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Synthesis of Oligoenes that Contain up to 15 Double Bonds from 1,6-Heptadiynes

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Abstract: This paper reports the synthesis of polyene oligomers ("oligoenes") that contain up to 15 double bonds that are identical to the "all five-membered ring" species formed through cyclopolymerization of diisopropyldipropargylmalonate. The oligoenes contain an isopropylidene unit at each end. The isolated oligoenes range from the "dimer" (a pentaene, (*E*)-di-1,2-[1-(2-methyl-propenyl)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-enyl]-ethene (**3b$_2$**)) to the "heptamer" (**3b$_7$**, a pentadecaene). Oligoenes **3b$_2$**, **3b$_3$**, **3b$_4$**, **3b$_5$**, and **3b$_7$** were prepared through Wittig-like reactions between aldehydes and the appropriate monometallic Mo alkylidene or bimetallic Mo bisalkylidene species whose alkylidene is derived from an identical five-membered ring monomeric unit. Compounds **3b$_2$**, **3b$_4$**, and **3b$_6$** were prepared through McMurry coupling reactions of aldehydes. A representative aldehyde (the "monomeric" aldehyde) is diisopropyl-3-formyl-4-(2-methylprop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate (**2b**), McMurry coupling of which yields **3b$_2$**. A heptaene that contains a six-membered ring in the central unit also was prepared in a Wittig-like reaction involving a bimetallic Mo alkylidene; this species is a model for oligoenes that contain both six-membered and five-membered rings. X-ray structures of two bimetallic species that are employed in the synthesis of the oligoenes are reported.

Introduction

Considerable progress has been made in the synthesis and optical characterization of conjugated polymers such as all-*trans* polyacetylene. These studies have been motivated in large part by the semiconducting properties of these systems and the advent of rational synthetic approaches toward the design of molecules for displays, lasers, photovoltaics, and nonlinear optical materials.[1] Polyacetylene, the simplest π-conjugated organic polymer, is highly conductive when doped and possesses a high third-order susceptibility ($\chi^{(3)}$), a measure of the change in refractive index under the action of an electromagnetic field. Materials that have a high third-order susceptibility are attractive candidates for photonic switches and other devices. Potential disadvantages of polyacetylene include its relatively high sensitivity to oxygen and its insolubility in common organic solvents. (*tert*-Butyl-capped polyenes are known to become relatively insoluble after $N \approx 13$, where N is the number of double bonds.[2]) Substituted polyacetylenes such as polyphenylacetylenes[3] or poly[1,6-heptadiynes][4] are often more soluble. However, substituted polyacetylenes are not necessarily regioregular, and regioerrors in the polyene chain can degrade or destroy electronic and optical properties. Research into potential applications of conjugated organic polymers has expanded to include many other conjugated polymers (or related oligomers) such as polyparaphenylenevinylenes, polyparaphenyleneethynylenes, polythiophenes, polypyrroles, etc.

In addition to their potential applications in optoelectronic devices, conjugated polymers are of fundamental interest as models for understanding the electronic and optical properties of one-dimensional, conjugated π-electron systems. Short, model polyenes have received considerable experimental and theoretical attention in recent years.[5] One- and two-photon absorption, fluorescence, and fluorescence excitation experiments and the measurement of excited-state decays have led to a deeper

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[†] Massachusetts Institute of Technology.

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(1) (a) Samuel, I. D. W. *Philos. Trans. R. Soc. London, Ser. A* **2000**, *358*, 193. (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121.

(2) Knoll, K.; Krouse, S. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4424.

(3) (a) Masuda, T.; Abdul Karim, S. M.; Nomura, R. *J. Mol. Catal. A: Chem.* **2000**, *160*, 125. (b) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1986**, *81*, 122. (c) Mizumoto, T.; Masuda, T.; Higashimura, T. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2555. (d) Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984**, *17*, 51. (e) Masuda, T.; Fujimori, J. I.; Abrahman, M. Z.; Higashimura, T. *Polym. J.* **1993**, *25*, 535.

(4) (a) Choi, S.-K.; Gal, Y.-S.; Jin, S.-H.; Kim, H. K. *Chem. Rev.* **2000**, *100*, 1645. (b) Lam, J. W. Y.; Tang, B. Z. *J. Polym. Sci.* **2003**, *41*, 2607. (c) Krause, J. O.; Wang, D.; Anders, U.; Weberskirch, R.; Zarka, M. T.; Nuyken, O.; Jaeger, C.; Haarer, D.; Buchmeiser, M. R. *Macromol. Symp.* **2004**, *217*, 179. (d) Buchmeiser, M. R. *Monatsh. Chem.* **2003**, *134*, 327.

(5) Christensen, R. L. The Electronic States of Carotenoids. In *The Photochemistry of Carotenoids*; Frank, H. A., Young, A. J., Britton, G., Cogdell, R. J., Eds.; Kluwer Academic Publishers: Dordrecht, 1999; Vol. 8, pp 137–159.

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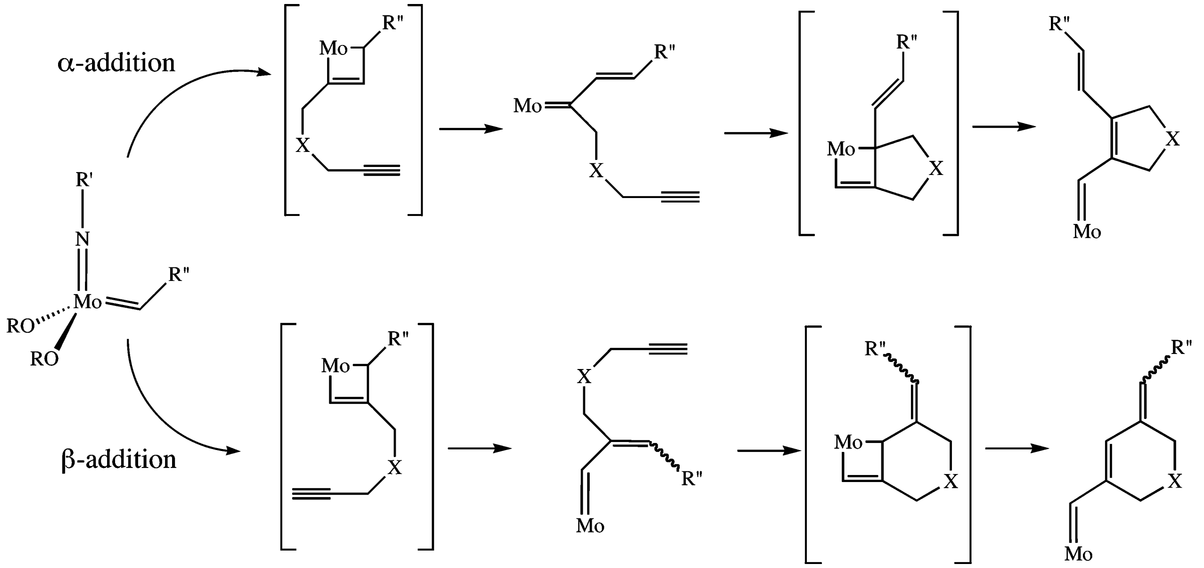
Scheme 1. Reaction of Mo(NR′)(CHR″)(OR)$_2$ with 1,6-Heptadiyne Derivatives (e.g., X = C(CO$_2$Et)$_2$)



understanding of the basic photophysics and photochemistry of these systems.[6] One important outcome of the work on simple polyenes was the discovery of a low energy, symmetry forbidden ($1^1A_g^- \rightarrow {}^1A_g^-$) transition ($S_0 \rightarrow S_1$) that lies below the strongly allowed $1^1A_g^- \rightarrow 1^1B_u^+$ transition ($S_0 \rightarrow S_2$) associated with the excitation of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in simple versions of molecular orbital theory.[7]

There also is considerable interest in the spectroscopy and photochemistry of longer polyenes and, in particular, how the energies and dynamics of polyene excited states change with increasing π-electron delocalization. Naturally occurring polyenes in the form of carotenoids play important roles in photobiology, e.g., in vision and photosynthesis, and their strongly allowed $S_0 \rightarrow S_2$ transitions provide a broad palette of colors to plants and animals. Carotenoids function as light-harvesting pigments in photosynthesis, absorbing light and transferring energy to other antenna pigments and chlorophylls in reaction centers.[8] Carotenoids also play crucial protective roles in these biological systems; their low-energy triplet states quench chlorophyll triplet states, thus preventing irreversible damage due to the photosensitization of singlet oxygen. Synthetic polyenes/oligoenes could play similar roles in artificial photosynthetic systems. Understanding how excited-state energies and lifetimes change with conjugation length and other structural modifications would allow optimization of light harvesting and photoprotection in the design of light-driven, synthetic systems.

Systematic study of the optical and electronic properties of "long" polyenes has been limited to molecules with $N \leq 15$ as a consequence of a lack of synthetic routes to longer polyenes and their limited solubilities. It also is interesting to note that $N \leq 13$ for the longest natural carotenoids such as β-carotene ($N = 11$), lycopene ($N = 11$), and astaxanthin ($N = 13$).[9] Much work remains to be done to extend our understanding of the optical properties of the short polyenes and carotenoids to much longer oligomers and ultimately polymers. As mentioned earlier, substituted polyenes tend to suffer from conformational disorder[10] and in some cases regioerrors, which complicate the interpretation of their optical spectra and other electronic properties. Investigation of the optical properties of a range of soluble, planar, regioregular polyenes/oligoenes with known structures would offer critical advantages in relating their optical and electronic properties to conjugation length, geometry, and other variations in molecular structure.

Poly[1,6-heptadiynes] such as poly[dialkyldipropargylmalonates] are highly conjugated and relatively soluble and appear to be relatively stable in air.[4] These polymers were first prepared using "classical" olefin metathesis (alkylidene) catalysts that are prepared from Mo or W halides or oxyhalides and some alkylating agent.[4] In general these polymers do not have a regular structure. As a consequence of addition of the first triple bond to the alkylidene to give either an α- or a β-substituted metallacyclobutene, both six-membered rings and five-membered rings are usually formed (Scheme 1).

We first explored the polymerization of diethyldipropargylmalonate (DEDPM) and related derivatives with well-defined Mo-based olefin metathesis catalysts, primarily Mo(NAr)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ (Ar = 2,6-i-Pr$_2$C$_6$H$_3$, OR$_{F6}$ = OCMe(CF$_3$)$_2$), in 1992.[11] These studies confirmed that high oxidation state Mo alkylidenes were catalysts for cyclopolymerization reactions of this general type. The resulting polymer formed using Mo(NAr)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ as the initiator was shown to contain both five-membered and six-membered rings. Later we showed that polyenes that contain all six-membered rings were formed when dicarboxylate catalysts of the type

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(6) Polívka, T.; Sundström, V. *Chem. Rev.* **2004**, *104*, 2021.

(7) (a) Hudson, B.; Kohler, B. *Ann. Rev. Phys. Chem.* **1974**, *25*, 437. (b) Hudson, B. S.; Kohler, B. E.; Schulten, K. Linear Polyene Electronic Structure and Potential Surfaces. In *Excited States*; Lim, E. D., Ed.; Academic Press: New York, 1982; Vol. 6, pp 1−95. (c) Christensen, R. L.; Barney, E. A.; Broene, R. D.; Galinato, M. G. I.; Frank, H. A. *Arch. Biochem. Biophys.* **2004**, *430*, 30.

(8) (a) Frank, H. A.; Cogdell, R. J. *Photochem. Photobiol.* **1996**, *63*, 257. (b) Frank, H. A.; Young, A. J.; Britton, G.; Cogdell, R. J. In *Advances in Photosynthesis*; Govindjee, Ed.; Kluwer Academic Publishers: Dordrecht, 1999.

(9) Zechmeister, L. *Cis-trans Isomeric Carotenoids, Vitamins A, and Arylpolyenes*; Academic Press: New York, 1962.

(10) Wood, P.; Samuel, I. D. W.; Schrock, R. R.; Christensen, R. L. *J. Chem. Phys.* **2001**, *115*, 10955.

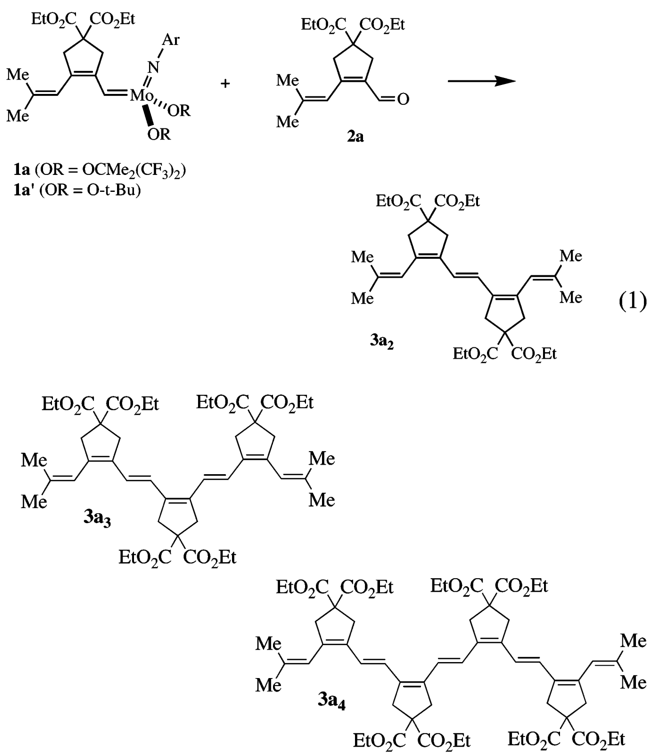
(11) (a) Fox, H. H.; Schrock, R. R. *Organometallics* **1992**, *11*, 2763. (b) Fox, H. H.; Wolf, M. O.; O'Dell, R.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827.

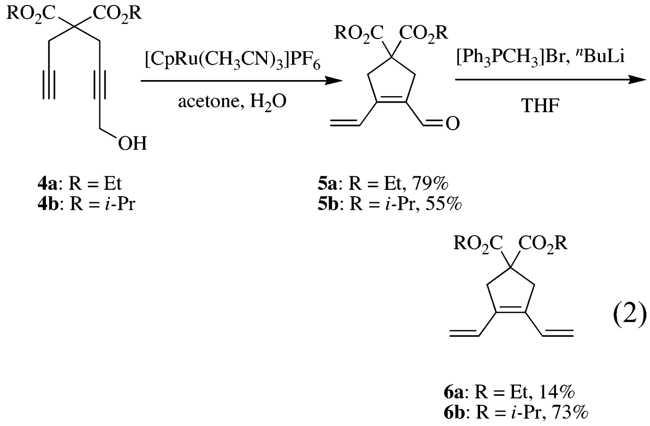
$Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_3)(O_2CCPh_3)_2$ were employed.[12] DEDPM polymers that contain only six-membered rings have λ_{max} values that are lower by 20−30 nm for a given apparent chain length than those for polymers that contain both five- and six-membered rings, consistent with a lower effective conjugation length, presumably as a consequence of twisting of the polymer chain. Buchmeiser and co-workers have shown that $Mo(NAr)(CHCMe_2Ph)(OCMe_3)_2$ catalysts will polymerize DEDPM to yield polymers that contain >95% five-membered rings.[13] Advantages of poly[1,6-heptadiynes] that contain only five-membered rings include the single alternating *cis*,*trans* structure and the potentially relatively rigid extended chain if conjugation is maintained. Since *all* polymerizations that begin with neopentylidene or neophylidene initiators have a high rate of polymerization versus initiation in polymerizations of this type, we recently prepared initiators that will initiate rapidly relative to the rate of propagation, including one that contains the very type of five-membered ring being formed in a cyclopolymerization reaction, i.e., **1a'** in eq 1.[14] We also showed that **1a** would react with aldehyde **2a** to yield the "dimer", **3a$_2$**, cleanly and in relatively high yield, in a Wittig-like reaction. Finally, we showed that upon treatment of **1a′** with 1.5 equiv of DEDPM, followed by quenching with **2a**, it was possible to isolate from the product mixture the "trimer" **3a$_3$** and "tetramer" **3a$_4$** as pure slightly air-sensitive compounds. We have prepared relatively short *tert*-butyl-capped polyenes previously through stoichiometric Wittig-like reactions related to the reaction shown in eq 1.[15]

One might imagine that variations of the reaction shown in eq 1 could be employed to prepare longer oligomeric polyenes analogous to **3a$_3$** and **3a$_4$** that have a single structure and chain length. Spectroscopic studies of a well-defined series of such compounds are of interest from a theoretical perspective, especially if $N > 11$. Systematic studies of this type are rare.[16] In this paper we report the synthesis of oligomers analogous to **3a$_3$** and **3a$_4$** that contain up to 7 monomer units ($N = 15$). These results establish a methodology that could prove useful for preparing long oligomers of other dialkyldipropargylmalonates, and possibly also long oligomers of other 1,6-heptadiynes. Studies of this type we hope will allow us to understand how variations in molecular structure alter the physical and optical properties of those materials. We can then return to applications that involve analogous polymeric materials with some confidence that we understand the fundamental properties of such materials as a function of structure and chain length.

Results and Discussion

Synthesis of Bimetallic 5- and 6-Membered Ring Species. One strategy for the synthesis of symmetric oligomers of type **3** is to prepare bimetallic species related to **1**. Dienal **5a** was prepared employing a ruthenium catalyzed cyclization of diynol





4a following a protocol published by Trost and co-workers (eq 2).[17] A Wittig olefination of **5a** yielded triene **6a**. Triene **6a** could be isolated only in low yield even though different reaction conditions (DMSO/NaH, THF/NaH, THF/*n*-BuLi) and various chromatographic separation techniques were employed. Significant decomposition of **6a** was observed at room temperature, even under dinitrogen. Therefore we believe that **6a** may be thermally unstable. Nevertheless, if compound **6a** is used immediately after it is prepared, bimetallic **7** can be isolated in good yield (eq 3). NMR studies are consistent with **7** having the *syn*,*syn* alkylidene configuration shown. The alkylidene H_α resonance is found at 12.65 ppm in CD_2Cl_2 with $J_{CH} = 125$ Hz. (Such coupling constants are usually routinely obtained through detection of ^{13}C satellites in high quality proton NMR spectra.) A J_{CH} value of 125 Hz is a typical *syn* alkylidene CH coupling constant in a high oxidation state alkylidene of this general type.[18]

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(12) Schattenmann, F. J.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3295.

(13) (a) Anders, U.; Nuyken, O.; Buchmeiser, M. R.; Wurst, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 4044. (b) Anders, U.; Nuyken, O.; Buchmeiser, M. R.; Wurst, K. *Macromolecules* **2002**, *35*, 9029. (c) Anders, U.; Nuyken, O.; Buchmeiser, M. R. *J. Mol. Catal. A: Chem.* **2004**, *213*, 89.

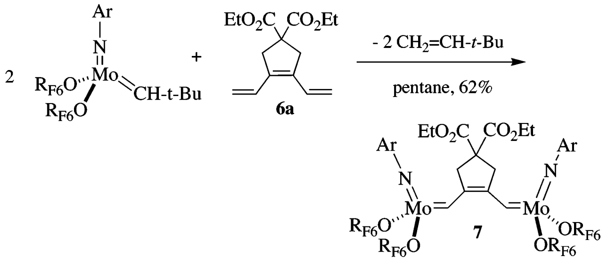
(14) Adamchuk, J.; Schrock, R. R.; Tonzetich, Z. J.; Müller, P. *Organometallics* **2006**, *25*, 2364.

(15) Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.

(16) Christensen, R. L.; Fakash, A.; Meyers, J. A.; Samuel, I. D. W.; Wood, P.; Schrock, R. R.; Hultzsch, K. C. *J. Phys. Chem.* **2004**, *108*, 8229.

(17) (a) Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2005**, *127*, 4763. (b) Trost, B. M.; Older, C. M. *Organometallics* **2002**, *21*, 2544.

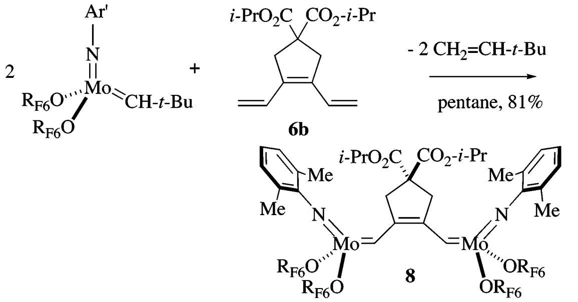
(18) (a) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1. (b) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.



(3)

Crystals of **7** suitable for an X-ray crystallographic analysis could be obtained readily. Its structure (Figure 1 and Table 1) is unremarkable and, therefore, is not discussed in detail. Selected distances and angles can be found in Table 2. It should be noted that the isopropyl groups in the imido ligands are turned away from the esters slightly, consistent with some steric crowding.

The difficulty of preparing and handling **6a** prompted us to explore analogues that contain other esters, in particular, isopropyl esters. Compounds **5b** and **6b** (eq 2) proved to be highly crystalline and readily isolated after minimal workup; only passage through a silica gel plug is necessary. In contrast to **6a**, **6b** showed no signs of decomposition upon storage in the solid state under dinitrogen. Interestingly, attempts to isolate the bimetallic isopropyl ester analogue of **7** failed, possibly for steric reasons that were hinted at in the X-ray structure of **7** (vide supra). However, a compound related to **7** could be prepared in good yield by employing the sterically less bulky 2,6-di*methyl*phenylimido ligand (Ar' = 2,6-$Me_2C_6H_3$), as shown in eq 4. NMR data for **8** are analogous to those for **7** (δH_α = 12.66 ppm in CD_2Cl_2, J_{CH} = 128 Hz, δC_α = 275.3 ppm).



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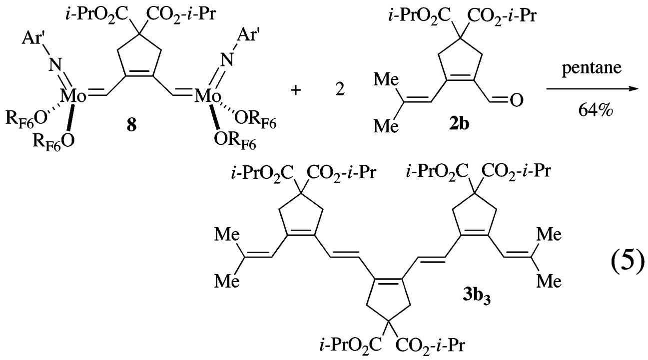
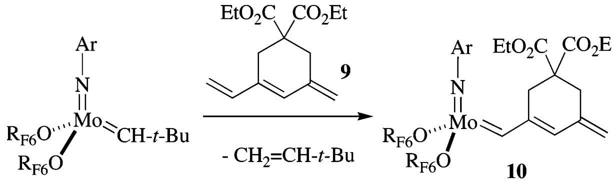


(5)

Upon treatment of **8** with **2b** (which was prepared in a Ru-catalyzed cyclization similar to compound **2a**; eq 1), the trimeric heptaene **3b$_3$** could be obtained in good yield as a pale yellow solid (eq 5). Compound **3b$_3$** is analogous to the ethyl ester version (**3a$_3$**) that was described in the introduction. In all such Wittig-like reactions the initial Mo product is believed to be Mo(O)(NR)(OR')$_2$. Such species have never proved isolable and are believed to be unstable with respect to bimolecular ligand scrambling reactions; therefore they are left out of equations that describe reactions in which they presumably are formed initially.

The reaction between 1-vinyl-3-methylene-5,5-bis(carboxyethyl)cyclohex-1-ene (**9**) and Mo(NAr)($CHCMe_3$)(OR_{F6})$_2$ has been reported to produce Mo(NAr)[1-methylidene-3-methylen-5,5-bis(carboxyethyl)cyclohex-1-ene)](OR_{F6})$_2$ (**10**; eq 6) in low yield.[11b] An X-ray structure of a compound analogous to **10**, but lacking the exo methylene group on the six-membered ring, has been reported.[14] A reaction analogous to that shown in eq 6 with a molybdenum complex that contains the less sterically demanding 2-*tert*-butyl-phenyl-imido ligand yields the bimetallic species (**11**) shown in eq 7. Compound **11** is obtained as a brown powder that is significantly more soluble than the other bimetallic compounds discussed thus far. It can be separated from traces of the starting neopentylidene complex through recrystallization from pentane. The spectroscopic features of the molecule are consistent with the proposed bimetallic structure shown in eq 7. The primary alkylidene proton resonance is found as a singlet at 12.38 ppm in benzene-d_6 with a J_{CH} value of 125 Hz, consistent with formulation of the species as a *syn* alkylidene. The ^{13}C NMR spectrum shows two alkylidene resonances at 271.06 and 259.03 ppm. The upfield resonance is assigned to the primary alkylidene carbon on the basis of an observed coupling of the alkylidene carbon to one proton.



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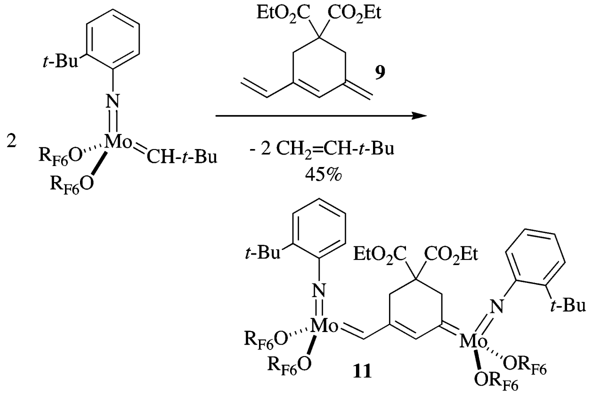


(7)

Also consistent with the proposed formulation of **11** is its reaction with 2 equiv of aldehyde **2a** to yield a “trimer” (**12**, eq 8) that contains a six-membered ring in the center. Two isomers of **12** are observed in a ratio of ~2:1. All NMR data are consistent with formation of *E* and *Z* isomers, as shown in eq 8. This result suggests that oligomers or polymers that contain both five-membered and six-membered rings are likely to contain many isomers as a consequence of *E* and *Z* isomers being formed. This may be one reason why polymers that contain both five-membered and six-membered rings generally are more soluble than those that contain only five-membered

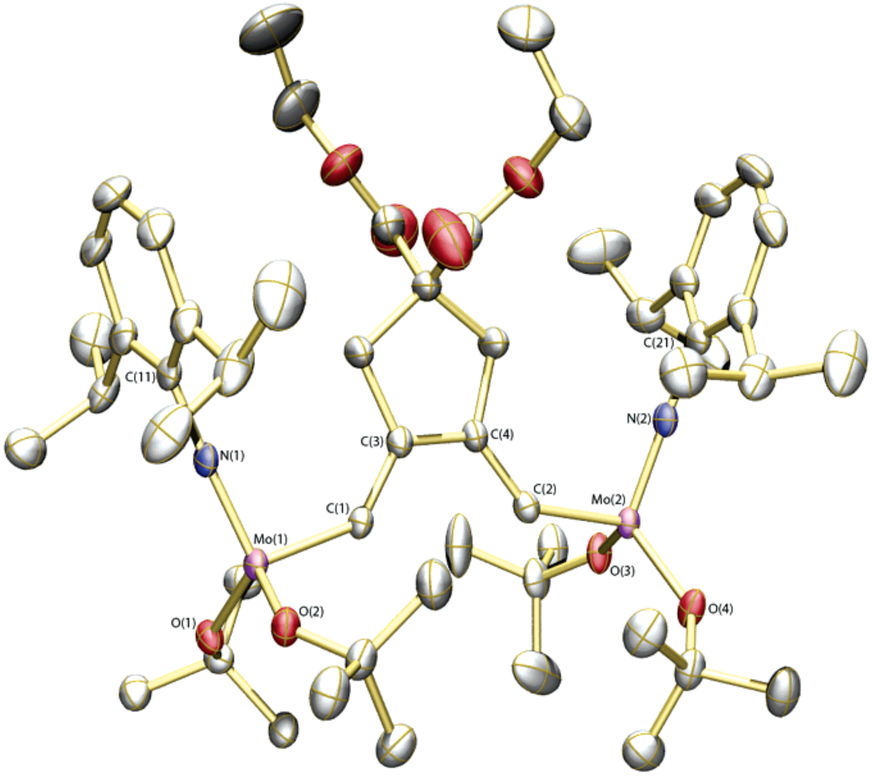


Figure 1. POV-ray rendering (ellipsoids at 50%) of the molecular structure of **7**. Fluorine atoms, hydrogen atoms, and the cocrystallized pentane molecule are omitted for clarity.

Table 1. Crystal Data and Structure Refinement Parameters for **7** and **17**[a]

compound	7	17
reciprocal net ident.	**05196**	**05149**
empirical formula	$C_{55.50}H_{68}F_{24}Mo_2N_2O_8$	$C_{79}H_{110}F_{24}Mo_2N_2O_{14}$
formula weight	1539.00	1959.57
crystal system	monoclinic	monoclinic
space group	$P2(1)/n$	$P2(1)/n$
unit cell dimensions	$a = 11.0704(4)$ Å	$a = 10.1034(7)$ Å
	$b = 27.1993(10)$ Å	$b = 29.987(2)$ Å
	$c = 22.5569(9)$ Å	$c = 14.9740(10)$ Å
	$\alpha = \gamma = 90°$	$\alpha = \gamma = 90°$
	$\beta = 90.8330(10)°$	$\beta = 104.099(2)°$
volume	6791.3(4) Å^3	4400.0(5) Å^3
Z	4	2
density (calculated)	1.505 g/cm^3	1.479 g/cm^3
absorption coefficient	0.484 mm^{-1}	0.396 mm^{-1}
$F(000)$	3116	2020
theta range for data collection	1.75° to 28.70°	1.95° to 22.72°
index ranges	$-14 \leq h \leq 14$	$-10 \leq h \leq 10$
	$-36 \leq k \leq 36$,	$0 \leq k \leq 32$
	$-30 \leq l \leq 30$	$0 \leq l \leq 16$
reflections collected	135 769	57 906
independent reflections	17 523 [R(int) = 0.0699]	5908 [R(int) = 0.0417]
completeness to theta = 28.70°	100.0%	100.0%
max. and min. transmission	0.9623 and 0.9180	0.9615 and 0.9075
data/restraints/parameters	17 523/131/913	5908/1360/863
goodness-of-fit on F^2	1.066	1.120
final R indices [$I > 2\sigma(I)$]	R1 = 0.0485, wR2 = 0.1199	R1 = 0.0983, wR2 = 0.2184
R indices (all data)	R1 = 0.0767, wR2 = 0.1332	R1 = 0.1112, wR2 = 0.2280
largest diff. peak and hole	1.613 and −0.375 eÅ^{-3}	1.447 and −1.044 eÅ^{-3}

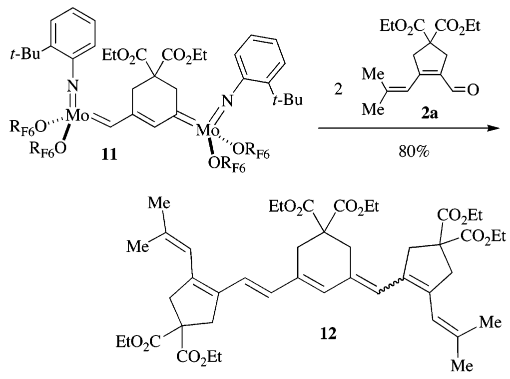
[a] In each case crystal data were recorded at 100 K with $\lambda = 0.710\,73$ Å; the refinement method was full-matrix least-squares on F^2, and the absorption correction was semiempirical from equivalents.

rings. The λ_{max} value for **12** is 384 nm (in CH_2Cl_2), 20 nm lower than λ_{max} for the all five-membered ring trimer in CH_2Cl_2 (404 nm, vide infra and Table 3). Although more studies of other oligoenes that contain six-membered ring "errors" are necessary, it would appear that the presence of one six-membered ring leads to a significant decrease in λ_{max}.

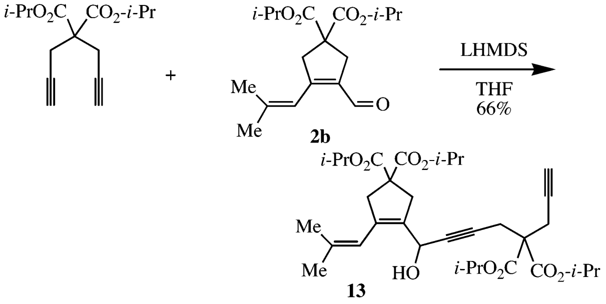
"Dimeric" and "Trimeric" Aldehydes and Reactions That Employ Them. We envisioned that the same methodology used to prepare aldehydes **2a** and **2b** might be employed to synthesize longer chain analogues. In order to test this hypothesis, aldehyde **2b** was treated with monodeprotonated diisopropyldipropargylmalonate (eq 9). The resulting propargylic alcohol (**13**) proved,

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **7** and **17**

7		17	
Mo(1)−N(1)	1.718(3)	Mo(1)−N(1)	1.697(7)
Mo(1)−C(1)	1.911(3)	Mo(1)−C(1)	1.925(8)
Mo(1)−O(1)	1.918(2)	Mo(1)−O(1)	1.938(5)
Mo(1)−O(2)	1.923(2)	Mo(1)−O(2)	1.927(7)
Mo(2)−N(2)	1.725(3)	Mo(1)−O(1E)	2.388(11)
Mo(2)−C(2)	1.914(3)	C(1)−C(2)	1.411(11)
Mo(2)−O(4)	1.927(2)	C(2)−C(6)	1.354(11)
Mo(2)−O(3)	1.940(2)	C(6)−C(7)	1.428(11)
C(1)−C(3)	1.434(4)	C(7)−C(7A)	1.343(15)
C(2)−C(4)	1.421(4)	N(1)−Mo(1)−C(1)	98.6(3)
C(3)−C(4)	1.378(4)	N(1)−Mo(1)−O(1)	113.1(3)
N(1)−Mo(1)−C(1)	98.98(13)	N(1)−Mo(1)−O(2)	119.2(3)
O(1)−Mo(1)−O(2)	115.38(10)	O(1E)−Mo(1)−C(1)	167.7(5)
Mo(1)−N(1)−C(11)	177.4(2)	O(1E)−Mo(1)−N(1)	93.4(5)
Mo(1)−C(1)−C(3)	138.2(2)	O(1)−Mo(1)−O(2)	120.9(3)
N(2)−Mo(2)−C(2)	98.51(13)	Mo(1)−N(1)−C(14)	171.8(6)
O(3)−Mo(2)−O(4)	116.98(10)	Mo(1)−C(1)−C(2)	137.3(6)
Mo(2)−N(2)−C(21)	176.7(2)	C(1)−C(2)−C(6)	127.1(7)
Mo(2)−C(2)−C(4)	139.7(2)	C(2)−C(6)−C(7)	127.0(7)
C(4)−C(3)−C(1)	126.4(3)	C(6)−C(7)−C(7A)	125.5(9)
C(3)−C(4)−C(2)	125.7(3)		

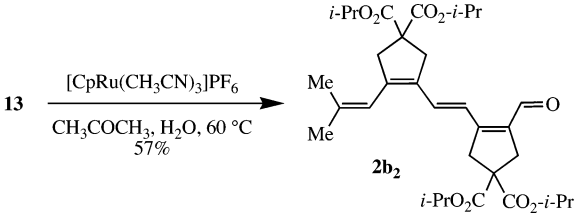


(8)



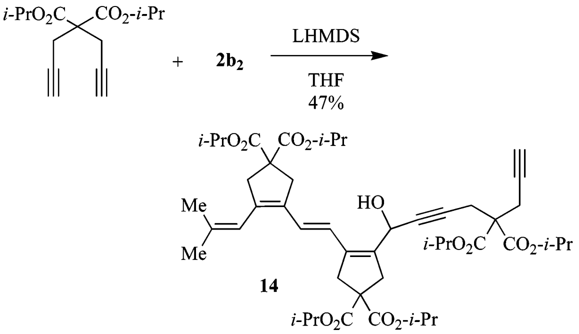
(9)

not unexpectedly, to be sensitive to traces of acid. For example, when **13** was dissolved in CDCl$_3$, which contained traces of HCl, clean formation of the cumulene through loss of water was observed over the course of 1 h. Nevertheless **13** could be cyclized to the "dimeric" aldehyde **2b$_2$** (eq 10). The reaction

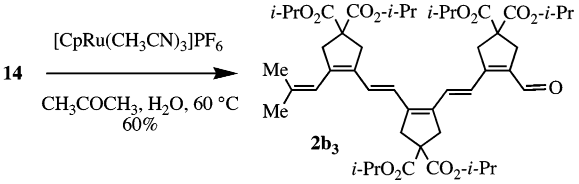


(10)

conditions for this cyclization had to be chosen carefully. It was found that a 9:1 mixture of acetone and water at reflux as well as a high catalyst loading was necessary. For example, with a low catalyst loading (2%) the starting material was consumed quickly, but only traces of the desired product could be isolated. Dimeric aldehyde **2b$_2$** is bright yellow, is stable in air, and can be stored for long periods. The reaction sequence shown in eqs 11 and 12 produced the "trimeric" aldehyde **2b$_3$** as a deep yellow solid. Like **2b$_2$**, aldehyde **2b$_3$** crystallizes readily in pure form after filtering the reaction mixture through a silica gel plug and evaporating the solvent. This methodology has not yet been employed to prepare longer polyenals.

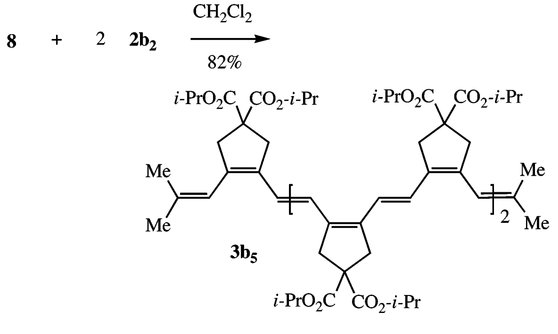


(11)

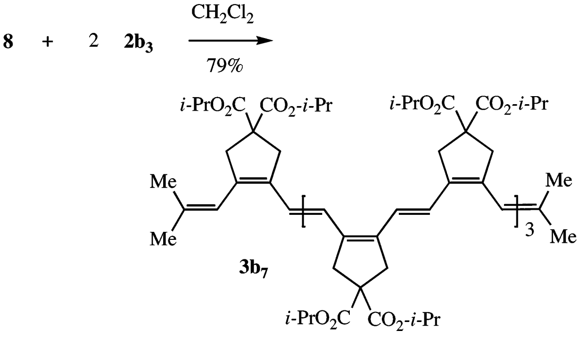


(12)

With **8**, **2b$_2$**, and **2b$_3$** in hand, the stage was set to synthesize longer odd-numbered analogues of **3b$_3$**. Reactions between **8** and **2b$_2$** and **2b$_3$** in methylene chloride yielded the "pentameric" undecaene (eq 13) and the "heptameric" pentadecaene (eq 14), respectively, in good yields as red microcrystalline solids. The reactions are relatively rapid (minutes), and the products can be precipitated readily from solution in high purity. They are



(13)

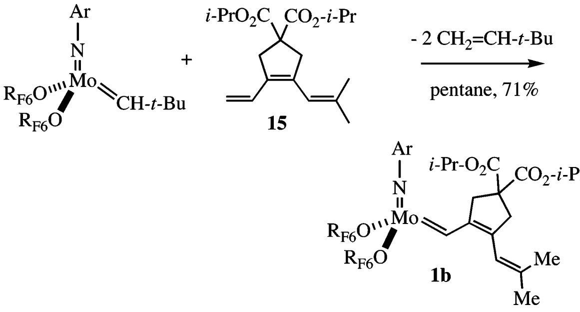


(14)

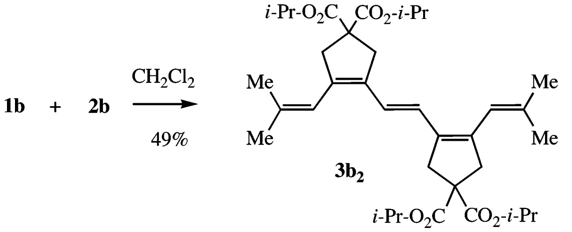
Table 3. Electronic Transitions of Oligoenes in Dichloromethane, Acetonitrile, and Benzene[a]

oligomer	solvent	E(0–2)	E(0–1)	λ_{max}(0–1)	E(0–0)	ϵ(0–1)/10^4
dimer (**3b$_2$**)	CH_2Cl_2	29 411	28 090	356	26 810	
trimer (**3b$_3$**)	CH_2Cl_2	25 773	24 752	404	23 640	4.4
tetramer (**3b$_4$**)	CH_2Cl_2	24 038	23 041	434	21 978	
pentamer (**3b$_5$**)	CH_2Cl_2	23 041	21 739	460	20 661	9.5
hexamer (**3b$_6$**)	CH_2Cl_2	21 930	21 008	476	19 841	11.0
heptamer (**3b$_7$**)	CH_2Cl_2	21 459	20 243	494	19 157	14.0
dimer	CH_3CN	29 762	28 409	352	27 100	
trimer	CH_3CN	26 042	25 000	400	23 809	
tetramer	CH_3CN	24 510	23 364	428	22 371	
pentamer	CH_3CN	23 256	22 026	454	20 964	
hexamer	CH_3CN	22 222	21 368	468	20 284	
heptamer	CH_3CN	21 930	20 576	486	19 455	
dimer	C_6H_6			340		6.9
trimer	C_6H_6			388		8.2
tetramer	C_6H_6			432		9.2
pentamer	C_6H_6			458		10.0
heptamer	C_6H_6			492		11.0

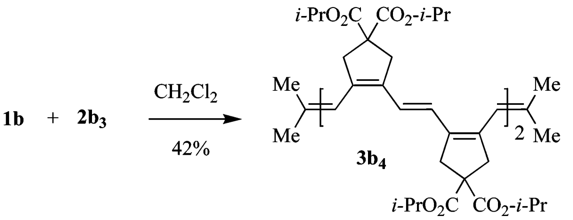
[a] The units of the transition energies are cm^{-1}, the units of λ are nm, and the units of ϵ are cm^{-1} M^{-1}.



(15)



(16)

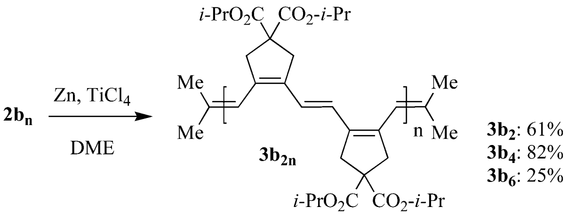


(17)

relatively insoluble in pentane, ether, or benzene but soluble in dichloromethane. Unfortunately, the oligoenes tend to form microcrystalline fibrous solids that resemble cotton candy. So far we have not been able to prepare single crystals that are suitable for X-ray studies.

Reactions of the type shown in eqs 5, 13, and 14 yield oligoenes that contain an odd number of repeat units. Even-membered oligoenes are not accessible directly in pure form using this method. (Of course, mixtures that contain even-membered oligoenes could be generated in reactions between **8** and a mixture of **2b$_2$** and **2b$_3$**, for example.) We envisioned that reaction of a complex related to **1a** bearing a suitably substituted vinyl-cyclopenten-alkylidene would provide access to both odd and even oligoenes upon reaction with aldehydes **2b**, **2b$_2$**, and **2b$_3$**. Triene **15** was prepared readily in a manner analogous to that described for the synthesis of **6b** (eq 4) and added to Mo(NAr)(CH-*t*-Bu)(OR_{F6})$_2$ to yield **1b** in good yield (eq 15). Reaction of **1b** with the monomeric aldehyde **2b** or trimeric aldehyde **2b$_3$** yielded the pale yellow, dimeric pentaene **3b$_2$** and the deep orange, tetrameric nonaene **3b$_4$**, respectively (eqs 16 and 17).

The methodology for synthesizing odd- and even-membered oligoenes employing Mo complexes as Wittig reagents consumes Mo reagents on a stoichiometric basis, although the reactions are clean and the yields are high. An alternative pathway for the synthesis of even-membered oligoenes involves McMurry coupling of two aldehydes. Initially it was not clear that highly conjugated oligoenes would tolerate the low valent titanium species present in a McMurry reaction. We were pleased to find that reaction of aldehydes **2b**, **2b$_2$**, or **2b$_3$** with an excess of a mixture of $TiCl_4$ and Zn afforded dimeric pentaene **3b$_2$**, tetrameric nonaene **3b$_4$**, and hexameric tridecaene **3b$_6$**, respectively (eq 18). The lower yield of **3b$_6$** is not surprising in reactions of this type given the likely increasing sensitivity of longer chain polyenes under the reaction conditions.



(18)

Transition energies for the strongly allowed $S_0 \rightarrow S_2$ transitions in polyenes have been shown to follow eq 19 where N is the number of double bonds.[16,19]

$$E(N) = A + B/N \tag{19}$$

Absorption spectra of the isolated oligoenes (**3b$_2$**, **3b$_3$**, **3b$_4$**, **3b$_5$**, and **3b$_7$**) in dichloromethane are shown in Figure 2. Transition energies, λ_{max} values (for the 0−1 transition), and selected molar absorptivities in dichloromethane, acetonitrile, and benzene are listed in Table 3. Figure 3 shows the correlation of the $E(0-0)$, $E(0-1)$, and $E(0-2)$ transition energies for the $S_0 \rightarrow S_2$ transition with $1/N$. The parameters A and B obtained from fits to eq 19 are in good agreement with results obtained previously.[19a]

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(19) Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989.

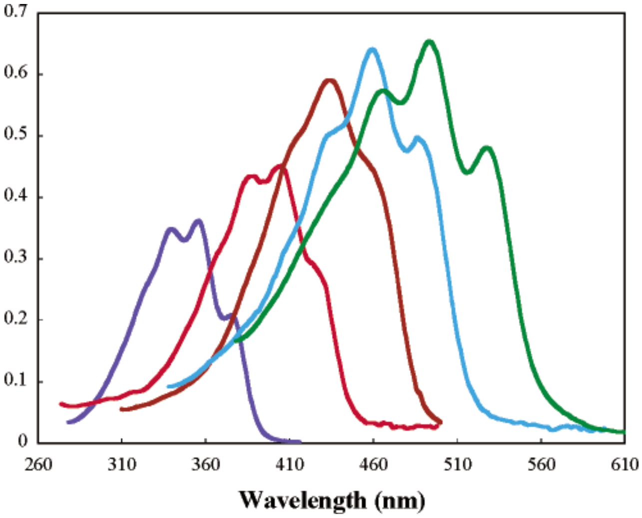


Figure 2. Absorption spectra of oligoenes **3b$_2$** (violet), **3b$_3$** (red), **3b$_4$** (brown), **3b$_5$** (blue), and **3b$_7$** (green) in dichloromethane at the same concentration (N = 5, 7, 9, 11, and 15, respectively).

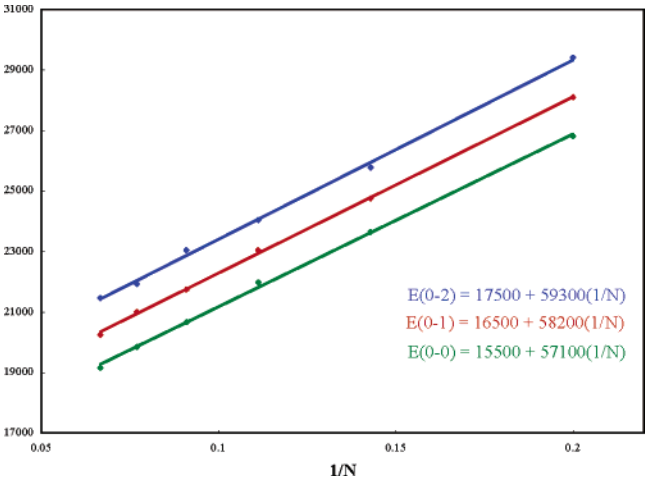
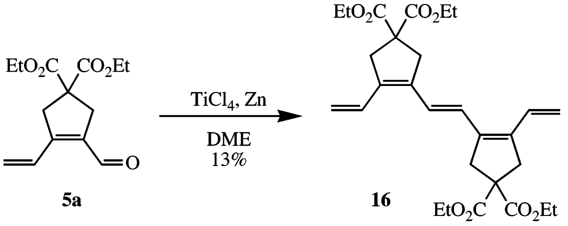


Figure 3. Plots of $E(0-0)$, $E(0-1)$, and $E(0-2)$ vs $1/N$ for oligomers in CH_2Cl_2.

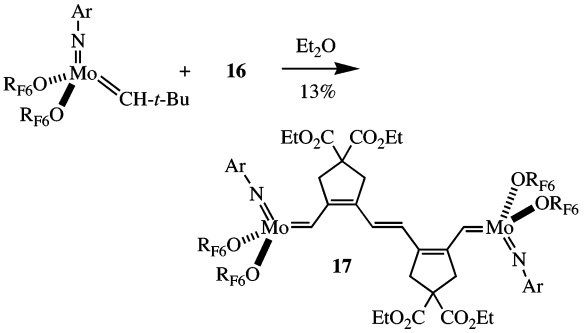
Extrapolation of N to infinity yields a limit of $E(0-0) \approx 15\,500$ cm^{-1} ($\lambda = 650$ nm) in dichloromethane.

Synthesis of a Dimeric Bimetallic Species and Its X-ray Structure. The key to the stoichiometric synthesis of symmetric oligoenes of some significant length is the bimetallic species **8**. We wanted to know whether bimetallic relatives could be prepared that contain more than one monomer "repeat" unit. Therefore we sought to prepare a bimetallic species that contains two monomer repeat units.

McMurry coupling of **5a** produced the pentaene **16** in low yield (eq 20). As expected, the lack of sterically protecting methyl groups at the ends of the oligoene and the presence of ethyl esters instead of isopropyl esters render **16** prone to decomposition. Therefore, it must be used immediately after it is prepared and purified. Reaction of **16** with Mo(NAr)(CH-*t*-Bu)(OR$_{F6}$)$_2$ produced the bimetallic species **17**, which was isolated in low yield from diethyl ether as deep purple crystals (eq 21). NMR data suggest that **17** has the same alkylidene configuration at each end (presumably *syn*,*syn*) with δH_α = 13.15 ppm in C_6D_6. Crystals suitable for an X-ray crystallographic analysis were grown from diethyl ether. (See Table 1 for crystal and structural refinement data.) The structure is shown in Figure 4, and selected bond distances and angles are listed in Table 2. In contrast to **7** two diethyl ether solvent molecules are weakly bound to the metal center *trans* to the alkylidene, a feature of related bimetallic species that have been structurally characterized recently.[14,20] A projection along the conjugated system reveals a high degree of planarity of the oligoene system with the metal centers and α carbons slightly out of the plane (Figure 5). (Individual deviations are 0.1080 (0.0033) for Mo(1), −0.1735 (0.0056) for C(1), 0.0225 (0.0051) for C(2), 0.0187 (0.0053) for C(6), −0.0737 (0.0068) for C(7), 0.0737 (0.0068) for C(7A), −0.0187 (0.0053) for C(6A), −0.0225 (0.0051) for C(2A), 0.1735 (0.0056) for C(1A), and −0.1080 (0.0033) for Mo(1A).) Although there was little doubt as to the alternating *trans*,*cis* structure of the repeat five-membered units in oligoenes prepared from DEDPM, to our knowledge this is the first confirmation of that structure, at least in a "dimer" with a Mo attached to each end.



(20)



(21)

Conclusions

We have described a method of preparing oligoenes that represent portions of polymers obtained by ring-closing metathesis polymerization of dialkyldipropargylmalonates to give polyenes that contain all five-membered rings. These oligoenes are accessible through reactions that involve new mono- or bimetallic Mo alkylidene complexes, although McMurry coupling has also been successful for synthesizing several. The spectroscopic properties of these compounds are in agreement with what one would expect for highly conjugated polyenes. We also were able to show that incorporation of a single six-membered ring in the center of a "trimer" produces two oligoene isomers and that λ_{max} in this species is lower than what it is in the trimer that contains three five-membered rings. We hope to be able to use this new methodology to synthesize longer polyenes and 1,6-heptadiyne variations, including those that incorporate photochemically or electrochemically active functionalities.

Experimental Section

General Comments. All manipulations of air- and moisture-sensitive materials were performed in oven-dried (200 °C) glassware under an

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(20) Schrock, R. R.; Gabert, A. J.; Singh, R.; Hock, A. S. *Organometallics* **2005**, *24*, 5058.

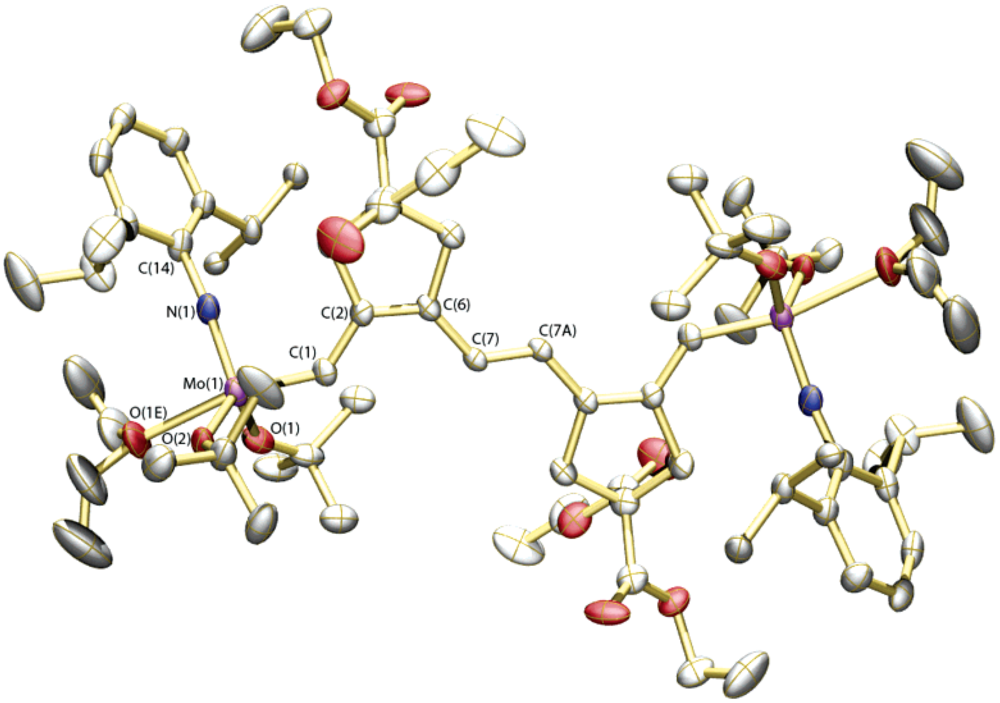

Figure 4. POV-ray rendering (ellipsoids at 35%) of the molecular structure of **17**. Fluorine atoms, hydrogen atoms, and the cocrystallized pentane molecule are omitted for clarity. Atoms related by the crystallographic inversion center are not labeled.

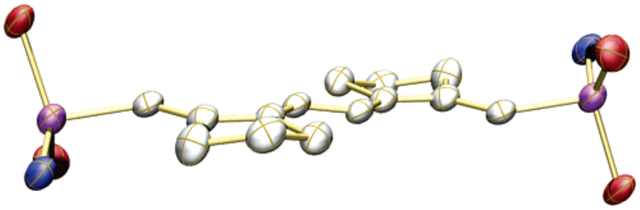

Figure 5. Selected view of **17** showing the planarity of the conjugated ring system.

atmosphere of nitrogen on a dual-manifold Schlenk line or in a Vacuum Atmospheres glovebox. HPLC grade organic solvents were sparged with nitrogen and dried by passage through activated alumina (for diethyl ether, toluene, pentane, THF, and methylene chloride) followed by passage through Q-5 supported copper catalyst (for benzene) prior to use and then stored over 4 Å Linde-type molecular sieves. Benzene-d_6 and toluene-d_8 were dried over sodium/benzophenone ketyl and vacuum-distilled. Methylene chloride-d_2 was dried over CaH$_2$, vacuum distilled, and stored over 4 Å Linde-type molecular sieves. Chloroform-d_1 was used as received. NMR spectra were recorded on a Varian 500 or Varian 300 spectrometer. Chemical shifts for ^{1}H and ^{13}C spectra were referenced to the residual ^{1}H/^{13}C resonances of the deuterated solvent (^{1}H: CDCl$_3$, δ 7.26; C$_6$D$_6$, δ 7.16; CD$_2$Cl$_2$, δ 5.32; C$_7$D$_8$, δ 2.09. ^{13}C: CDCl$_3$, δ 77.0; C$_6$D$_6$, δ 128.39; CD$_2$Cl$_2$, δ 54.00) and are reported as parts per million relative to tetramethylsilane. ^{19}F NMR spectra were referenced externally to fluorobenzene (δ −113.15 ppm upfield of CFCl$_3$). UV−vis spectra were recorded using a Hewlett-Packard 8452A diode array spectrophotometer at approximately 22 °C. High-resolution mass spectrometry measurements were performed at the MIT Department of Chemistry Instrument Facility, and elemental analyses were performed by the H. Kolbe Microanalytical Laboratory, Mülheim an der Ruhr, Germany.

Mo(CHCMe$_3$)(N-2,6-i-Pr$_2$C$_6$H$_3$)(OR$_{F6}$)$_2$,[21] Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)(OR$_{F6}$)$_2$,[22] Mo(CHCMe$_3$)(N-2-t-BuC$_6$H$_4$)(OR$_{F6}$)$_2$,[22] Mo(CH-[5])(NAr)(OR$_{F6}$)$_2$,[14] and RuCp(NCMe)$_3$PF$_6$[17b] were prepared according to previously reported methods (OR$_{F6}$ = OCMe(CF$_3$)$_2$, CH[5] = diethyl 3-(2-methylprop-1-enyl)-4-vinylcyclopent-3-ene-1,1-dicarboxylate). 2-(4-Chloro-but-2-ynyloxy)-tetrahydropyran[17a] and diethyldipropargyl malonate[23] were prepared as described in the literature. Synthetic details for all organic compounds (except the symmetric polyenes) can be found in the Supporting Information.

Crystal Structures. Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), performing φ- and ω-scans. All structures were solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least-squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U-value of the atoms they are linked to (1.5 times for methyl groups).

The crystals obtained for compound **17** diffracted only to the relatively mediocre resolution of $2\theta_{\max}$ = 45.4°, leading to a relatively low data-to-parameter ratio of about 7:1. In addition the structure determination was troubled by several complicated disorders, all of which were refined with the help of similarity restraints on 1−2 and 1−3 distances. To counteract correlation effects arising from the low data-to-parameter ratio, similarity restraints on displacement parameters as well as rigid bond restraints for anisotropic displacement parameters were applied to all atoms. In spite of the below-average data quality, the hydrogen atom bound to C(1) could be located in the difference Fourier synthesis and was refined semifreely with the help of a distance restraint, while constraining its U-value to 1.2 times the U_{eq} value of C(1).

Compound **7** cocrystallizes with one-half molecule of pentane per asymmetric unit. The pentane is disordered over four positions that involve the crystallographic inversion center. The ratio between the two crystallographically independent components was refined freely, and similarity restraints on 1−2 and 1−3 distances and displacement

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(21) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(22) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organometal. Chem.* **1993**, *459*, 185.

(23) Atkinson, R. S.; Grimshire, M. J. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1215.

parameters as well as rigid bond restraints for anisotropic displacement parameters were applied to all solvent atoms. Nevertheless, mathematical correlation between coordinates and anisotropic displacement parameters of the disordered atoms gives rise to unusually shaped thermal ellipsoids for some of the pentane atoms. This should not affect the accuracy of the structure of the main molecule, and the low residual values of the refinement attest to the overall high quality of the structure of **7**. The hydrogen atoms bound to C(1) and C(2) were taken from the difference Fourier synthesis and refined semifreely with the help of distance restraints, while constraining their *U*-values to 1.2 times the U_{eq} value of the atom to which they are bound. Further details of the data quality and a summary of the residual values of the refinements are listed in Table 1.

Mo(CH[5](CO$_2$-*i*-Pr)$_2$)(NAr)(OR$_{\mathrm{F6}}$)$_2$ (1b). Triene **15** (1.41 g, 4.60 mmol) was dissolved in pentane (5 mL), and molecular sieves (4 Å) were added. After 2 h, the solution was decanted and added to a solution of $\mathrm{Mo(CHCMe_3)(NAr)(OR_{F6})_2}$ (3.24 g, 4.60 mmol) in pentane (30 mL), and the mixture was stirred for 1 h. The orange precipitate was collected on a frit and washed with cold pentane; the yield of **1b** was 3.03 g (3.27 mmol, 71%): ^{1}H NMR (500 MHz, $\mathrm{CD_2Cl_2}$) δ 12.80 (s, 1H, $J_{\mathrm{CH}} = 130$ Hz, Mo═C*H*R), 7.27 (t, 1H, $J = 7.5$ Hz, *p*-Ar), 7.18 (d, 2H, $J = 7.5$ Hz, *m*-Ar), 5.97 (s, 1H, C*H*═CMe$_2$), 4.86 (sept, 2H, $J = 6.5$ Hz, OC*H*Me$_2$), 3.70 (s, 2H, C*H*$_2$), 3.53 (sept, 2H, $J = 6.3$ Hz, C*H*Me$_2$), 3.18 (s, 2H, C*H*$_2$), 1.96 (s, 3H, Me), 1.91 (s, 3H, Me), 1.43 (s, 6H, C(CF$_3$)$_2$*Me*), 1.20 (d, 12H, $J = 6.5$ Hz, CH*Me*$_2$), 0.92 (d, 6H, $J = 6.3$ Hz, OCH*Me*$_2$), 1.00 (d, 6H, $J = 6.3$ Hz, OCH*Me*$_2$); ^{13}C NMR (125 MHz, $\mathrm{CD_2Cl_2}$) δ 258.9, 171.4, 154.7, 148.6, 143.9, 140.1, 130.1, 126.8, 124.4 (q, $J_{\mathrm{CF}} = 288$ Hz, *C*F$_3$), 124.1 (q, $J_{\mathrm{CF}} = 288$ Hz, *C*F$_3$), 123.8, 119.2, 81.3 (quin, $J = 29$ Hz, *C*(CF$_3$)$_2$Me), 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, $\mathrm{C_6D_6}$) δ −77.79. Anal. Calcd for $\mathrm{C_{38}H_{49}NF_{12}MoO_6}$: C, 48.57; H, 5.26; N, 1.49. Found: C, 48.95; H, 5.47; N, 1.49.

[Mo(NAr)(OR$_{\mathrm{F6}}$)$_2$]CH[5](CO$_2$Et)$_2$CH[Mo(NAr)(OR$_{\mathrm{F6}}$)$_2$] (7). Triene **6a** (35.0 mg, 0.132 mmol) was dissolved in pentane (5 mL), and the solution was treated with molecular sieves (4 Å) for 15 min. Pentane (5 mL) was then used to dissolve $\mathrm{Mo(NAr)(CHCMe_3)(OR_{F6})_2}$ (186 mg, 0.265 mmol). The solution of **6a** was slowly added to the Mo solution, and the mixture was stirred for 4 h. The solution was then concentrated and stored at −40 °C to yield two crops of crystals (124 mg, 82.0 μmol, 62%). Crystals suitable for X-ray studies were selected from this batch: ^{1}H NMR (500 MHz, $\mathrm{CD_2Cl_2}$) δ 12.65 (s, 2H, $J_{\mathrm{CH}} = 125$ Hz, Mo═C*H*R), 7.28 (t, 2H, $J = 7.5$ Hz, *p*-Ar), 7.17 (d, 4H, $J = 7.5$ Hz, *m*-Ar), 3.84 (q, 4H, $J = 7.0$ Hz, OC*H*$_2$), 3.60 (s, 4H, C*H*$_2$), 3.47 (sept, 4H, $J = 7.0$ Hz, C*H*Me$_2$), 1.39 (s, 12H, C(CF$_3$)$_2$*Me*), 1.17 (d, 24H, $J = 7.0$ Hz, CH*Me*$_2$), 0.93 (t, 6H, $J = 7.0$ Hz, OCH$_2$C*H*$_3$); ^{19}F NMR (282 MHz, $\mathrm{C_6D_6}$) δ −78.19 (br s), −78.36 (br s).

[Mo(NAr′)(OR$_{\mathrm{F6}}$)$_2$]CH[5](CO$_2$-*i*-Pr)$_2$CH[Mo(NAr′)(OR$_{\mathrm{F6}}$)$_2$] (8). A 50 mL round-bottom flask was charged with $\mathrm{Mo(NAr')(CHCMe_2Ph)(OR_{F6})_2}$ (609 mg, 0.858 mmol), which was subsequently dissolved in diethyl ether (12 mL). Triene **6b** (125 mg, 0.429 mmol) was dissolved in diethyl ether (8 mL), and the solution was stood over molecular sieves (4 Å) for 30 min. It was then added slowly to the complex solution, and the mixture was stirred for 18 h. The solvent was removed in vacuo, and the residue was 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, $\mathrm{CD_2Cl_2}$) δ 12.66 (s, 2H, $J_{\mathrm{CH}} = 128$ Hz, Mo═C*H*R), 7.13 (m, 6H, Ar), 4.78 (septet, 2H, $J = 6.5$ Hz, OC*H*Me$_2$), 3.62 (s, 4H, C*H*$_2$), 2.39 (s, 12H, Ar*Me*), 1.37 (s, 12H, C(CF$_3$)$_2$*Me*) 0.96 (d, 12H, $J = 6.5$ Hz, CH*Me*$_2$); ^{13}C NMR (125 MHz, $\mathrm{CD_2Cl_2}$) δ 275.3, 170.9, 157.5, 138.1, 133.1, 129.8, 128.5, 124.1 (q, $J_{\mathrm{CF}} = 286$ Hz, *C*F$_3$), 123.9 (q, $J_{\mathrm{CF}} = 288$ Hz, *C*F$_3$), 81.9 (sept, $J_{\mathrm{CF}} = 27$ Hz, *C*(CF$_3$)$_2$Me), 69.3, 56.7, 45.1, 30.2, 21.6, 19.4; ^{19}F NMR (282 MHz, $\mathrm{CD_2Cl_2}$) δ −78.06 (br s), −78.39 (br s). Anal. Calcd for $\mathrm{C_{47}H_{50}N_2F_{24}Mo_2O_8}$: C, 39.79; H, 3.55; N, 1.97. Found: C, 39.72; H, 3.51; N, 1.96.

[Mo(NAr)(OR$_{\mathrm{F6}}$)$_2$]CH[5](CO$_2$Et)$_2$CH═CH[5](CO$_2$Et)$_2$CH[Mo(NAr)(OR$_{\mathrm{F6}}$)$_2$] (17). Activated zinc (1.99 g, 30.4 mmol) was suspended in degassed DME (20 mL), and the mixture was cooled to 0 °C. $\mathrm{TiCl_4}$ (2.85 g, 15.0 mmol) was added dropwise. After the mixture was stirred for 5 min, it was heated to reflux for 2 h. After cooling to 0 °C a solution of **5a** (953 mg, 3.58 mmol) in DME (10 mL) was added dropwise. The blue suspension was allowed to warm to room tempterature over a period of 18 h and then heated to reflux for 2 h. After cooling to 0 °C a mixture of saturated aqueous $\mathrm{NaHCO_3}$ and saturated $\mathrm{K_2CO_3}$ (5:1) was added along with ether. The gray-blue suspension was filtered over Celite and washed with $\mathrm{Et_2O}$. The combined organic phases were dried over $\mathrm{Na_2SO_4}$, and the solvents were evaporated. Flash column chromatography (silica gel, deactivated with $\mathrm{NEt_3}$, hexanes/ethyl acetate 25:1) gave pentaene **16** as a colorless oil (120 mg, 0.240 mmol, 13%). The product was used immediately in the next step.

Pentaene **16** (31.5 mg, 63.0 μmol) was dissolved in diethyl ether (2 mL), and the solution was stored over molecular sieves (4 Å) for 2 h. $\mathrm{Mo(NAr)(CHCMe_3)(OR_{F6})_2}$ (96.5 mg, 0.126 mmol) was dissolved in diethyl ether (0.5 mL), and the pentaene solution was added dropwise at room temperature. The mixture was strirred for 18 h. The solvent was evaporated, and the residue was triturated with pentane. The dark solid was recrystallized from $\mathrm{Et_2O}$/pentane to give **17** as purple crystals (14.0 mg, 8.05 μmol, 13%): ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$) δ 13.15 (s, 2H, Mo═C*H*R), 6.93−6.85 (m, 6H, Ar), 6.64 (s, 2H, CH═C*H*), 3.77−3.94 (m, 16H, C*H*$_2$ and OC*H*$_2$), 3.62 (septet, $J = 6.9$ Hz, 4H, C*H*Me$_2$), 1.33 (s, 12H, C(CF$_3$)$_2$*Me*), 1.23 (d, $J = 6.9$ Hz, 24H, CH*Me*$_2$), 0.84 (t, $J = 6.9$ Hz, 12H, OCH$_2$C*H*$_3$); ^{19}F NMR (282 MHz, $\mathrm{C_6D_6}$) δ −78.32 (s). Anal. Calcd for $\mathrm{C_{66}H_{78}N_2F_{24}Mo_2O_{12}}$: C, 45.58; H, 4.52; N, 1.61. Found: C, 45.46; H, 4.44; N, 1.54.

{Mo(N-2-*t*-BuC$_6$H$_4$)(OR$_{\mathrm{F6}}$)$_2$}$_2$-*μ*-(CH[6](CO$_2$Et)$_2$C) (11). A flask was charged with 0.203 g (0.301 mmol) of Mo(N-2-*t*-BuC$_6$H$_4$)(CH-*t*-Bu)(OR$_{\mathrm{F6}}$)$_2$, and 5 mL of $\mathrm{Et_2O}$ was added. To the stirring solution was added a solution of 0.0700 g (0.264 mmol) of triene **9** in 10 mL of $\mathrm{Et_2O}$. The solution became deep red and was allowed to stir at room temperature for 18 h. The volatiles were removed in vacuo, and the residue dissolved in a minimal amount of pentane. The pentane solution was then set aside at −25 °C for several days during which time the desired complex precipitated as 0.100 g (45%) of a brown powder. Repeated crystallization from cold pentane removed any traces of Mo(N-2-*t*-BuC$_6$H$_4$)(CH-*t*-Bu)(OR$_{\mathrm{F6}}$)$_2$: ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$) δ 12.36 (s, 1H, $J_{\mathrm{CH}} = 125$ Hz, Mo═C*H*R), 7.74 (d, 1H, $J = 7.5$ Hz, Ar), 7.57 (d, 1H, $J = 7.5$ Hz, Ar), 7.52 (s, 1H, C≡C*H*), 7.04 (t, 2H, $J = 7.5$ Hz, Ar), 6.86 (m, 4H, Ar), 4.94 (s, 2H, C*H*$_2$), 3.69 (m, 4H, OC*H*$_2$), 3.67 (s, 2H, C*H*$_2$), 1.53 (s, 6H, C(CF$_3$)$_2$*Me*), 1.40 (s, 9H, C*Me*$_3$), 1.38 (s, 9H, C*Me*$_3$), 1.32 (br s, 3H, C(CF$_3$)$_2$*Me*), 0.75 (t, 6H, $J = 7.0$ Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (125 MHz, $\mathrm{C_6D_6}$) δ 271.1 (MoC_α), 259.0 (MoC_αH), 170.3 (*C*O), 157.6, 156.3, 147.0, 146.7, 134.7, 134.2, 132.1, 130.2, 129.8, 127.5, 127.3, 127.1, 126.8, 124.5 (q, $J_{\mathrm{CF}} = 286$ Hz, *C*F$_3$), 124.4 (q, $J_{\mathrm{CF}} = 289$ Hz, *C*F$_3$), 124.2 (br q, $J_{\mathrm{CF}} = 286$ Hz, *C*F$_3$), 113.7, 83.0 (br m, *C*(CF$_3$)$_2$Me), 82.75 (sep, $J_{\mathrm{CF}} = 29.9$ Hz, *C*(CF$_3$)$_2$Me), 61.78 (O*C*H$_2$), 55.02 (C_{quat}-[6]), 47.22, 36.16, 36.09, 35.84, 30.75, 30.62, 19.59 (br, C(CF$_3$)$_2$*Me*), 19.08 (C(CF$_3$)$_2$*Me*), 14.16 (OCH$_2$*C*H$_3$); ^{19}F NMR (282 MHz, $\mathrm{C_6D_6}$) δ −77.66 (q, 6 C*F*$_3$), −78.02 (q, 6 C*F*$_3$), −78.13 (br, 12 C*F*$_3$). Anal. Calcd for $\mathrm{C_{49}H_{54}F_{24}Mo_2N_2O_8}$: C, 40.68; H, 3.76; N, 1.94. Found: C, 40.43; H, 3.82; N, 1.93.

(*E*)-Di-1,2-[1-(2-methyl-propenyl)-4,4-di-*iso*-propyl-carboxy-cyclopent-1-enyl]-ethene (3b$_2$). A solution of **2b** (13 mg, 0.043 mmol) in dichloromethane (0.5 mL) was stored over molecular sieves (4 Å) for 30 min and added to a solution of **1b** (41 mg, 0.043 mmol) in dichloromethane (2 mL). The reaction was stirred vigorously for 3 h. Solvent was removed in vacuo, and the residue was eluted through an activated basic alumina plug with diethyl ether. The solvent was evaporated, and the residue was triturated with pentane (slightly soluble) to yield **3b$_2$** (13 mg, 0.021 mmol, 49%) as an off-white solid: ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$) δ 6.75 (s, 2H, ═C*H*), 6.02 (s, 2H, C*H*═CMe$_2$), 5.01 (sept, 4H, $J = 6.0$ Hz, OC*H*Me$_2$), 3.65 (s, 8H, C*H*$_2$), 1.67 (s, 6H, Me), 1.54 (s, 6H, Me), 0.98 (m, 24H, OCH*Me*$_2$); ^{13}C NMR (125 MHz, C_6D_6) 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 ($CDCl_3$) cm^{-1} 3141 (w), 2984, 2907, 1724 (s), 1446, 1368, 1259 (s), 1192, 1095, 1074, 1011. HRMS (EI, [M]$^+$). Calcd for $C_{36}H_{52}O_8$: 612.3657. Found: 612.3637. $\lambda_{max} = 340$ nm; $\epsilon = 6.9 \times 10^4$ cm^{-1} M^{-1} in benzene (9.5×10^{-6} M).

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 ($3b_3$). Aldehyde **2b** (35.4 mg, 0.115 mmol) was dissolved in dichloromethane (2 mL). The solution was stored over molecular sieves (4 Å) for 30 min and then added to a solution of **8** (81.4 mg, 57.0 μmol) in dichloromethane (3 mL). The reaction was stirred vigorously for 3 h to yield a brownish-yellow solution. The solvent was removed in vacuo, and the residue was dissolved in diethyl ether and passed through an activated basic alumina plug. After evaporation of the solvent the product was obtained as a yellowish solid (32 mg, 37.0 μmol, 64%): ^{1}H NMR (500 MHz, C_6D_6) δ 6.83 (d, 2H, $J = 15.5$ Hz, C*H*═CH), 6.76 (d, 2H, $J = 15.5$ Hz, C*H*═CH), 6.00 (s, 2H, C*H*═CMe$_2$), 5.04 (sept, 4H, $J = 6.5$ Hz, OC*H*Me$_2$), 5.01 (sept, 2H, $J = 6.5$ Hz, OC*H*Me$_2$), 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, Me), 1.55 (s, 6H, Me), 1.01 (m, 24H, OCH*Me*$_2$), 0.97 (d, 12H, $J = 6.0$ Hz, OCH*Me*$_2$); ^{13}C 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 ($CDCl_3$) cm^{-1} 2983, 2936(w), 1722(s), 1467, 1376, 1262(s), 1196, 1104(s), 1068. HRMS (EI, [M]$^+$) Calcd for $C_{51}H_{72}O_{12}$: 876.5018. Found: 876.4996. $\lambda_{max} = 388$ nm (C_6H_6), 404 nm (CH_2Cl_2); $\epsilon = 8.2 \times 10^4$ cm^{-1} M^{-1} in benzene and 4.4×10^4 cm^{-1} M^{-1} in dichloromethane.

(*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 ($3b_4$). The trimeric aldehyde **$2b_3$** (21 mg, 0.025 mmol) was dissolved in dichloromethane (2 mL). The solution was stored over molecular sieves (4 Å) for 30 min and added to a solution of **1b** (24 mg, 0.025 mmol) in dichloromethane (2 mL). The reaction was stirred vigorously for 3.5 h. The solvent was removed in vacuo, and the residue was eluted through an activated basic alumina plug with a mixture of diethyl ether/tetrahydrofuran (2:1). The solvent was removed from the filtrate, and the residue was washed with pentane to yield **$3b_4$** (12 mg, 0.010 mmol, 42%) as an orange solid: ^{1}H NMR (500 MHz, 54:46 C_6D_6/$CDCl_3$) δ 6.64 (m, 4H, C*H*═C*H*), 6.51 (m, 2H, C*H*═CMe$_2$), 5.94 (s, 2H, ═C*H*), 4.95 (m, 8H, OC*H*Me$_2$), 3.40 (s, 4H, C*H*$_2$), 3.38 (s, 4H, C*H*$_2$), 3.35 (s, 4H, C*H*$_2$), 3.31 (s, 4H, C*H*$_2$), 1.68 (s, 6H, Me), 1.66 (s, 6H, Me), 1.05 (m, 48H, OCH*Me*$_2$); ^{13}C NMR (125 MHz, 54:46 C_6D_6/$CDCl_3$) 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 ($CDCl_3$) cm^{-1} 3236 (w), 2991, 2913, 1722 (s), 1619, 1454, 1331, 1262 (s), 1165, 1097, 1016. HRMS (ESI, [M + Na]$^+$). Calcd for $C_{66}H_{92}O_{16}Na$: 1163.6278. Found: 1163.6244. $\lambda_{max} = 432$ nm; $\epsilon = 9.2 \times 10^4$ cm^{-1} M^{-1} in benzene.

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 ($3b_5$). The dimeric aldehyde, **$2b_2$** (78 mg, 0.12 mmol), was dissolved in dichloromethane (2 mL), and the solution was stored over molecular sieves (4 Å) for 30 min. It was then added to a solution of **8** (94 mg, 0.066 mmol) in dichloromethane (4 mL). The reaction was stirred for 3 h. Solvent was removed in vacuo, and the residue was eluted through an activated basic alumina plug with diethyl ether/tetrahydrofuran (2:1) and benzene to give pentamer **$3b_5$** (76 mg, 0.054 mmol, 82%) as an orange solid: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.00 (s, 4H, ═C*H*), 6.61 (d, 2H, $J = 15.5$ Hz, C*H*═C*H*), 6.49 (d, 2H, $J = 15.5$ Hz, C*H*═C*H*), 6.05 (s, 2H, C*H*═CMe$_2$), 5.02 (m, 10H, OC*H*Me$_2$), 3.33 (m, 8H, C*H*$_2$), 3.29 (m, 8H, C*H*$_2$), 3.21 (s, 4H, C*H*$_2$), 1.88 (s, 6H, Me), 1.81 (s, 6H, Me), 1.23 (m, 60H, OCH*Me*$_2$); ^{13}C NMR (125 MHz, CD_2Cl_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 ($CDCl_3$) cm^{-1} 3041 (w), 2984, 2938 (w), 1722 (s), 1467, 1454, 1376, 1270, 1197, 1105, 1068. HRMS (ESI, [M + Na]$^+$). Calcd for $C_{81}H_{112}O_{20}Na$: 1427.7639. Found: 1428.7645. $\lambda_{max} = 458$ nm (C_6H_6), 460 nm (CH_2Cl_2); $\epsilon = 1.0 \times 10^5$ cm^{-1} M^{-1} in benzene and 9.5×10^4 cm^{-1} M^{-1} in dichloromethane.

McMurry Coupling of $2b_3$ to give $3b_6$. A 25 mL two-necked flask with a reflux condensor was charged with activated zinc (217 mg, 3.30 mmol) and dimethoxyethane (10 mL). After cooling to 0 °C titanium tetrachloride (313 mg, 1.65 mmol) was added dropwise. The blue suspension was heated to reflux for 2 h. After the suspension cooled to 0 °C, a solution of trimeric aldehyde **$2b_3$** (330 mg, 0.388 mmol) in dimethoxyethane (2 mL) was added dropwise and the mixture was allowed to warm to rt over 12 h. The red-brown suspension was heated to reflux for 1 h. After the suspension cooled to rt, it was filtered through celite and the solid was washed with dichloromethane (50 mL). The solvent was evaporated. The residue was dissolved in a minimum amount of dichloromethane and excess pentane added. After stirring for 4 h at rt the red precipitate was filtered off, redissolved in dichloromethane, and filtered through a neutral aluminum oxide plug (1 cm × 2 cm) using dichloromethane as eluent. After evaporation of the solvent the product was obtained as a brick-red powder (81.0 mg, 48.0 μmol, 25%): ^{1}H NMR (300 MHz, CH_2Cl_2) δ 6.72 (br s, 6H, C*H*═C*H*), 6.59 (d, $J = 15.9$ Hz, 2H, CH═C*H*), 6.50 (d, $J = 15.9$ Hz, 2H, C*H*═CH), 6.07 (s, 2H, C*H*═CMe$_2$), 5.03 (m, 12H, OC*H*Me$_2$), 3.36 (br m, 12H, C*H*$_2$), 3.30 (br m, 8H, C*H*$_2$), 3.22 (br s, 4H, C*H*$_2$), 1.89 (s, 6H, Me), 1.82 (s, 6H, Me), 1.25 (br m, 72H, OCH*Me*$_2$); ^{13}C NMR (75 MHz, CH_2Cl_2) δ 171.93, 171.86, 171.86, 138.06, 137.83, 137.75, 137.57, 137.28, 136.28, 134.21, 128.83, 125.49, 123.80, 123.60, 123.23, 122.00, 119.60, 69.75, 69.57, 58.26, 57.51, 57.46, 45.03, 41.87, 41.71, 40.35, 27.88, 21.86, 21.83, 21.81, 20.77; IR ($CDCl_3$) cm^{-1} 3016, 2984, 1722, 1467, 1376, 1271, 1195, 1104, 1068, 949. HRMS (ESI, [M + Na]$^+$). Calcd for $C_{96}H_{132}O_{24}Na$: 1691.9001. Found: 1691.9069. $\lambda_{max} = 476$ nm; $\epsilon = 1.1 \times 10^5$ cm^{-1} M^{-1} in methylene chloride.

Oligomers **$3b_2$** and **$3b_4$** can be prepared similarly from **$2b_1$** and **$2b_2$**, respectively.

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 ($3b_7$). Trimeric aldehyde **$2b_3$** (253 mg, 0.297 mmol) was dissolved in dichloromethane (7 mL). The solution was stored over molecular sieves (4 Å) for 45 min and added to a solution of **8** (211 mg, 0.149 mmol) in dichloromethane (3 mL). The reaction was stirred vigorously for 4 h. The solvent was removed in vacuo, and the residue was eluted through an activated basic alumina plug with diethyl ether/tetrahydrofuran (6:1) and benzene to yield **$3b_7$** (226 mg, 0.117 mmol, 79%) as a reddish solid: ^{1}H NMR (500 MHz, C_6D_6) δ 6.73 (s, 4H, ═C*H*), 6.72 (s, 4H, C*H*═C*H*), 6.62 (d, 2H, $J = 15.4$ Hz, C*H*═CH), 6.53 (d, 2H, $J = 15.4$ Hz, CH═C*H*), 6.07 (s, 2H, C*H*═CMe$_2$), 5.03 (m, 14H, OC*H*Me$_2$), 3.30 (m, 28H, C*H*$_2$), 1.89 (s, 6H, Me), 1.82 (s, 6H, Me), 1.24 (m, 84H, OCH*Me*$_2$); ^{13}C NMR (125 MHz, C_6D_6) δ 171.9, 171.8, 138.0, 137.9, 137.8, 137.7, 137.7, 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, 42.1, 42.1, 40.8, 27.7, 21.9, 21.9, 21.9, 21.9, 21.9, 20.8; IR ($CDCl_3$) ν = 3042 (w), 2984, 2938, 2865 (w), 1723 (s), 1466, 1371, 1262 (s), 1195, 1105 (s), 1068 cm^{-1}. HRMS (ESI, [M + Na]$^+$). Calcd for $C_{111}H_{152}O_{28}Na$: 1956.0362. Found: 1956.0392. $\lambda_{max} = 492$ nm (C_6H_6), 494 nm (CH_2Cl_2); $\epsilon = 1.1 \times 10^5$ cm^{-1} M^{-1} in benzene and 1.4×10^5 cm^{-1} M^{-1} in methylene chloride.

Diethyl 5-((4,4-Di(ethoxycarbonyl)-2-(2-methylprop-1-enyl)cyclopent-1-enyl)methylene)-3-((1*E*)-2-(4,4-di(ethoxycarbonyl)-2-(2-methylprop-1-enyl)cyclopent-1-enyl)vinyl)cyclohex-3-ene-1,1-dicarboxylate (12). A flask was charged with 0.113 g (77.8 μmol) of complex **11** and 8 mL of ether. To the stirring solution was added 0.0569 g (190 μmol) of aldehyde **2a**. Upon addition of the aldehyde, an immediate color change from brown to deep red occurred. The solution was stirred for 24 h at room temperature during which time the color lightened to yellow-brown. The solvent volume was reduced in vacuo to ~5 mL, and 10 mL of pentane was added. The solution was loaded onto a short silica gel column and eluted with 2:1 hexanes/ethyl acetate. The product fractions ($R_f = 0.45$) were pooled, and the solvent was removed in vacuo yielding 0.0500 g (80%) of a bright yellow film. The compound exists as a 2:1 mixture of isomers as determined by NMR: ^{1}H NMR (500 MHz, $CDCl_3$) *Major isomer* δ 6.61 (s, 1H), 6.56 (d, 1H, $J = 16.0$ Hz, C*H*=CH), 6.25 (d, 1H, $J = 16.0$ Hz, CH=C*H*), 6.02 (s, 1H), 5.97 (s, 1H), 5.84 (s, 1H), 4.20 (m, 12H, OCH_2), 3.38 (s, 2H, CH_2), 3.34 (s, 2H, CH_2), 3.23 (s, 2H, CH_2), 3.20 (s, 2H, CH_2), 2.88 (s, 2H, CH_2), 2.86 (s, 2H, CH_2), 1.87 (s, 3H, Me), 1.82 (s, 3H, Me), 1.81 (s, 3H, Me), 1.73 (s, 3H, Me), 1.25 (m, 18H, OCH_2CH_3); *Minor isomer* δ 6.51 (d, 1H, $J = 16.0$ Hz, C*H*=CH), 6.19 (d, 1H, $J = 16.0$ Hz, CH=C*H*), 6.15 (s, 1H), 6.08 (s, 1H), 6.01 (s, 1H), 5.84 (s, 1H), 4.20 (m, 12H, OCH_2), 3.40 (s, 2H, CH_2), 3.32 (s, 2H, CH_2), 3.20 (s, 2H, CH_2), 3.18 (s, 2H, CH_2), 3.07 (s, 2H, CH_2), 2.85 (s, 2H, CH_2), 1.87 (s, 3H, Me), 1.83 (s, 3H, Me), 1.80 (s, 3H, Me), 1.71 (s, 3H, Me), 1.25 (m, 18H, OCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) *Both isomers* δ 172.3, 172.2, 172.2, 171.2, 171.1, 138.4, 137.9, 137.6, 137.5, 137.2, 137.1, 136.4, 136.1, 136.0, 134.4, 133.8, 133.7, 133.2, 132.8, 132.7, 132.4, 131.9, 131.4, 130.8, 126.8, 125.4, 123.3, 122.5, 121.8, 120.1, 120.0, 119.5, 61.9, 61.8, 61.8, 61.7, 59.0, 58.9, 58.0, 57.9, 54.4, 54.2, 44.7, 44.6, 43.7, 43.4, 42.7, 40.3, 40.2, 38.5, 32.3, 30.8, 30.4, 27.8, 27.4, 20.7, 20.6, 20.5, 14.3, 14.2, 14.2, 14.1. HRMS (ESI, $[MH]^+$): Calcd for $C_{45}H_{61}O_{12}$: 793.4158. Found: 793.4170. UV−vis: $\lambda_{max} = 384$ nm (CH_2Cl_2).

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Supporting Information Available: Experimental details for all organic compounds except the polyene oligomers. Fully labeled thermal ellipsoid drawings for **7** and **17**. Data for the structures are available to the public at http://www.reciprocal-net.org (numbers 05149 for **17** and 05196 for **7**). This material is available free of charge via the Internet at http://pubs.acs.org.

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