H, ^{iPr}C*H₃*), 0.93 (m, 12H, ^{iPr}C*H₃*). **¹³C NMR** (125 MHz, C₆D₆): δ = 186.1, 186.0, 171.6, 171.1, 152.8, 141.7, 139.2, 136.4, 133.8, 130.8, 120.5, 120.0, 69.5 (m), 58.5, 57.4, 45.8, 42.4, 40.8, 40.1, 27.6, 21.9 (m), 21.7 (m), 20.8. **IR** (cm⁻¹, CDCl₃) 2984, 2938 (w), 1720 (s), 1654, 1597, 1467, 1376, 1267 (s), 1196, 1104 (s), 1069. **HRMS** (EI, [M]⁺). Calc'd for C₃₃H₄₆O₉: 586.3136: Found: 586.3250. λ_{max} = 358 nm; ε = 3.2 x 10⁴ cm⁻¹M⁻¹ in a 1.8 x 10⁻⁵ M benzene solution.

Di-1,2-[{1-(*E*)-(2-Methyl-propenyl)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-enyl]-vinyl}-1-(*E*)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-enyl]-vinyl)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-ene (11)
(Pentamer)
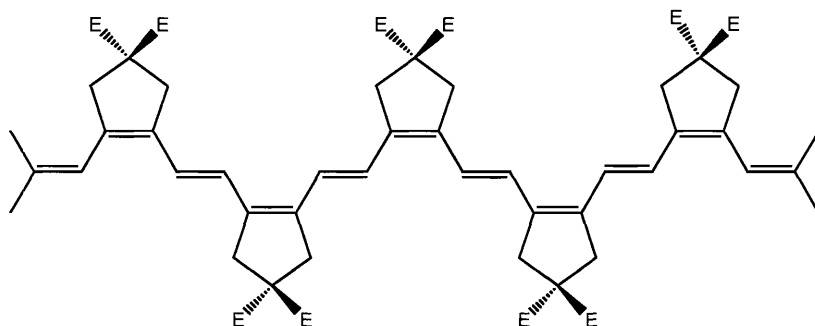
E = CO₂iPr

Recrystallized and dried dimeraldehyde (10) (78 mg, 0.123 mmol) was dissolved in dichloromethane (2 mL), stored over molecular sieves (4Å) for 30 min and added to a solution of (5b) (94 mg, 0.066 mmol) in dichloromethane (4 mL). The reaction was stirred vigorously for 3

h. Solvent was removed en vaccuo and eluted through an activated basic alumina plug with diethyl ether/tetrahydrofuran (2:1) and benzene to give (11) (76 mg, 0.054 mmol, 82%) as an orange solid. The UV-VIS spectrum was taken using a 7.4 x 10^{-6} M solution in benzene and 6.8 x 10^{-6} M solution in dichloromethane.

^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ = 7.00 (s, 4H, =CHR), 6.61 (d, 2H, J = 15.5 Hz, RCH =CHR), 6.49 (d, 2H, J = 15.5 Hz, RCH =CHR), 6.05 (s, 2H, =CHR), 5.02 (m, 10H, ^{iPr}CH), 3.33 (m, 8H, ^{ring}CH_2), 3.29 (m, 8H, ^{ring}CH_2), 3.21 (s, 4H, ^{ring}CH_2), 1.88 (s, 6H, CH_3), 1.81 (s, 6H, CH_3), 1.23 (m, 60H, ^{iPr}CH_3). ^{13}C NMR (500 MHz, CD$_2$Cl$_2$): δ = 171.9, 171.8, 138.0, 137.8, 137.7, 137.3, 136.3, 134.2, 125.5, 123.7, 123.3, 122.0, 119.6, 69.7, 69.6, 58.3, 57.5, 57.4, 45.0, 41.9, 41.7, 40.3, 27.9, 23.9 (m), 20.8. IR (cm^{-1}, CDCl$_3$) 3041 (w), 2984, 2938 (w), 1722 (s), 1467, 1454, 1376, 1270, 1197, 1105, 1068. HRMS (ESI, [M+Na]$^+$). Calc'd for C$_{81}$H$_{112}$O$_{20}$Na: 1427.7639: Found: 1428.7645. λ_{max} = 458 nm, 460 nm; ε = 1.0 x 10^5 cm^{-1}M^{-1}, 9.5 x 10^4 cm^{-1}M^{-1} in benzene and dichloromethane, respectively.

2-{{2-(E)-2-[2-(2-Methyl-propenyl)-4,4-di-iso-propyl-carboxy-cyclopent-1-enyl]-vinyl}-2-(E)-4,4-di-iso-propyl-carboxy-cyclopent-1-enyl]-vinyl}-4,4- di-iso-propyl-carboxy -cyclopent-1-enecarbaldehyde (12)[20]
(Trimeraldehyde)
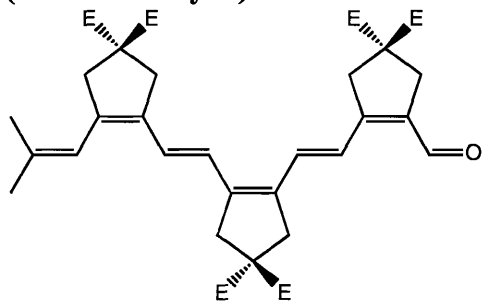
E = CO$_2$iPr

^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ = 10.18 (s, 1H, =C(O)H), 7.03 (s, 2H, =CHR), 6.61 (s, 2H, =CHR), 6.07 (s, 1H, =CHR), 5.03 (sept, 6H, J = 6.5 Hz, ^{iPr}CH), 3.51 (s, 2H, ^{ring}CH_2), 3.26 (m, 10H, ^{ring}CH_2), 1.90 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.23 (m, 36H, ^{iPr}CH_3). ^{13}C NMR (125 MHz, CD$_2$Cl$_2$): δ = 186.9, 171.9, 171.6, 171.2, 154.0, 141.9, 139.3, 138.7, 136.2, 135.1, 133.9, 129.6, 127.2, 121.4, 120.8, 119.5, 80.7, 70.0, 69.9, 69.6, 58.3, 57.3, 57.1, 45.1, 42.4, 41.9, 41.4, 40.3, 39.4, 27.9, 21.8 (m), 20.8. IR (cm^{-1}, CDCl$_3$) 2981, 2936, 2874, 1723 (s), 1653, 1571, 1454,

1376, 1265 (s), 1196, 1107 (s). **HRMS** (EI, $[M]^+$). Calc'd for $C_{48}H_{66}O_{13}$: 850.4498: Found: 850.4477. λ_{max} = 416 nm; ϵ = 4.3 x 10^4 cm^{-1}M^{-1}.

Di-1,2-[(1-(E)-(2-Methyl-propenyl)-4,4-di-iso-propyl-carboxy-cyclopent-1-enyl]-vinyl)-{1-(E)-(2-Methyl-propenyl)-4,4-di-iso-propyl-carboxy-cyclopent-1-enyl]-vinyl}-1-(E)-4,4-di-iso-propyl-carboxy-cyclopent-1-enyl]-vinyl)-4,4-di-iso-propyl-carboxy-cyclopent-1-ene (13) (Heptamer)
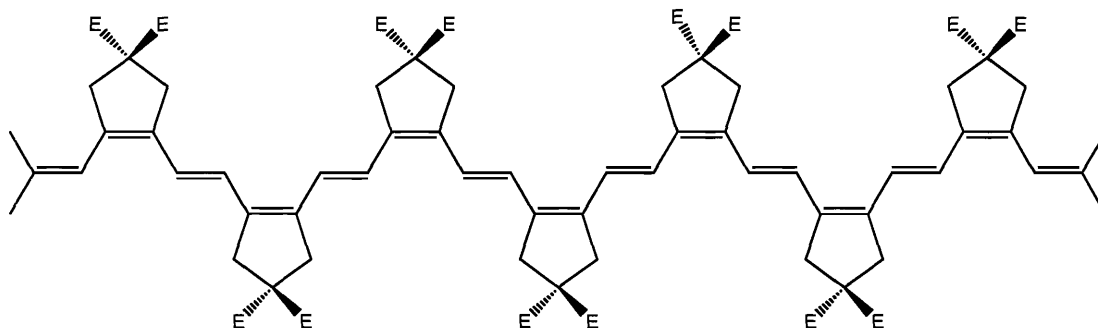
E = CO₂iPr

Recrystallized and dried trimeric five-membered ring aldehyde (12) (253 mg, 0.297 mmol) was dissolved in dichloromethane 7 mL, stored over molecular sieves (4Å) for 45 minutes and added to a solution of (5b) (211 mg, 0.149 mmol) in dichloromethane (3 mL). The reaction was stirred vigorously for 4 h. The solvent was removed in vaccuo and eluted through an activated basic alumina plug with diethyl ether/tetrahydrofuran (6:1) and benzene to yield (226 mg, 0.117 mmol, 78.5%) (13) as a reddish solid. The UV-VIS spectrum was taken using a 2.9 x 10^{-6} M solution in benzene and 4.1 x 10^{-6} M solution in dichloromethane.

¹H NMR (500 MHz, C_6D_6): δ = 6.73 (s, 4H, =CHR), 6.715 (s, 4H, =CHR), 6.64 (s, 1H, =CHR), 6.59 (s, 1H, =CHR), 6.53 (s, 1H, =CHR), 6.48 (s, 1H, =CHR), 6.07 (s, 2H, =CHR), 5.03 (m, 14H, ^{iPr}CH) 3.30 (m, 28H, $^{ring}CH_2$), 1.89 (s, 6H, CH_3), 1.82 (s, 6H, CH_3) 1.24 (m, 84H, $^{iPr}CH_3$).
¹³C NMR (125 MHz, C_6D_6): δ = 171.9, 171.8, 138.0, 137.9, 137.8, 137.7, 137.71, 137.5, 136.7, 134.5, 125.9, 124.2, 124.1, 123.7, 122.6, 120.3, 118.4, 69.5, 69.3, 58.6, 57.9, 45.6, 42.2, 42.12, 42.1, 40.8, 27.7, 21.92, 21.91, 21.90, 21.89, 21.86, 20.8. **IR** (CDCl₃, cm^{-1}) 3042 (w), 2984, 2938, 2865 (w), 1723 (s), 1466, 1371, 1262 (s), 1195, 1105 (s), 1068. **HRMS** (ESI, $[M+Na]^+$). Calc'd for $C_{111}H_{152}O_{28}$: 1956.0362: Found: 1956.0392. λ_{max} = 492 nm, 494 nm; ϵ = 1.1 x 10^5 cm^{-1}M^{-1}, 1.4 x 10^5 cm^{-1}M^{-1}.

Diisopropyl-3-formyl-4-(2-ferrocenylprop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate (14)[20]

(Fc-FMR-aldehyde)

E = CO$_2$iPr
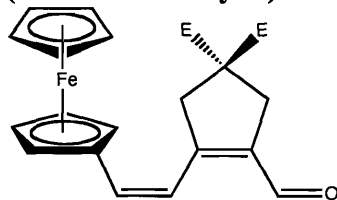
^{1}**H NMR** (500 MHz, C$_6$D$_6$): δ = 10.08 (s, 1H, =C(O)H), 7.04 (d, 1H, J = 16 Hz, =CHR), 6.51 (d, 1H, J = 16Hz, =CHR), 4.98 (sept, 2H, J = 6 Hz, ^{iPr}CH), 4.20 (s, 2H, Cp), 4.12 (s, 2H, Cp), 3.93 (s, 5H, Cp) 3.67 (s, 2H, ^{ring}CH_2), 3.62 (s, 2H, ^{ring}CH_2), 1.00 (d, 6H, J = 6 Hz, ^{iPr}CH_3), 0.95 (d, 6H, J = 6 Hz, ^{iPr}CH_3). ^{13}**C NMR** (125 MHz, C$_6$D$_6$): δ = 186.0, 171.2, 153.2, 137.7, 134.2, 117.4, 82.0, 70.9, 70.2, 69.6, 68.5, 57.6, 42.8, 40.0, 21.8, 21.7. **IR** (CDCl$_3$, cm^{-1}) 2984, 2938 (w), 1724 (s), 1655, 1609 (s), 1376 (w), 1270 (s), 1196, 1106 (s). λ_{max} = 340 nm; ε = 1.5 x 10^4 cm^{-1}M^{-1}.

Di-1,2-[1-(E)-(2-ferrocenyl-propenyl)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-enyl]-vinyl)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-ene (15)
(Fc-capped Trimer)

E = CO$_2$iPr
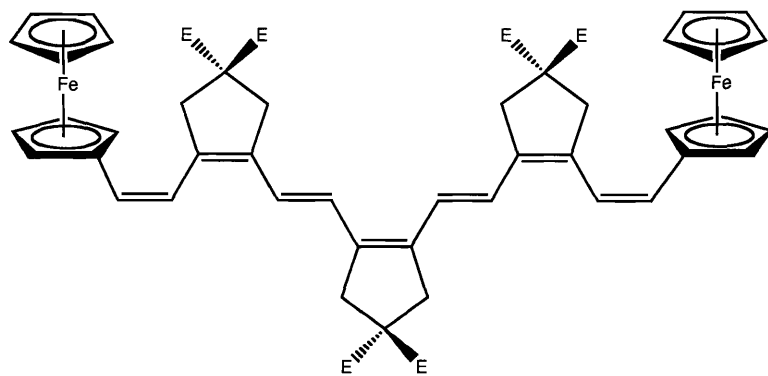
Fc-FMR-aldehyde (14) (95.2 mg, 0.199 mmol) was dissolved in dichloromethane (3 mL), stored over molecular sieves (4Å) for 45 min, and added to a solution of (5b) (141 mg, 0.099 mmol) in dichloromethane (3 mL). The reaction was stirred vigorously for 3 h. The solvent was removed in vaccuo and eluted through an activated basic alumina plug with diethyl ether to give (28 mg, 0.024 mmol, 24%) of a reddish powder. The UV-VIS spectrum was taken using a 3.5 x 10^{-5} M solution in benzene.

^{1}**H NMR** (500 MHz, C$_6$D$_6$): δ = 6.99 (m, 4H, =CHR), 6.87 (m, 2H, =CHR), 6.39 (m, 2H, =CHR), 5.05 (m, 6H, ^{iPr}CH), 4.17 (s, 4H, Cp), 4.07 (s, 4H, Cp), 3.95 (s, 10H, Cp), 3.68 (m, 12H,

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$^{ring}CH_2$), 1.04 (m, 24H, $^{iPr}CH_3$), 0.98 (d, 12H, $J_{CH} = 6$ Hz, $^{iPr}CH_3$). ^{13}C NMR (125 MHz, C_6D_6): δ = 171.8, 171.7, 137.7, 137.1, 134.4, 130.7, 127.9, 124.2, 123.2, 120.0, 84.0, 70.1, 70.0, 69.4, 69.2, 67.9, 58.1, 42.7, 42.3, 41.9, 21.9. IR ($CDCl_3$, cm^{-1}) 3149 (w), 2963, 2122, 1722 (s), 1467, 1377, 1261, 1101 (s), 1015. $\lambda_{max} = 384$ nm; ε $= 9.8$ x 10^3 cm^{-1}M^{-1}.

Diisopropyl-3-(2-methylprop-1-enyl)-4-vinylcyclopent-3-ene-1,1-dicarboxylate (16)
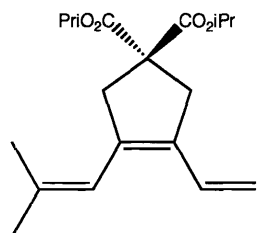
An oven-dried 250 mL Schlenck flask was charged with methyltriphenylphosphonium bromide (6.68 g, 10.3 mmol) and cooled under high vacuum. Dry THF (150 mL) was cannula-transferred into the reaction flask, cooled to -78 °C and n-BuLi (3.28 mL, 9.62 mmol) added to reveal a bright yellow ylide solution. After warming to room temperature to ensure complete reaction, the reaction was cooled to -78 °C and (8) (2.12 g, 6.87 mmol) was added under a nitrogen spurge. After 1.5 hours, TLC in hexane/ethyl acetate (6:1) revealed one product. Silica gel column chromatography pre-treated with NEt_3 using pentane/diethyl ether (8:2) yielded (16) (1.41 g, 4.60 mmol, 67%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.57 (dd, 2H, $J = 17.1$, 10.8 Hz, CHR=CHR), 5.902 (s, 1H, =CHR), 5.07 (m, 4H, ^{iPr}CH), 3.25 (s, 2H, $^{ring}CH_2$), 3.13 (s, 2H, $^{ring}CH_2$), 1.83 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 1.24 (2d, 12H, $J = 6.3$ Hz, $^{iPr}CH_3$). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 171.5, 136.7, 135.6, 133.2, 130.8, 118.9, 113.9, 68.8, 57.5, 44.3, 39.5, 27.1, 21.4, 20.1. IR (cm^{-1}, KBr) 3088, 2980, 2935, 1729, 1635, 1616, 1453, 1375, 1261, 1191, 1105, 1067, 1050, 985, 912, 888, 827.

Mo(CH[5]')(NAr)(OR$_{F6}$)$_2$ (17)
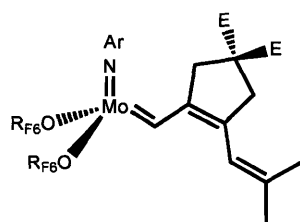
E = CO$_2$iPr
R$_{F6}$ = CMe(CF$_3$)$_2$

Triene (10) (1.41 g, 4.60 mmol) was dissolved in pentane (5 mL) and molecular sieves (4Å) added. After 2 h, the solution was added to a solution of Mo(NAr)(CHCMe$_3$)(OR$_{F6}$)$_2$ (3.24 g, 4.60 mmol) in pentane (30 mL) and stirred for 1 h. The precipitate was collected on a frit and washed with cold pentane to yield (17) as an orange solid (3.03 g, 3.27 mmol, 71%).

^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ = 12.80 (s, 1H, J_{CH} = 130 Hz, Mo=CHR), 7.27 (t, 1H, J = 7.5 Hz, Ar), 7.18 (d, 2H, J = 7.5 Hz, Ar), 5.97 (s, 1H, CHMe$_2$), 4.86 (sept, 2H, J = 6.5 Hz, ^{iPr}CH_E), 3.70 (s, 2H, ^{ring}CH_2), 3.53 (sept, 2H, J = 6.3 Hz, ^{iPr}CH_{Ar}), 3.18 (s, 2H, ^{ring}CH_2), 1.96 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.43 (s, 6H, OR$_{F6}$), 1.20 (d, 12H, J = 6.5 Hz, ^{iPr}C$H_{3,Ar}$), 0.92 (d, 6H, J = 6.3 Hz, ^{iPr}C$H_{3,E}$), 1.00 (d, 6H, J = 6.3 Hz, ^{iPr}C$H_{3,E}$). **^{13}C NMR** (500 MHz, CD$_2$Cl$_2$): δ = 258.9, 171.4, 154.7, 148.6, 143.9, 140.1, 130.1, 126.8, 124. 7 (dq, J_{CF} = 285, 29 Hz), 123.8, 119.2, 81.3 (quin, 29 Hz), 69.4, 58.0, 45.4, 43.4, 29.1, 28.1, 23.9, 21.7, 20.3, 19.4. **^{19}F NMR** (282 MHz, C$_6$D$_6$): δ = -77.79. **Anal.** Calcd. for C$_{38}$H$_{49}$NF$_{12}$MoO$_6$; C, 48.57; H, 5.26; N, 1.49. Found C, 48.95; H, 5.47, N, 1.49.

(E)-Di-1,2-[1-(2-Methyl-propenyl)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-enyl]-ethene (18) Dimer (iPr)

E = CO$_2$iPr
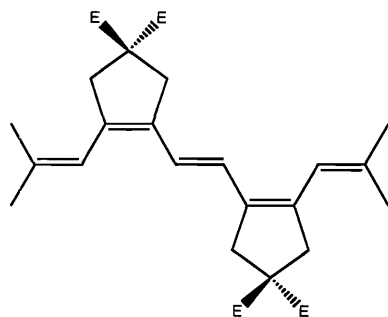
Recrystallized and dried (8) (13.3 mg, 0.043 mmol) was dissolved in dichloromethane (0.5 mL), stored over molecular sieves (4Å) for 30 min, and added to a solution of (17) (41.3 mg, 0.043 mmol) in dichloromethane (2 mL). The reaction was stirred vigorously for 3 h. Solvent was removed in vaccuo and eluted through an activated basic alumina plug with diethyl ether. The solvent was removed and the residue was triterated with pentane (slightly soluble) to yield (18) (13 mg, 0.021 mmol, 49%) as an off-white solid. The UV-VIS spectrum was taken using a 9.5 x 10^{-6} M solution in benzene.

¹H NMR (500 MHz, C₆D₆): δ = 6.75 (s, 2H, =C*H*R), 6.02 (s, 2H, =C*H*R), 5.01 (sept, 4H, *J* = 6 Hz, ᶦᵖʳC*H*), 3.65 (s, 8H, ʳⁱⁿᵍC*H₂*), 1.67 (s, 6H, C*H₃*), 1.54 (s, 6H, C*H₃*), 0.98 (m, 24H, ᶦᵖʳC*H₃*). **¹³C NMR** (125 MHz, C₆D₆): δ = 171.9, 137.1, 136.9, 134.5, 124.5, 120.4, 69.1, 58.7, 45.7, 41.0, 27.6, 21.8 (m), 20.8. **IR** (CDCl₃, cm⁻¹) 3141 (w), 2984, 2907, 1724 (s), 1446, 1368, 1259 (s), 1192, 1095, 1074, 1011. **HRMS** (EI, [M]⁺). Calc'd for C₃₆H₅₂O₈: 612.3657: Found: 612.3637. λ_{max} = 340 nm; ε = 6.9 x 10⁴ cm⁻¹M⁻¹.

(*E*)-Di-1,2-[1-{(*E*)-2-[2-(2-Methyl-propenyl)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-enyl]-vinyl}-4,4-di-*iso*-propyl-carboxy -cyclopent-1-enyl]-ethene (19)
**Tetramer**
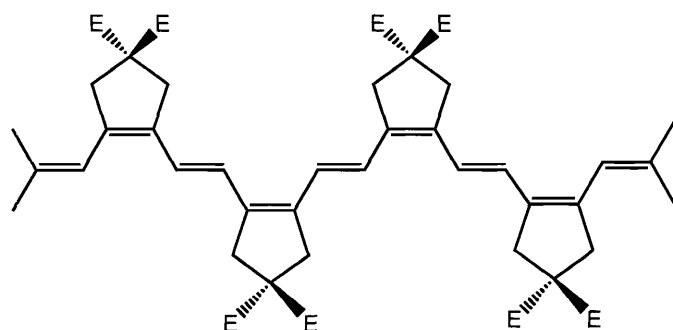
Recrystallized and dried trimeraldehyde (12) (21.0 mg, 0.025 mmol) was dissolved in dichloromethane (2 mL), stored over molecular sieves (4Å) for 30 min, and added to a solution of Mo(NAr)(CH[5])(OR_F6)₂⁸ (23.5 mg, 0.025 mmol) in dichloromethane (2 mL). The reaction was stirred vigorously for 3.5 h. Solvent was removed in vaccuo and eluted through an activated basic alumina plug with a mixture of diethyl ether/tetrahydrofuran (2:1). The solvent was removed and the residue was washed with pentane to yield (19) (11.8 mg, 0.010 mmol, 42%) as a yellowish-orange solid. The UV-VIS spectrum was taken using a 4.3 x 10⁻⁶ M solution in benzene.

¹H NMR (500 MHz, 54% C₆D₆/CD₂Cl₃): δ = 6.64 (m, 4H, =C*H*R), 6.51 (m, 2H, =C*H*R), 5.94 (s, 2H, =C*H*R), 4.95 (m, 8H, ᶦᵖʳC*H*), 3.40 (s, 4H, ʳⁱⁿᵍC*H₂*), 3.38 (s, 4H, ʳⁱⁿᵍC*H₂*), 3.35 (s, 4H, ʳⁱⁿᵍC*H₂*), 3.31 (s, 4H, ʳⁱⁿᵍC*H₂*), 1.68 (s, 6H, C*H₃*), 1.66 (s, 6H, C*H₃*), 1.05 (m, 48H, ᶦᵖʳC*H₃*). **¹³C NMR** (125 MHz, 54% C₆D₆/CD₂Cl₃): δ = 172.2, 172.0, 137.8, 137.7, 137.4, 136.4, 134.4, 125.8, 123.7, 122.4, 120.2 (m), 69.5 (m), 58.6, 57.8, 45.4, 42.2, 42.0, 40.7, 27.9, 22.0 (m), 21.0. **IR** (CDCl₃, cm⁻¹) 3236 (w), 2991, 2913, 1722 (s), 1619, 1454, 1331, 1262 (s), 1165, 1097, 1016. **HRMS** (ESI, [M+Na]⁺). Calc'd for C₆₆H₉₂O₁₆Na: 1163.6278: Found; 1163.6244. λ_{max} = 432 nm; ε = 9.2 x 10⁴ cm⁻¹M⁻¹.

**(_E_)-Di-1,2-[1-(2-Methyl-propenyl)-4,4-di-ethyl-carboxy-cyclopent-1-enyl]-ethene (20)
Dimer (Et)**

E = CO₂Et
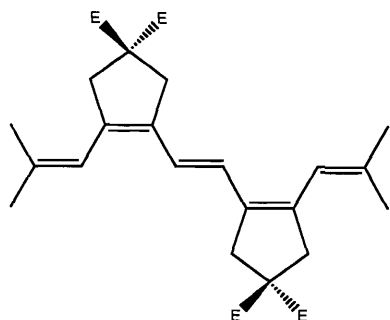
Recrystallized and dried diisopropyl-3-formyl-4-(2-methylprop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate[8] (64.9 mg, 0.221 mmol) was dissolved in dichloromethane (1.5 mL), stored over molecular sieves (4Å) for 30 min, and added to a solution of Mo(NAr)(CH[5])(OR$_{F6}$)$_2$[8] (201 mg, 0.221 mmol) in dichloromethane (2 mL). The reaction was stirred vigorously for 3 h. Solvent was removed in vaccuo and eluted through an activated basic alumina plug with diethyl ether. The solvent was removed and the residue washed with pentane (slightly soluble) to yield (20) (58 mg, 0.104 mmol, 47%) as an off-white solid. The UV-VIS spectrum was taken using a 1.5 x 10^{-5} M solution in benzene.

¹H NMR (500 MHz, C$_6$D$_6$): δ = 6.74 (s, 2H, , =CHR), 6.04 (s, 2H, =CHR), 3.95 (m, 8H, ^{Er}CH_2), 3.65 (s, 4H, ^{ring}CH_2), 3.61 (s, 4H, ^{ring}CH_2), 1.66 (s, 6H, CH_3), 1.56 (s, 6H, CH_3), 0.87 (m, 12H, ^{Er}CH_3). **¹³C NMR** (125 MHz, C$_6$D$_6$): δ = 172.3, 137.2, 136.8, 134.5, 124.4, 120.3, 61.8, 58.7, 45.6, 41.0, 45.6, 41.0, 27.7, 20.7, 14.3. **IR** (CDCl$_3$, cm⁻¹) 3149 (w), 2982, 2909, 1726 (s), 1446, 1368, 1258, 1190, 1097, 1074, 1013. **HRMS** (EI, [M]⁺). Calc'd for C$_{32}$H$_{44}$O$_8$: 556.3031: Found; 556.3045. λ_{max} = 340 nm; ε = 4.8 x 10^4 cm⁻¹M⁻¹.

Mo(CH[5]')(NAr)(OR)₂ (21)

**E = CO₂iPr
R = CMe₃**

55
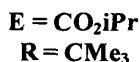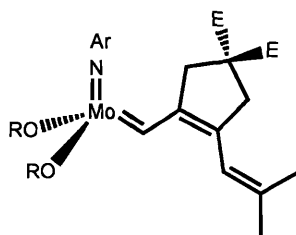
Generated in situ by addition of 2.3 equivalents of LiOCMe$_3$ to (17).

^{1}**H NMR** (300 MHz, C$_6$D$_6$): δ = ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 12.23 (s, 1H, J_{CH} = 123 Hz, Mo=C*H*R), 7.05 (m, 3H, Ar), 6.24 (s, 1H, C*H*Me$_2$), 4.95 (septet, 2H, J = 6.5 Hz, ^{iPr}C*H*$_E$), 4.07 (septet, 2H, J = 7 Hz, ^{iPr}C*H*$_{Ar}$), 3.99 (s, 2H, ^{ring}C*H*$_2$), 3.67 (s, 2H, ^{ring}C*H*$_2$), 1.73 (s, 6H, C*H*$_3$), 1.36 (s, 18H, O*t*-Bu), 3.10 (d, 12H, J = 7 Hz, ^{iPr}C*H*$_{3,Ar}$), 0.94 (d, 6H, J = 6.5 Hz, ^{iPr}C*H*$_{3,E}$), 0.87 (d, 6H, J = 6.5 Hz, ^{iPr}C*H*$_{3,E}$).. Used without further purification.

General Polymerization Method

The substrate (approximately 100 mg) was dissolved in dichloromethane (2 mL) and stored over molecular sieves for 30 min and then added to a vigorously stirring solution of 5 mol% catalyst in dichloromethane (2nM-20nM). After 2 h the reaction is quenched with 10 equivalents of benzaldehyde, stirred for another hour, and the solution concentrated in vaccuo. Polymer was precipitated with pentane, collected on a frit and washed with pentane (200 mL). The product was dried in vaccuo.

Appendix I

Reduced Tungsten Dimeric Compounds

INTRODUCTION

After the initial discovery of unbridged $W^{IV}=W^{IV}$ dimers resulting from decomposition of catalytic alkylidene complexes[27], a simplified preparation was sought. Since bimolecular decomposition is a major pathway to the depletion of high oxidation state alkylidene catalyst concentration, a better understanding of the nature of such decomposition products could prove useful.

The original synthetic scheme enroute to bimetallic tungsten compounds entailed the thermally activated bimolecular decomposition of an alkylidene-containing complex. [27] The first compounds of the type; unbridged double bonded W^{IV} metals, to be fully characterized by NMR and X-ray crystallography were the heterochiral $[W(NAr)(CH_2CMe_3)(OC_6F_5)]_2$ and $[W(NAr')(OCMe_2CF_3)_2]_2$ (Ar = 2,6-diisopropylphenyl and Ar' = 2,6-dimethylphenyl).[27]

Analogous tungsten dimers of alkylidene compounds that are stable at high temperatures have also become accessible through decomposition methods. The same route used to produce the $Re^V=Re^V$ dimer, $\{Re(C_tBu)(OCMe(CF_3)_2]\}_2$, from the thermally stable $Re(C_tBu)(CH_tBu)[OCMe(CF_3)_2]_2$ compound was utilized in such cases.[28] Through the addition of ethyl vinyl ether, the bulky neopentylidene group was lost via the evolution of $EtOCH=CH_tBu$ and the much less stable methylidene was formed, which was susceptible to bimolecular decomposition. By this method, both the heterochiral and homochiral dimer was formed from the stable neopentylidene-containing starting material, $\{W(NAr)(CH_2CMe_3)[OCMe(CF_3)_2]_2\}$.[29]

The synthetic procedure for $[W(NAr')(OCMe_2CF_3)_2]_2$ required the alkylidene complex be made; a five step route, after which the compound underwent heating to promote decomposition. Subsequently, yield was only modestly optimized from the first step to completion. Also, many dimeric compounds, due to similar solubility of the starting material and other reaction impurities, were rendered inaccessible due to separation difficulties; such species we have only observed by NMR.[29]

Previously, it was found that these $W^{IV}=W^{IV}$ species are capable of olefin metathesis reactions such as ROMP of norbornene and RCM of diallyl ether and diallyl tosyl amine, Standard metathesis results have also been displayed for cis-2-pentene and cis-3-hexene.[30] Until recently, there was much debate if such reactions were catalyzed by the dimeric compound. Since the former compounds had been formed through bimolecular decomposition, there

remained a chance that there was a small amount of d^0 catalyst that still lingered in the reaction mixture.

Such assumptions aside, there are three possibilities that may be causing this sort of unexpected behavior from double bonded bimetallic compounds. In the case of Nb and Ta, rearrangements of olefins with d^2 metal systems to yield d^0 alkylidenes have been observed.[31,32,33] By another possibility, the formation of a metallacyclopentane and subsequent ring contraction was found for Ta,[34] Re,[35] and W.[36] Finally, a mechanism analogous to the chop-chop reaction of internal alkynes with $(^tBuO)_3W\equiv W(^tBuO)_3$[37] is an option. Recent studies have been built upon this information in order to better understand what is occurring in the case of the aforementioned metathesis activity of the W(IV)=W(IV) compounds.[30]

In the interest of easier synthetic access to these dimeric tungsten compounds, a new and successful route was employed that required no alkylidene formation. More importantly, no olefin-containing compounds were present at any time. The new procedure reported here is a convenient pathway only two steps further than the previously reported tungsten-imido tetrachloride complex. Both reactions occur under ambient conditions and with excellent yields. After further studies, there is now tentative evidence that the $W^{IV}=W^{IV}$ compound is actually reacting with olefins in an ill-defined manner to produce high oxidation state alkylidenes.

Results and Discussion

I.i. Synthesis of Previously Known Dimeric Compounds

Beginning with the known imido complex, $W(NAr')Cl_4(THF)$ (Ar' = 2,6-dimethylphenyl)[38], $W(NAr')(OR)_2Cl_2(THF)$ (I.2) was synthesized via reaction with two equivalents of LiOR (R = CMe_2CF_3) (**Scheme I.1**). It should be noted that these compounds are close analogs to $W(NAr)(OCMe_3)_2Cl_2(THF)$[38] reported by our group in 1990 where Ar = 2,6-diisopropylphenyl (a precursor to a tungsten alkylidene complex via the PCl_5 route) and also to $W(N\text{-}^tBu)(OSi(^tBu)_3)_2Cl_2$[39] reported by Wolczanski et al.

Scheme I.1

R = CMe_2CF_3 (a)
R = $CMe(CF_3)_2$ (b)
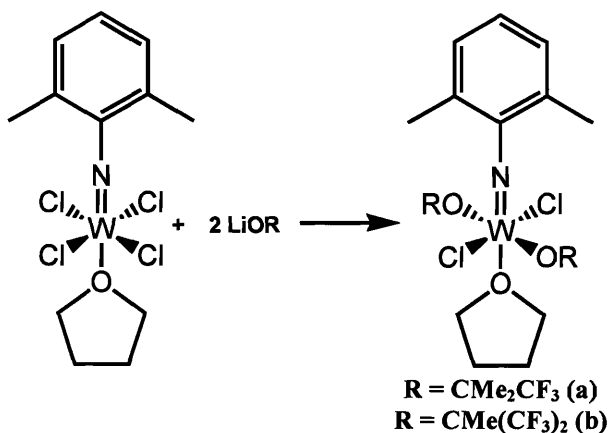
Here, solvent choice, as well as slow addition at low temperatures, proved crucial to gain pure product in good yield. Recrystallization from mixed products is possible, although tedious, due to similar solubility in pentane. Alkoxide exchange also occurs intermolecularly among compounds with differing substitution patterns. Within one day at 50 °C in d^6-benzene, there was a noticeable change when $W(NAr')Cl_4(THF)$ and (a) were combined. The percentage of products went from an approximate 70:30 mixture to mostly the mono-substituted product, $W(NAr')(OR)_2Cl_2(THF)$ [24% $W(NAr')Cl_4(THF)$, 70% $W(NAr')(OR)Cl_3(THF)$, 6% (a)]. After the first 24 hours, integral change was negligible as found by ^1H NMR even with a slight increase of ten degrees for two days. No degradation was evident within that temperature range.

Using the optimized solvent and reactant ratios, the mono-, di-, and tri-substituted alkoxide compounds proved accessible as the THF adduct (**Table I.1**). The same reaction conditions were employed when the lithium salt, $LiOCMe(CF_3)_2$, was used. It was found that if the reaction solvent was THF, the di-substituted alkoxide was not the major product using two equivalents of lithium salt. It is worthy to note here that the lithium chloride precipitate is

soluble in THF, which indicates that there is a potential stabilization of the salt in the reaction mixture that could have prevented the reaction from going to completion. It is also possible that for a timely reaction to occur, the THF must be more labilized, which is difficult with THF as a reaction solvent. However, any excess lithium alkoxide used caused the formation of the tri-substituted product (NMR data for such reactions were corroborated using shifts from the clean reactions shown in **Table I.1**). If an approximate mixture of 3:1 diethyl ether to THF was used in Scheme I, then the reaction was found to go almost to completion (**Table I.1**).

Table I.1
Yields and ^{1}H NMR shifts of various alkoxide substitution patters

Compound	Yield	^{1}H NMR $[Ar(CH_3)_2]$
W(NAr')(OR)Cl$_3$(THF)	83%	3.06 ppm
*W(NAr')(OR)$_2$Cl$_2$(THF)	90%	2.93 ppm
W(NAr')(OR)$_3$Cl(THF)	71%	2.87 ppm
W(NAr')(OR')Cl$_3$(THF)	87%	3.08 ppm
W(NAr')(OR')$_2$Cl$_2$(THF)	85%	2.94 ppm
W(NAr')(OR')$_3$Cl$_1$(THF)	74%	2.86 ppm

Ar' = 2,6-dimethylphenyl, R = C(Me)$_2$CF$_3$, R' = CMe(CF$_3$)$_2$
*Yield based on large scale synthesis (19 mmol) versus .19 mmol metal starting material scale

In accordance with the results of an alcoholysis reaction using a chiral bidentate ligand,[40] (I.1) was prepared by a similar route (**Scheme I.2**); using the corresponding alcohol and a 1.1 equivalents of triethylamine. The reaction was attempted in both THF and toluene. In THF, the reaction did not go to completion within a week. After 36 hours, a dark red color, indicative of the mono-substituted product, persisted for five days before a small percentage of expected product was observable by ^{1}H NMR. Most likely, this is due to the formation of the six-coordinate base adduct starting material. With the lower acidity of the fluorinated alcohol used, 2-trifluoromethyl-2-propanol, the rate-determining step is most likely the addition of the alcohol directly to the metal. Consequently, the hydrogen is labilized due to the Lewis acid effect, and triethylamine is protonated. For this to occur, the THF adduct must become labile to allow for addition, which is severely limited with THF as a reaction solvent. In toluene, the reaction goes to completion in order to yield a mixture of differently substituted complexes (thought to be due to a destabilization from the ammonium salt). These results are in stark contrast to what was

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found with the aromatic chelating ligand, biphenanthroline, which formed the base adduct in the presence of THF and an "-ate" complex in benzene.[40] At this point, further exploration was not done due to the fact that the reaction is lower yielding than the salt metathesis reactions (**Scheme I.1**).
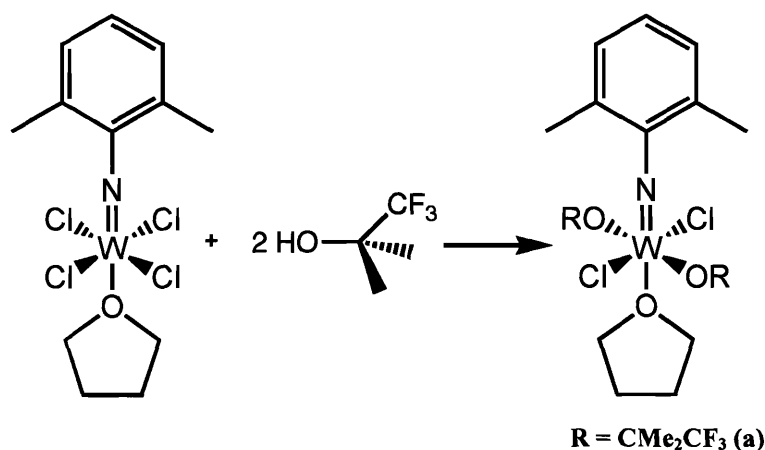
Scheme I.2

R = CMe₂CF₃ (a)

Electrochemical investigation of (a) (**Figure I.1**) did not indicate two fully reversible reactions that would seem necessary to synthetically access the unbridged dimer, addressed in previous work, [W(NAr')(OCMe₂CF₃)₂]₂ by reduction of W(NAr')(OCMe₂CF₃)₂Cl₂(THF). The electrochemical window of fluorobenzene did not allow for the complete viewing of the second reduction potential if present, but the first potential was diagnosed as not fully reversible at -1.4 V relative to ferrocene. However, since [W(NAr')(OCMe₂CF₃)₂]₂ was found to be a thermodynamic sink in the decomposition of the corresponding alkylidene compound, the reduction was probed even in light of this information. Similar reductions have been carried out in the Wolczanski group.[39,41] The formerly mentioned tungsten compound, W(N-ᵗBu)(OSi(ᵗBu)₃)₂Cl₂, yielded a three coordinate complex, W(N-ᵗBu)(OSi(ᵗBu)₃)₂, using Mg dust.[39] A molybdenum analog yielded {Mo(N-ᵗBu)[OSi(ᵗBu)₃]₂}₂(μ-Hg) where the d²/d² molybdenum dimer was arranged linearly to a central bridging mercury atom when sodium amalgam was employed.[41] In the case of (a), a dimer compound similar in all respects to the W(IV)/W(IV) unsupported dimer as found via decomposition methods[27] was synthesized by reduction using potassium graphite (**Scheme I.3**). Both ¹H NMR, ¹⁹F NMR and ethylene adduct formation all support the findings that this is the same compound as previously reported.[27,30] Both potassium graphite and 0.5 weight percent sodium amalgam produced fairly clean results. Other reductants

evaluated were magnesium sand and cobaltacene, but neither yielded the desired compound. The ease of use and cleanliness of the reaction made potassium graphite the reductant of choice for the synthesis of (c). Unfortunately, due to the heterogeneous nature of the reaction, and therefore necessity of vigorous stirring, a large-scale reaction was hindered significantly. When mixing was slowed in an NMR scale reaction, alkoxide exchange was seen to occur as well as the formation of dimer after 20 minutes in both d^6-benzene and d^8-toluene.

Figure I.1
Cyclic Voltammetry of $W(NAr')(OCMe_2CF_3)_2Cl_2(THF)$ (a)
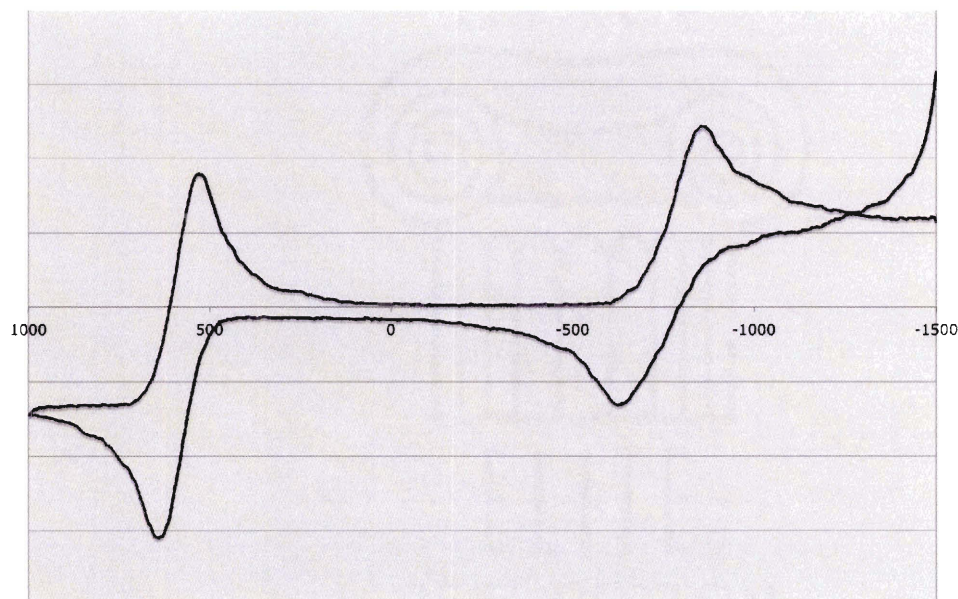
Cyclic Voltammetry scan from -1500 to 1000 mV in fluorobenzene solvent using pseudo-silver working electrode referenced to ferrocene. **Note: Larger peak separation of 144 mV and also a reduction potential of -1.285 V for the target compound versus reference

R = CMe_2CF_3

Scheme I.3

(a)   (c)
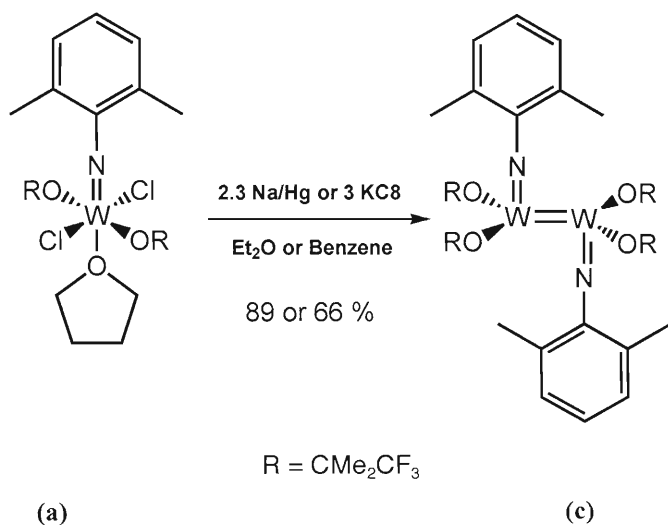
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I.ii Attempts to Prepare Novel Dimeric Tungsten Compounds

Since other starting materials with varying alkoxide ligands are readily available (**Table I.1**), reduction was attempted. As the alkoxide ligand becomes more electron withdrawing (e.g. R= CMe(CF$_3$)$_2$), reductions theoretically become easier, and therefore reaction conditions to achieve dimerization must be altered. This stipulation has not yet been proven by cyclic voltammetry, but electrochemical studies were done for W(NAr)(OCMe$_3$)$_2$Cl$_2$(THF).[38] The expected trend, a lower reduction potential, was evident.[29] At this point, optimal reaction conditions to reach either of these W(IV)/W(IV) analogs by reduction has not been found.

In addition to the effects of fluorinated alkoxide ligands with respect to dimerization, a different imido group was looked into as well. In particular, the adamantyl imido analog was interesting due to previous work with molybdenum. The imido-bridged dimer, {Mo(μ-NAd)[OCMe(CF$_3$)$_2$]$_2$}$_2$, was found as a crystal that had been grown over a period of 10 years in a sealed NMR tube from the reaction between two equivalents of 2,3-bis(trifluoromethyl)norbornadiene and Mo(NAd)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$.[42] A bridged tungsten dimer of this sort has not yet been found.

When the ethylene adduct of (I.3) was heated to 80 °C, the methyl group of 2,6-dimethylphenyl imido underwent CH activation to yield two tungsten-carbon single bonds within the newly bridged dimeric structure.[30] So the question remains what structure would be found in the presence of an imido group that does not contain a pendent hydrogen-containing substituent. Aforementioned, a molybdenum analogue with an adamantly imido group formed a bridged dimer, although over a span of years. If the tungsten analogue was found to be an unsupported dimer in this case as well, it would be an indication that CH activation is not necessarily the reason that bridging is not seen for these dimeric species. It should not be overlooked, though, that the two metals discussed here have different electrochemical properties and the compounds have been made by two different methods. The route to W[N(Ad)]Cl$_4$ was investigated using the previously published synthesis for aryl imido ligands in which the corresponding isocyanate compound is added to a toluene solution of W(O)Cl$_4$ and refluxed until CO$_2$ evolution ceases.[38] No desired product was formed, and it is surmised that the reaction conditions are too harsh for the more electron-rich imido ligand. Perhaps due to possible radical pathways, the nitride compound was formed as a reaction byproduct. The addition of 1-admantyl azide to

WCl$_4$(DME) has already been attempted unsuccessfully with the initial observations that the naked species (i.e. no base adduct) is partially unstable.[43]

I.iii Exploration of d^2/d^2 Dimer Reactivity

After the initial reduction to form a pure dimer (c) that was identical in all respects to the original dimer, $[W(NAr')(OCMe_2CF_3)_2]_2$, reactivity was tested. This was done to begin answering the question of whether or not the previously noted reactivity is due to a residual amount of alkylidene since it was formed via decomposition. 10 equivalents of norbornene and $[W(NAr')(OCMe_2CF_3)_2]_2$ were dissolved in 1 mL d^8-toluene and the reaction followed by ^1H NMR. The dimer was found active for the polymerization of norbornene (87% cis-polymer) in the same fashion as the previous samples. Kinetics data revealed a nonlinear plot, which could be due to low initiation rates and concentrations of propagating species (**Figure I.2**). It is interesting, however, to look at the ^{19}F NMR. The norbornene adduct of the dimer is suggested by the characteristic four pattern splitting, which grows in and out slowly throughout the polymerization reaction. Adduct formation is supported by similar ^{19}F NMR spectra for the 2-butyne and ethylene adduct (**Figure I.3**). The proposal of adduct formation corroborates the non-linear plot of the ring-opening metathesis polymerization. The dimer most likely undergoes one of the aforementioned rearrangements to a high oxidation state alkylidene complex in order to catalyze the polymerization of norbornene seen by ^1H NMR. The formation of an adduct could serve as a reservoir for the reactive alkylidene. The polymerization of 10 equivalents norbornene is over within 10 hours. Previous studies of polymer molecular weights have shown that they are in average 38 times larger than expected for a living system.

Figure I.2

Three Half-Lives of ROMP of Norbornene using $\{W(NAr')[OCMe_2CF_3]_2\}_2$ Followed by 1H NMR
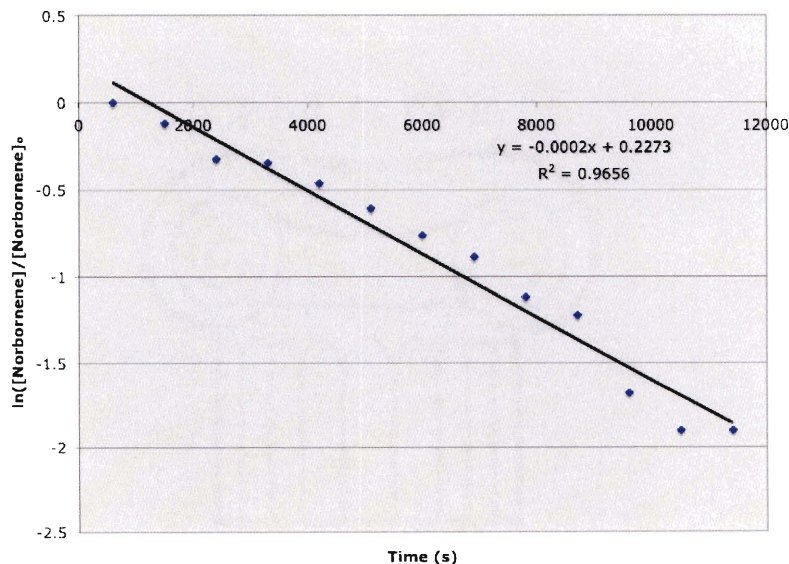
Figure I.3
Proposed norbornene adduct of dimer
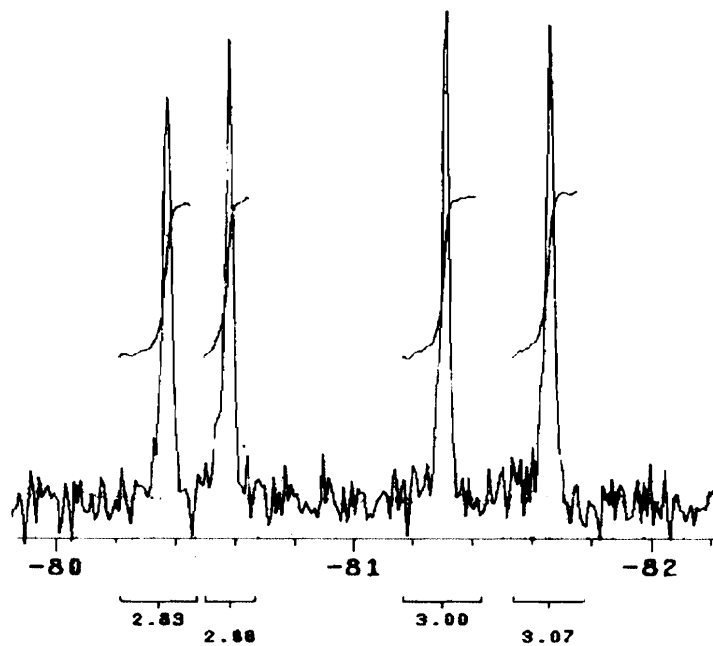
I.iv Related W(IV) Chemistry

Monomeric W(IV) chemistry was briefly explored, but desired products were not formed. The monomeric form of the ethylene adduct was sought in order to begin to understand more about tungsten (IV) chemistry with potential capability as active catalysts. It is still unknown at this point whether or not it is *only* the dimer form of these species that are potentially capable of rearrangement to an alkylidene-type catalyst. Two methods could be used to form an olefin complex of the monomer, W(NAr')(OR)$_2$(olefin). The stable analogue, W(NAr)[OCMe(CF$_3$)$_2$]$_2$(CH$_2$=CHSiMe$_3$)[29], has been prepared in accordance with previous studies in which Mo(CH-t-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ was shown to react with excess vinyltrimethylsilane.[42] One method to encourage formation of such compounds without using an alkylidene starting material is β-hydrogen abstraction that has been shown to occur as a decomposition method for dialkyl complexes. Another option is the reduction of the dichloride W(VI) starting material in the presence of the desired olefin.

A reduction of W(NAr')(OCMe$_2$(CF$_3$))$_2$Cl$_2$(THF) using sodium amalgam in the presence of ethylene yielded the ethylene adduct of the dimer as well as a small amount of (c). It is thought that ethylene, even at one atmosphere of pressure, was too small to impede the very fast rearrangement to the dimeric structure immediately following reduction. There is a constant struggle between a fast reduction to produce the dimer and a slower reaction that would allow time for the olefin to coordinate to the W(IV) metal center but promotes other bimolecular reactions such as rearrangements. In the case of a slow reduction, such as when a sodium mirror is used instead of sodium amalgam or potassium graphite, the trisubstituted alkoxide, W(NAr')[OCMe$_2$(CF$_3$)]$_3$Cl(THF), is the major product. Therefore, a different route was implemented in an effort to realize the desired product, W(NAr')[OCMe$_2$(CF$_3$)]$_2$(C$_2$H$_4$), which is based upon research done by the Floriani group. Various olefin adducts of calix[4]-arene—tungsten(IV) were synthesized via reduction of the dichloride W(VI) precursor by sodium in the presence of cyclohexene.[44] The latter has been replaced by norbornene, acenaphthylene, stilbene, and 2-butyne among other variations. Similar to the results with W(NAr')[OCMe$_2$(CF$_3$)]$_2$Cl$_2$(THF), when the reduction is carried out without an alkene or alkyne excess in the reaction mixture, a W(IV)/W(IV) dimer is formed. The exact reaction conditions for the reduction of (b) in the presence of cyclohexene have not yet been determined. Various

solvents including benzene, diethyl ether, THF/diethyl ether and reductants such as Na, Na/Hg, Mg dust, and KC_8 with up to 20 fold excess of cyclohexene proved futile.

In a subsequent paper, Floriani showed that a diazoalkane could labilize the cyclohexene adduct as well.[45] In this case, the reaction did not result in N—C bond cleavage with the release of N_2 as is the typical pathway of diazoalkane. However, perhaps without the large, chelating ligand that mimics a metal-oxo surface used by Floriani, this would prove an interesting route to an alkylidene complex, although this has not yet been attempted since the cyclohexene adduct is still elusive.

Conclusions

Two synthetic routes have been devised for the reduction of W(NAr)(OCMe$_2$-CF$_3$)$_2$Cl$_2$(THF) to reach the previously known dimer, [W(NAr')(OCMe$_2$CF$_3$)$_2$]$_2$. Using evidence of the polymerization of norbornene with the dimer made by the method presented here, tentative evidence has been given to dimer reactivity. Other reactions, such as RCM and metathesis of cis-2-pentane that were shown to occur by catalytic activity of the dimer have not been corroborated yet. Steps were taken to better understand the mechanism that could potentially cause the rearrangement of olefins to high oxidation state alkylidenes within this dimer system. Although not many conclusions have been made, the groundwork has been laid for the preparation of possible new tungsten dimers such as one containing adamantyl imido and those of various alkoxide ligands that could exhibit different reactivities and snapshots of what is actually occurring during rearrangement.

Monomeric tungsten(IV) chemistry has not been probed to a great extent, and investigations have been made to create an olefin adduct of such. The question remains whether or not olefin rearrangement could take place to form alkylidenes or metallacycles.

EXPERIMENTAL DETAILS

All air- and moisture-sensitive work was carried out in a Vacuum Atmospheres dry box under a dinitrogen atmosphere or by using standard Schlenk techniques. All solvents were passed through a column of activated alumina under constant nitrogen flow. Deuterated d_6-benzene was dried over sodium and freeze-pump-thaw degassed before being brought into the drybox. Both hexamethyldisiloxane and deuterated d_2-methylene chloride were dried over CaH_2 and freeze-pump-thaw degassed as well. All alcohols used were degassed in the same manner. The aryl isocyanate utilized (Ar' = 2,6-dimethylphenyl) was distilled under vacuum and freeze-pump-thaw degassed. Molecular sieves (4 Å) was used to dry solvents and alcohols. All lithium salt reagents were made by the reaction of n-butyl lithium with the corresponding alcohol. $W(O)Cl_4$[46] was prepared by the previously described methods of Gibson et al. $W(NAr')Cl_4(THF)$[38] was prepared in a method similar to literature preparation of related compounds.

Unless otherwise stated, all reported ^{19}F NMR shifts are reported in parts per million referenced against $CFCl_3$. In addition, ^1H and ^{13}C shifts are reported in parts per million referenced to deuterated solvents. All spectra were acquired near 22 °C.

W(NAr')[OCMe₂(CF₃)]₂Cl₂ (a).   Two equivalents of $LiOMe_2CF_3$ (5.18 g, 38.6 mmol) were dissolved in minimal THF (35 mL) and cooled to -40 °C. The solution was added dropwise to a chilled stirring green suspension of $W(NAr')Cl_4(THF)$ (10.0 g, 19.34 mmol) in diethyl ether (110 mL) and allowed to stir for 20 h. The color changed from a dark green to a dark orange solution. The reaction mixture was evaporated to dryness, dissolved in pentane and filtered over celite to separate off the salt precipitate. The resulting filtrate was concentrated to yield 10.8 g of pure microcrystalline material that was collected via a second filtration. At reduced temperatures, pentane was used to claim the remainder of pure product from the filtrate (11.99 g, 90.2%). ^1H NMR (300 MHz, $C_6D_5CD_3$) δ = 6.82 (d, 2H, J = 7.8 Hz), 6.47 (t, 1H, J = 7.8 Hz), 4.25 (m, 4H), 2.90 (s, 6H), 1.47 (s, 12H), 1.41 (m, 4H). ^{19}F NMR (282 MHz, C_6D_6) δ - 81.5 (s). ^{13}C NMR (125 MHz, C_6D_6) δ = 149.9, 142.7, 130.1, 128.7, 127.5 (q, J_{CF} = 285 Hz), 86.1 (q, J_{CF} = 29 Hz), 72.1, 25.7, 23.2, 20.9. **Anal.** Calcd. for $C_{20}H_{29}NCl_2F_6O_3W$; C, 34.31; H, 4.17; N, 2.00. Found C, 34.28; H, 4.17, N, 1.93.

*Note: The same procedure was used for the synthesis of W(NAr')[OCMe₂(CF₃)]Cl₃(THF) and W(NAr')[OCMe₂(CF₃)]₃Cl(THF) through direct translation of equivalents LiOMe₂CF₃ used. Yields listed in **Table 1**.

W(NAr')[OCMe(CF₃)₂]₂Cl₂ (b). Two equivalents of LiOCMe(CF₃)₂ (0.073 g, 0.387 mmol) was dissolved in minimal THF (3 mL) and cooled to -40 °C. The solution was added drop-wise to a chilled stirring green suspension of W(NAr')Cl₄(THF) (0.100 g, 0.1934 mmol) in diethyl ether (9 mL) and allowed to stir for 8 h. The color changed from dark green to purple-red to a resulting dark orange solution. The reaction mixture was evaporated to dryness, dissolved in pentane and filtered over celite to separate off the salt precipitate. The resulting filtrate was concentrated in vaccuo and two crops collected at reduced temperatures (0.130 g, 85%). ^{1}**H NMR** (300 MHz, C₆D₆) δ = 6.78 (d, 2H, J = 7.5 Hz), 6.36 (t, 1H, J = 7.5 Hz), 4.26 (m, 4H), 2.94 (s, 6H), 1.54 (s, 6H), 1.28 (m, 4H). ^{19}**F NMR** (282 MHz, C₆D₆) δ = -75.8 (s). ^{13}**C NMR** (125 MHz, C₆D₆) δ = 149.1, 145.3, 131.9, 128.7, 124.5 (q, J_{CF} = 287 Hz), 86.2 (q, J_{CF} = 30 Hz), 72.6, 25.5, 20.3), 16.8. **Anal.** Calcd. for C₂₀H₂₃NCl₂F₁₂O₃W; C, 29.72; H, 2.87; N, 1.73. Found C, 29.77; H, 2.82, N, 1.70.

*Note: The same procedure was used for the synthesis of W(NAr')[OCMe(CF₃)₂]Cl₃(THF) and W(NAr')[OCMe(CF₃)₂]₃Cl(THF) through direct translation of equivalents LiOCMe(CF₃)₂ used. Yields listed in **Table 1**.

[W(NAr)[OCMe₂(CF₃)]₂]₂ (c). **a)** The reduction of W(NAr)[OCMe₂(CF₃)]₂Cl₂ was carried out using 3 equivalents of freshly prepared KC₈ (0.439 g, 3.25 mmol). A benzene solution (12 mL) of WCl₂(NAr)[OCMe₂(CF₃)]₂ (0.760 g, 1.08 mmol) was added at a steady rate to KC₈ and allowed to stir for 10 h. The solution was then filtered over celite and the solvent removed in high vaccuo. Recrystallization via Pentane/THF gave a brown microcrystalline material (0.902 g, 66%). **b)** A diethyl ether solution (3 mL) of W(NAr)[OCMe₂(CF₃)]₂Cl₂ (1.46 g, 2.09 mmol) was added dropwise to Na/Hg (0.5 wt.%, 0.111 g Na, 4.81 mmol Na) at -40 °C, and allowed to stir for 3.5 h at room temperature. The solution was evaporated in vaccuo, rinsed with pentane and filtered over celite. The sample was then dried in high vaccuo for a crude yield

of 1.06 g (81%). The sample was then purified by recrystallization in concentrated pentane with residual diethyl ether from the reaction mixture. The microcrystalline material is insoluble in pentane. ^{1}H NMR (C_6D_6) δ 7.01 (m, 5H), 2.57 (s, 12H), 1.27 (s, 12H) 1.20 (s, 12H). ^{19}F NMR (C_6D_6) δ -82.5 (s).

Appendix II:

Crystallographic data Tables for {Mo(NAr)[OCMe(CF$_3$)$_2$]}$_2$CH[5]CH

- Labeled ORTEP
- Crystal data and structure refinement details
- Atomic coordinates and equivalent isotropic displacement parameters
- Bond lengths and angles
- Anisotropic displacement parameters
- Hydrogen coordinates and isotropic displacement parameters

Table II.1. Crystal data and structure refinement

Identification code   05196

Empirical formula   C55.50 H68 F24 Mo2 N2 O8

Formula weight   1539.00

Temperature   100(2) K

Wavelength   0.71073 ≈

Crystal system   Monoclinic

Space group   P2(1)/n

Unit cell dimensions   a = 11.0704(4) ≈   a= 90∞.

     b = 27.1993(10) ≈   b= 90.8330(10)∞.

     c = 22.5569(9) ≈   g = 90∞.

Volume   6791.3(4) ≈^{3}

Z   4

Density (calculated)   1.505 Mg/m^3

Absorption coefficient   0.484 mm^{-1}

F(000)   3116

Crystal size   0.18 x 0.16 x 0.08 mm^3

Theta range for data collection   1.75 to 28.70∞.

Index ranges   -14<=h<=14, -36<=k<=36, -30<=l<=30

Reflections collected   135769

Independent reflections   17523 [R(int) = 0.0699]

Completeness to theta = 28.70∞   100.0 %

Absorption correction   Semi-empirical from equivalents

Max. and min. transmission   0.9623 and 0.9180

Refinement method   Full-matrix least-squares on F^2

Data / restraints / parameters   17523 / 131 / 913

Goodness-of-fit on F^2 1.066

Final R indices [I>2sigma(I)]   R1 = 0.0485, wR2 = 0.1199

R indices (all data)   R1 = 0.0767, wR2 = 0.1332

Largest diff. peak and hole   1.613 and -0.375 e.≈$^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

	x	y	z	U(eq)
Mo(1)	7820(1)	2228(1)	7860(1)	20(1)
Mo(2)	9858(1)	4477(1)	8702(1)	22(1)
C(1)	8173(3)	2910(1)	7958(1)	24(1)
C(2)	9134(3)	3926(1)	8308(1)	24(1)
C(3)	7953(3)	3363(1)	7649(1)	26(1)
C(4)	8372(3)	3822(1)	7811(1)	26(1)
C(5)	7882(4)	4215(1)	7404(2)	37(1)
C(6)	7224(4)	3930(1)	6897(2)	35(1)
C(7)	7114(4)	3394(1)	7118(2)	39(1)
N(1)	7361(2)	2236(1)	7129(1)	24(1)
C(11)	7033(3)	2228(1)	6532(2)	30(1)
C(12)	5788(4)	2272(1)	6383(2)	35(1)
C(13)	5489(4)	2296(1)	5785(2)	47(1)
C(14)	6370(5)	2273(2)	5362(2)	54(1)
C(15)	7571(5)	2222(1)	5515(2)	49(1)
C(16)	7943(4)	2197(1)	6108(2)	36(1)
C(121)	4845(3)	2262(2)	6862(2)	41(1)
C(122)	3727(5)	2567(3)	6714(3)	86(2)
C(123)	4529(5)	1729(2)	7001(2)	64(1)
C(161)	9257(4)	2152(2)	6288(2)	44(1)
C(162)	9826(4)	2662(2)	6362(2)	53(1)
C(163)	9998(5)	1838(2)	5855(2)	70(2)
N(2)	9318(2)	4936(1)	8242(1)	24(1)
C(21)	8914(3)	5294(1)	7842(1)	28(1)
C(22)	7800(3)	5525(1)	7932(2)	32(1)
C(23)	7372(4)	5839(1)	7491(2)	40(1)

C(24)	8025(4)	5921(1)	6988(2)	50(1)
C(25)	9135(4)	5706(1)	6912(2)	48(1)
C(26)	9626(4)	5387(1)	7335(2)	37(1)
C(221)	7115(3)	5442(1)	8499(2)	36(1)
C(222)	5746(4)	5511(2)	8426(2)	61(1)
C(223)	7615(4)	5781(2)	8984(2)	48(1)
C(261)	10855(4)	5157(1)	7277(2)	49(1)
C(262)	11754(4)	5435(2)	7671(2)	56(1)
C(263)	11291(6)	5134(2)	6642(2)	77(2)
O(1)	9280(2)	1864(1)	8003(1)	28(1)
C(31)	10484(3)	1912(1)	8183(2)	30(1)
C(32)	11086(3)	2369(2)	7926(2)	44(1)
C(33)	11128(3)	1450(2)	7961(2)	46(1)
F(1)	11116(2)	1441(1)	7375(1)	73(1)
F(2)	10606(2)	1041(1)	8145(2)	72(1)
F(3)	12283(2)	1435(1)	8148(1)	56(1)
C(34)	10514(4)	1943(2)	8855(2)	45(1)
F(4)	9984(3)	1569(1)	9112(1)	72(1)
F(5)	11634(2)	1976(1)	9081(1)	62(1)
F(6)	9929(3)	2352(1)	9023(1)	70(1)
O(2)	6536(2)	2101(1)	8405(1)	29(1)
C(35)	5947(3)	2309(1)	8889(2)	34(1)
C(36)	5881(4)	2865(2)	8873(2)	57(1)
C(37)	6636(5)	2136(3)	9442(2)	73(2)
F(7)	7726(3)	2327(2)	9446(2)	129(2)
F(8)	6093(3)	2267(2)	9943(1)	106(2)
F(9)	6756(4)	1655(2)	9457(2)	126(2)
C(38)	4662(4)	2104(2)	8870(2)	43(1)
F(10)	4631(3)	1621(1)	8867(2)	84(1)
F(11)	4101(2)	2258(1)	8384(1)	66(1)
F(12)	4008(2)	2256(1)	9327(1)	54(1)

O(3)	11588(2)	4373(1)	8658(1)	29(1)
C(41)	12414(3)	4009(1)	8503(2)	32(1)
C(42)	12154(4)	3782(2)	7902(2)	46(1)
C(43)	13666(3)	4256(2)	8500(2)	43(1)
F(13)	13917(2)	4507(1)	8985(1)	59(1)
F(14)	13742(2)	4565(1)	8042(1)	62(1)
F(15)	14561(2)	3929(1)	8437(1)	55(1)
C(44)	12394(3)	3611(1)	8991(2)	41(1)
F(16)	13055(2)	3220(1)	8863(1)	66(1)
F(17)	12780(3)	3773(1)	9514(1)	69(1)
F(18)	11275(2)	3446(1)	9060(1)	55(1)
O(4)	9161(2)	4468(1)	9479(1)	26(1)
C(45)	8253(3)	4260(1)	9819(1)	27(1)
C(46)	7066(3)	4183(2)	9477(2)	38(1)
C(47)	8721(3)	3763(1)	10059(2)	32(1)
F(19)	9790(2)	3799(1)	10324(1)	47(1)
F(20)	7962(2)	3556(1)	10443(1)	49(1)
F(21)	8843(2)	3442(1)	9613(1)	43(1)
C(48)	8055(3)	4622(1)	10335(2)	34(1)
F(22)	7181(2)	4471(1)	10695(1)	46(1)
F(23)	7746(2)	5059(1)	10123(1)	48(1)
F(24)	9050(2)	4684(1)	10670(1)	39(1)
O(5)	5036(3)	3999(1)	6959(2)	72(1)
O(6)	6124(3)	4583(1)	6498(2)	67(1)
O(7)	8895(4)	4135(1)	6274(2)	76(1)
O(8)	7357(3)	3692(1)	5906(1)	56(1)
C(61)	5981(5)	4159(2)	6787(2)	50(1)
C(62)	5036(6)	4875(2)	6389(3)	97(2)
C(63)	5346(10)	5225(3)	5912(4)	173(5)
C(64)	7934(4)	3943(2)	6335(2)	46(1)
C(65)	7930(6)	3663(2)	5326(2)	65(1)

C(66)	7473(7)	4065(2)	4947(2)	93(2)
C(1X)	6410(20)	462(6)	9648(7)	76(4)
C(2X)	6949(18)	668(6)	10245(6)	64(3)
C(3X)	6667(15)	1025(5)	10658(6)	58(3)
C(4X)	7651(14)	1200(6)	11001(7)	66(3)
C(5X)	8826(12)	1431(5)	10634(5)	49(3)
C(1Y)	8578(16)	1038(6)	10273(7)	32(3)
C(2Y)	7290(20)	874(8)	10504(10)	51(3)
C(3Y)	6760(20)	455(8)	10245(11)	57(3)
C(4Y)	5680(20)	458(9)	9929(12)	64(4)
C(5Y)	4710(30)	-1(16)	10000(30)	94(8)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3.   Bond lengths [Å] and angles [°]

Mo(1)-N(1)	1.718(3)
Mo(1)-C(1)	1.911(3)
Mo(1)-O(1)	1.918(2)
Mo(1)-O(2)	1.923(2)
Mo(2)-N(2)	1.725(3)
Mo(2)-C(2)	1.914(3)
Mo(2)-O(4)	1.927(2)
Mo(2)-O(3)	1.940(2)
C(1)-C(3)	1.434(4)
C(2)-C(4)	1.421(4)
C(3)-C(4)	1.378(4)
C(3)-C(7)	1.507(5)
C(4)-C(5)	1.505(5)
C(5)-C(6)	1.554(5)
C(6)-C(64)	1.501(6)
C(6)-C(61)	1.526(6)
C(6)-C(7)	1.547(5)
N(1)-C(11)	1.389(4)
C(11)-C(16)	1.402(5)
C(11)-C(12)	1.420(5)
C(12)-C(13)	1.384(5)
C(12)-C(121)	1.515(6)
C(13)-C(14)	1.376(7)
C(14)-C(15)	1.376(7)
C(15)-C(16)	1.394(5)
C(16)-C(161)	1.510(6)
C(121)-C(122)	1.523(6)
C(121)-C(123)	1.525(6)
C(161)-C(162)	1.531(6)

C(161)-C(163)	1.542(6)
N(2)-C(21)	1.397(4)
C(21)-C(22)	1.401(5)
C(21)-C(26)	1.421(5)
C(22)-C(23)	1.389(5)
C(22)-C(221)	1.514(5)
C(23)-C(24)	1.373(6)
C(24)-C(25)	1.374(6)
C(25)-C(26)	1.395(5)
C(26)-C(261)	1.504(6)
C(221)-C(223)	1.526(6)
C(221)-C(222)	1.534(6)
C(261)-C(263)	1.520(6)
C(261)-C(262)	1.524(7)
O(1)-C(31)	1.394(4)
C(31)-C(34)	1.518(6)
C(31)-C(32)	1.529(5)
C(31)-C(33)	1.532(5)
C(33)-F(1)	1.323(5)
C(33)-F(2)	1.323(5)
C(33)-F(3)	1.341(4)
C(34)-F(4)	1.315(5)
C(34)-F(5)	1.336(5)
C(34)-F(6)	1.344(5)
O(2)-C(35)	1.399(4)
C(35)-C(36)	1.514(5)
C(35)-C(37)	1.528(6)
C(35)-C(38)	1.529(5)
C(37)-F(7)	1.314(7)
C(37)-F(9)	1.315(7)
C(37)-F(8)	1.337(5)

C(38)-F(10)	1.313(5)
C(38)-F(11)	1.321(5)
C(38)-F(12)	1.335(4)
O(3)-C(41)	1.394(4)
C(41)-C(42)	1.513(5)
C(41)-C(43)	1.541(5)
C(41)-C(44)	1.544(5)
C(43)-F(13)	1.317(5)
C(43)-F(14)	1.334(5)
C(43)-F(15)	1.341(4)
C(44)-F(16)	1.324(4)
C(44)-F(17)	1.325(5)
C(44)-F(18)	1.329(4)
O(4)-C(45)	1.392(4)
C(45)-C(46)	1.528(5)
C(45)-C(48)	1.543(5)
C(45)-C(47)	1.545(5)
C(47)-F(19)	1.321(4)
C(47)-F(20)	1.338(4)
C(47)-F(21)	1.341(4)
C(48)-F(23)	1.323(4)
C(48)-F(22)	1.336(4)
C(48)-F(24)	1.338(4)
O(5)-C(61)	1.203(6)
O(6)-C(61)	1.334(5)
O(6)-C(62)	1.461(6)
O(7)-C(64)	1.195(5)
O(8)-C(64)	1.339(5)
O(8)-C(65)	1.465(5)
C(62)-C(63)	1.482(12)
C(65)-C(66)	1.473(7)

C(1X)-C(2X)	1.571(17)
C(2X)-C(3X)	1.384(15)
C(3X)-C(4X)	1.409(16)
C(4X)-C(5X)	1.675(17)
C(1Y)-C(2Y)	1.59(2)
C(2Y)-C(3Y)	1.408(17)
C(3Y)-C(4Y)	1.382(18)
C(4Y)-C(5Y)	1.65(2)
N(1)-Mo(1)-C(1)	98.98(13)
N(1)-Mo(1)-O(1)	113.89(11)
C(1)-Mo(1)-O(1)	108.13(12)
N(1)-Mo(1)-O(2)	113.87(11)
C(1)-Mo(1)-O(2)	104.56(11)
O(1)-Mo(1)-O(2)	115.38(10)
N(2)-Mo(2)-C(2)	98.51(13)
N(2)-Mo(2)-O(4)	114.70(11)
C(2)-Mo(2)-O(4)	103.98(11)
N(2)-Mo(2)-O(3)	114.14(11)
C(2)-Mo(2)-O(3)	105.58(11)
O(4)-Mo(2)-O(3)	116.98(10)
C(3)-C(1)-Mo(1)	138.2(2)
C(4)-C(2)-Mo(2)	139.7(2)
C(4)-C(3)-C(1)	126.4(3)
C(4)-C(3)-C(7)	111.2(3)
C(1)-C(3)-C(7)	122.2(3)
C(3)-C(4)-C(2)	125.7(3)
C(3)-C(4)-C(5)	111.4(3)
C(2)-C(4)-C(5)	122.9(3)
C(4)-C(5)-C(6)	104.8(3)
C(64)-C(6)-C(61)	109.6(3)

C(64)-C(6)-C(7)	109.8(3)
C(61)-C(6)-C(7)	111.2(3)
C(64)-C(6)-C(5)	111.4(3)
C(61)-C(6)-C(5)	109.2(3)
C(7)-C(6)-C(5)	105.7(3)
C(3)-C(7)-C(6)	105.0(3)
C(11)-N(1)-Mo(1)	177.4(2)
N(1)-C(11)-C(16)	118.9(3)
N(1)-C(11)-C(12)	117.9(3)
C(16)-C(11)-C(12)	123.1(3)
C(13)-C(12)-C(11)	116.9(4)
C(13)-C(12)-C(121)	122.6(4)
C(11)-C(12)-C(121)	120.3(3)
C(14)-C(13)-C(12)	120.8(4)
C(13)-C(14)-C(15)	121.5(4)
C(14)-C(15)-C(16)	121.0(4)
C(15)-C(16)-C(11)	116.6(4)
C(15)-C(16)-C(161)	122.1(4)
C(11)-C(16)-C(161)	121.3(3)
C(12)-C(121)-C(122)	113.5(4)
C(12)-C(121)-C(123)	109.0(4)
C(122)-C(121)-C(123)	112.1(4)
C(16)-C(161)-C(162)	110.5(3)
C(16)-C(161)-C(163)	113.1(4)
C(162)-C(161)-C(163)	110.5(3)
C(21)-N(2)-Mo(2)	176.7(2)
N(2)-C(21)-C(22)	119.5(3)
N(2)-C(21)-C(26)	117.8(3)
C(22)-C(21)-C(26)	122.5(3)
C(23)-C(22)-C(21)	117.6(3)
C(23)-C(22)-C(221)	121.7(3)

C(21)-C(22)-C(221)	120.7(3)
C(24)-C(23)-C(22)	120.9(4)
C(23)-C(24)-C(25)	121.1(4)
C(24)-C(25)-C(26)	121.3(4)
C(25)-C(26)-C(21)	116.4(4)
C(25)-C(26)-C(261)	123.0(3)
C(21)-C(26)-C(261)	120.6(3)
C(22)-C(221)-C(223)	109.6(3)
C(22)-C(221)-C(222)	113.5(3)
C(223)-C(221)-C(222)	110.6(3)
C(26)-C(261)-C(263)	113.4(4)
C(26)-C(261)-C(262)	109.2(3)
C(263)-C(261)-C(262)	110.9(4)
C(31)-O(1)-Mo(1)	143.20(19)
O(1)-C(31)-C(34)	107.6(3)
O(1)-C(31)-C(32)	112.7(3)
C(34)-C(31)-C(32)	109.2(3)
O(1)-C(31)-C(33)	106.0(3)
C(34)-C(31)-C(33)	111.6(3)
C(32)-C(31)-C(33)	109.7(3)
F(1)-C(33)-F(2)	107.4(4)
F(1)-C(33)-F(3)	108.0(3)
F(2)-C(33)-F(3)	107.2(3)
F(1)-C(33)-C(31)	110.1(3)
F(2)-C(33)-C(31)	112.4(3)
F(3)-C(33)-C(31)	111.6(3)
F(4)-C(34)-F(5)	107.5(4)
F(4)-C(34)-F(6)	107.3(4)
F(5)-C(34)-F(6)	106.6(4)
F(4)-C(34)-C(31)	113.1(4)
F(5)-C(34)-C(31)	113.1(3)

F(6)-C(34)-C(31)	108.9(3)
C(35)-O(2)-Mo(1)	141.6(2)
O(2)-C(35)-C(36)	114.1(3)
O(2)-C(35)-C(37)	106.2(3)
C(36)-C(35)-C(37)	110.6(4)
O(2)-C(35)-C(38)	105.9(3)
C(36)-C(35)-C(38)	108.7(3)
C(37)-C(35)-C(38)	111.3(4)
F(7)-C(37)-F(9)	107.6(5)
F(7)-C(37)-F(8)	108.3(5)
F(9)-C(37)-F(8)	106.9(5)
F(7)-C(37)-C(35)	109.3(5)
F(9)-C(37)-C(35)	112.1(5)
F(8)-C(37)-C(35)	112.5(4)
F(10)-C(38)-F(11)	107.5(4)
F(10)-C(38)-F(12)	107.5(3)
F(11)-C(38)-F(12)	106.8(3)
F(10)-C(38)-C(35)	113.0(3)
F(11)-C(38)-C(35)	109.5(3)
F(12)-C(38)-C(35)	112.3(3)
C(41)-O(3)-Mo(2)	140.2(2)
O(3)-C(41)-C(42)	113.3(3)
O(3)-C(41)-C(43)	106.6(3)
C(42)-C(41)-C(43)	109.4(3)
O(3)-C(41)-C(44)	107.7(3)
C(42)-C(41)-C(44)	110.3(3)
C(43)-C(41)-C(44)	109.4(3)
F(13)-C(43)-F(14)	107.5(3)
F(13)-C(43)-F(15)	106.6(3)
F(14)-C(43)-F(15)	106.3(3)
F(13)-C(43)-C(41)	113.6(3)

F(14)-C(43)-C(41)	110.2(3)
F(15)-C(43)-C(41)	112.1(3)
F(16)-C(44)-F(17)	106.8(3)
F(16)-C(44)-F(18)	105.9(3)
F(17)-C(44)-F(18)	107.2(3)
F(16)-C(44)-C(41)	113.3(3)
F(17)-C(44)-C(41)	113.1(3)
F(18)-C(44)-C(41)	110.0(3)
C(45)-O(4)-Mo(2)	143.9(2)
O(4)-C(45)-C(46)	113.6(3)
O(4)-C(45)-C(48)	105.6(3)
C(46)-C(45)-C(48)	109.8(3)
O(4)-C(45)-C(47)	107.9(3)
C(46)-C(45)-C(47)	109.8(3)
C(48)-C(45)-C(47)	110.1(3)
F(19)-C(47)-F(20)	107.8(3)
F(19)-C(47)-F(21)	106.8(3)
F(20)-C(47)-F(21)	106.5(3)
F(19)-C(47)-C(45)	112.8(3)
F(20)-C(47)-C(45)	112.5(3)
F(21)-C(47)-C(45)	110.1(3)
F(23)-C(48)-F(22)	108.0(3)
F(23)-C(48)-F(24)	107.3(3)
F(22)-C(48)-F(24)	107.1(3)
F(23)-C(48)-C(45)	109.8(3)
F(22)-C(48)-C(45)	112.0(3)
F(24)-C(48)-C(45)	112.5(3)
C(61)-O(6)-C(62)	116.7(5)
C(64)-O(8)-C(65)	117.7(4)
O(5)-C(61)-O(6)	125.4(5)
O(5)-C(61)-C(6)	126.0(4)

O(6)-C(61)-C(6)	108.5(4)
O(6)-C(62)-C(63)	105.9(7)
O(7)-C(64)-O(8)	123.7(4)
O(7)-C(64)-C(6)	125.9(4)
O(8)-C(64)-C(6)	110.4(4)
O(8)-C(65)-C(66)	109.2(4)
C(3X)-C(2X)-C(1X)	137.7(16)
C(2X)-C(3X)-C(4X)	115.2(15)
C(3X)-C(4X)-C(5X)	117.1(11)
C(3Y)-C(2Y)-C(1Y)	117.8(19)
C(4Y)-C(3Y)-C(2Y)	124(2)
C(3Y)-C(4Y)-C(5Y)	120(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. <u>Anisotropic displacement parameters $(\text{Å}^2 \times 10^3)$</u>

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mo(1)	18(1)	16(1)	26(1)	-3(1)	2(1)	-1(1)
Mo(2)	28(1)	14(1)	24(1)	-1(1)	-2(1)	-3(1)
C(1)	24(2)	22(1)	25(2)	-3(1)	0(1)	-4(1)
C(2)	28(2)	16(1)	27(2)	0(1)	-1(1)	-2(1)
C(3)	32(2)	21(2)	25(2)	-4(1)	-2(1)	-1(1)
C(4)	34(2)	19(1)	25(2)	-1(1)	-1(1)	-2(1)
C(5)	61(2)	22(2)	29(2)	-1(1)	-14(2)	-3(2)
C(6)	53(2)	24(2)	29(2)	-1(1)	-13(2)	3(2)
C(7)	58(2)	22(2)	36(2)	0(1)	-18(2)	-4(2)
N(1)	26(1)	17(1)	30(1)	-3(1)	2(1)	-4(1)
C(11)	41(2)	17(1)	30(2)	-3(1)	-2(1)	-4(1)
C(12)	46(2)	22(2)	36(2)	-3(1)	-8(2)	-8(2)
C(13)	67(3)	31(2)	41(2)	0(2)	-20(2)	-9(2)
C(14)	103(4)	33(2)	26(2)	-2(2)	-14(2)	-11(2)
C(15)	86(3)	31(2)	31(2)	-3(2)	13(2)	-8(2)
C(16)	55(2)	23(2)	31(2)	0(1)	9(2)	-3(2)
C(121)	35(2)	45(2)	44(2)	2(2)	-9(2)	-7(2)
C(122)	44(3)	126(6)	89(4)	27(4)	-2(3)	20(3)
C(123)	82(4)	63(3)	47(3)	-4(2)	4(2)	-36(3)
C(161)	51(2)	41(2)	41(2)	6(2)	22(2)	5(2)
C(162)	50(3)	58(3)	53(3)	3(2)	12(2)	-6(2)
C(163)	85(4)	51(3)	75(3)	6(2)	50(3)	6(3)
N(2)	31(1)	16(1)	27(1)	-2(1)	-1(1)	-5(1)
C(21)	41(2)	14(1)	29(2)	0(1)	-3(1)	-5(1)
C(22)	38(2)	18(1)	39(2)	1(1)	-6(2)	-6(1)
C(23)	50(2)	19(2)	51(2)	5(2)	-12(2)	-1(2)
C(24)	80(3)	26(2)	44(2)	13(2)	-13(2)	1(2)
C(25)	83(3)	26(2)	34(2)	9(2)	7(2)	-7(2)
C(26)	53(2)	21(2)	36(2)	2(1)	8(2)	-7(2)
C(221)	35(2)	21(2)	51(2)	6(2)	3(2)	3(1)
C(222)	39(2)	63(3)	80(3)	-2(3)	6(2)	-3(2)

C(223)	51(2)	53(3)	39(2)	-3(2)	1(2)	8(2)
C(261)	60(3)	29(2)	58(3)	9(2)	26(2)	-2(2)
C(262)	47(3)	42(2)	81(3)	19(2)	17(2)	-3(2)
C(263)	98(4)	66(3)	68(3)	0(3)	46(3)	1(3)
O(1)	18(1)	19(1)	47(1)	-4(1)	-2(1)	-1(1)
C(31)	17(2)	26(2)	48(2)	-5(1)	1(1)	-1(1)
C(32)	22(2)	40(2)	69(3)	2(2)	-1(2)	-9(2)
C(33)	25(2)	37(2)	76(3)	-16(2)	-8(2)	5(2)
F(1)	53(2)	97(2)	69(2)	-41(2)	-6(1)	28(2)
F(2)	39(1)	27(1)	148(3)	-7(2)	-10(2)	3(1)
F(3)	25(1)	53(2)	90(2)	-22(1)	-8(1)	10(1)
C(34)	32(2)	57(3)	47(2)	-3(2)	-3(2)	6(2)
F(4)	55(2)	95(2)	65(2)	33(2)	-2(1)	-8(2)
F(5)	39(1)	90(2)	56(2)	-12(1)	-13(1)	5(1)
F(6)	63(2)	88(2)	58(2)	-32(2)	-6(1)	27(2)
O(2)	28(1)	24(1)	36(1)	-7(1)	14(1)	-2(1)
C(35)	26(2)	36(2)	40(2)	-13(2)	11(2)	2(1)
C(36)	45(2)	37(2)	90(4)	-27(2)	32(2)	-6(2)
C(37)	54(3)	121(5)	44(3)	-21(3)	4(2)	39(3)
F(7)	48(2)	241(6)	95(3)	-57(3)	-26(2)	27(3)
F(8)	97(3)	182(4)	40(2)	-27(2)	2(2)	65(3)
F(9)	187(4)	135(4)	57(2)	30(2)	25(2)	105(3)
C(38)	34(2)	39(2)	56(3)	-12(2)	19(2)	-6(2)
F(10)	73(2)	35(1)	145(3)	-24(2)	69(2)	-17(1)
F(11)	32(1)	104(2)	63(2)	-26(2)	-1(1)	-1(1)
F(12)	44(1)	52(1)	67(2)	-13(1)	33(1)	-4(1)
O(3)	30(1)	23(1)	35(1)	-5(1)	0(1)	1(1)
C(41)	31(2)	24(2)	40(2)	-1(1)	1(2)	4(1)
C(42)	51(2)	39(2)	49(2)	-11(2)	4(2)	4(2)
C(43)	34(2)	35(2)	59(3)	-2(2)	9(2)	0(2)
F(13)	38(1)	56(2)	82(2)	-25(1)	-1(1)	-7(1)
F(14)	47(2)	51(2)	88(2)	17(1)	11(1)	-5(1)
F(15)	36(1)	45(1)	84(2)	-1(1)	9(1)	7(1)
C(44)	36(2)	34(2)	53(2)	5(2)	-3(2)	2(2)
F(16)	52(2)	32(1)	112(2)	17(1)	9(2)	15(1)
F(17)	88(2)	65(2)	53(2)	15(1)	-26(2)	-6(2)

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F(18)	35(1)	56(2)	74(2)	33(1)	-2(1)	-1(1)
O(4)	32(1)	22(1)	25(1)	-1(1)	2(1)	-7(1)
C(45)	29(2)	25(2)	26(2)	2(1)	-1(1)	-4(1)
C(46)	34(2)	41(2)	39(2)	5(2)	-6(2)	-9(2)
C(47)	41(2)	23(2)	33(2)	2(1)	1(2)	-4(1)
F(19)	48(1)	33(1)	58(2)	5(1)	-18(1)	4(1)
F(20)	61(2)	40(1)	47(1)	15(1)	15(1)	-4(1)
F(21)	70(2)	22(1)	39(1)	-3(1)	5(1)	-2(1)
C(48)	39(2)	30(2)	32(2)	1(1)	3(2)	-2(2)
F(22)	45(1)	53(1)	42(1)	-6(1)	16(1)	-6(1)
F(23)	68(2)	31(1)	45(1)	-2(1)	6(1)	15(1)
F(24)	44(1)	37(1)	36(1)	-11(1)	-3(1)	-6(1)
O(5)	63(2)	74(3)	79(3)	-6(2)	-4(2)	11(2)
O(6)	90(3)	41(2)	68(2)	7(2)	-22(2)	21(2)
O(7)	98(3)	71(2)	58(2)	-14(2)	12(2)	-28(2)
O(8)	80(2)	52(2)	34(2)	-8(1)	-6(2)	-1(2)
C(61)	72(3)	38(2)	39(2)	-8(2)	-12(2)	14(2)
C(62)	115(5)	68(4)	108(5)	-8(4)	-41(4)	51(4)
C(63)	270(13)	113(7)	134(8)	9(6)	-90(8)	101(8)
C(64)	67(3)	32(2)	40(2)	-1(2)	-5(2)	-2(2)
C(65)	103(4)	54(3)	38(2)	-7(2)	3(3)	7(3)
C(66)	153(6)	81(4)	45(3)	11(3)	1(3)	11(4)
C(1X)	118(11)	57(8)	54(7)	17(6)	-16(7)	-5(8)
C(2X)	93(7)	48(6)	50(5)	17(4)	-6(5)	3(5)
C(3X)	85(6)	41(6)	49(5)	22(4)	-1(5)	0(5)
C(4X)	93(7)	45(6)	60(6)	13(5)	-9(5)	-1(5)
C(5X)	68(7)	45(7)	32(6)	-3(5)	-22(5)	13(5)
C(1Y)	63(8)	21(7)	11(6)	7(6)	-15(6)	14(6)
C(2Y)	81(7)	32(6)	40(6)	16(5)	-6(5)	0(5)
C(3Y)	86(7)	42(7)	43(6)	14(6)	-7(6)	-9(6)
C(4Y)	88(8)	56(7)	49(7)	6(7)	-11(6)	-1(7)
C(5Y)	86(17)	96(14)	98(15)	5(13)	-19(17)	-19(12)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2}U^{11} + \ldots\ + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

Table II.5. **Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($\mathring{A}^2$x 10 ^{3})**

	x	y	z	U(eq)
H(1)	8560(30)	2936(13)	8348(10)	28
H(2)	9370(30)	3621(9)	8515(14)	28
H(5A)	8544	4419	7246	45
H(5B)	7311	4431	7616	45
H(7A)	6273	3320	7231	46
H(7B)	7361	3160	6806	46
H(13)	4666	2328	5666	56
H(14)	6144	2294	4955	65
H(15)	8157	2204	5212	59
H(121)	5223	2406	7228	50
H(12A)	3973	2899	6595	130
H(12B)	3213	2588	7063	130
H(12C)	3275	2411	6387	130
H(12D)	4170	1574	6648	96
H(12E)	3950	1719	7325	96
H(12F)	5264	1551	7119	96
H(161)	9292	1986	6683	53
H(16A)	9767	2841	5986	80
H(16B)	10678	2627	6479	80
H(16C)	9398	2844	6670	80
H(16D)	9629	1512	5817	105
H(16E)	10827	1805	6008	105
H(16F)	10007	1998	5466	105
H(23)	6616	5998	7539	48
H(24)	7704	6131	6688	60
H(25)	9577	5777	6564	57
H(221)	7263	5096	8629	43
H(22A)	5568	5857	8340	91
H(22B)	5347	5415	8794	91
H(22C)	5447	5305	8099	91

H(22D)	8472	5708	9053	71
H(22E)	7169	5727	9350	71
H(22F)	7525	6124	8858	71
H(261)	10805	4812	7429	58
H(26A)	11779	5780	7550	85
H(26B)	12559	5289	7631	85
H(26C)	11504	5413	8085	85
H(26D)	10655	4993	6388	116
H(26E)	12015	4928	6624	116
H(26F)	11484	5466	6505	116
H(32A)	11046	2356	7492	66
H(32B)	11933	2382	8057	66
H(32C)	10666	2664	8064	66
H(36A)	6695	3002	8921	85
H(36B)	5371	2982	9195	85
H(36C)	5535	2971	8492	85
H(42A)	11382	3606	7912	69
H(42B)	12801	3552	7804	69
H(42C)	12110	4042	7602	69
H(46A)	6717	4503	9372	57
H(46B)	6501	4001	9724	57
H(46C)	7221	3996	9114	57
H(62A)	4804	5054	6752	117
H(62B)	4356	4662	6263	117
H(63A)	6084	5404	6023	260
H(63B)	4682	5459	5854	260
H(63C)	5477	5044	5542	260
H(65A)	7746	3342	5139	78
H(65B)	8818	3691	5374	78
H(66A)	6588	4068	4954	139
H(66B)	7741	4013	4539	139
H(66C)	7786	4379	5095	139
H(1X1)	6905	189	9510	115
H(1X2)	6393	723	9349	115
H(1X3)	5580	346	9713	115
H(2X1)	7032	369	10492	76

H(2X2)	7785	756	10136	76
H(3X1)	6055	889	10929	70
H(3X2)	6293	1307	10447	70
H(4X1)	7950	925	11252	80
H(4X2)	7348	1458	11270	80
H(5X1)	9467	1522	10917	73
H(5X2)	8567	1723	10411	73
H(5X3)	9132	1183	10359	73
H(1Y1)	8827	1342	10472	48
H(1Y2)	8531	1094	9844	48
H(1Y3)	9170	779	10359	48
H(2Y1)	7367	816	10936	61
H(2Y2)	6730	1154	10446	61
H(3Y1)	7366	314	9978	68
H(3Y2)	6655	215	10571	68
H(4Y1)	5877	482	9504	77
H(4Y2)	5247	764	10034	77
H(5Y1)	3982	67	9762	141
H(5Y2)	4496	-36	10417	141
H(5Y3)	5084	-306	9861	141

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Acknowledgements

First and foremost, I must thank Professor Richard R. Schrock for giving me this amazing opportunity to spend the last two years researching and learning chemistry in one of the top labs in the country. He is understanding and an inspiration to every student that has an aspiration to achieve great things. I cannot graduate, however, before thanking my labmates, without whom science and time in the lab would have been much more confusing and dismal. Special note must be given to my organic savior, chemistry mentor, and great friend, Dr. Constantin Czekelius. I must mention, as well, Dr. Pia Lopez who laid the ground work for the studies of dimeric tungsten compounds. As for the rest of the Schrock group, I thank them for interesting conversation and entertainment during the late nights, specifically Nathan, who never ceased to listen with interest to all of my never-ending rambling!

I also would like to thank Dr. Peter Müller for his expertise in x-ray crystallography, who mounted and solved the structure of (5a), and Dr. David Bray for help with NMR experiments.

Lastly, I cannot overlook my present and future family. Without my parent's abundant support, I couldn't have done half of what I have accomplished in my life thus far. They gave me the strength, courage, and confidence to make all of my decisions, no matter how tough, and all of the steps towards a better life for myself. And not least, I thank my fiancé,Tim, with all my heart. If it weren't for his ears and shoulders from the very beginning, I would not be writing this acknowledgment section today. He listened to every detail and supported me through this entire process even from afar. For that, I am indebted.