Synthesis of Oligo(1,6-heptadiynes) with a Single Structure and Terminal Methylene Groups Using Molybdenum-Based Wittig and Metathesis Chemistry. 1. 2,6-Dimethylphenylimido Systems

Corina Scriban, Richard R. Schrock,* and Peter Müller

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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In this paper we demonstrate a method of synthesizing oligomers of disopropylidipropargylmalonolate, \(\text{[CH}_2\text{][b][CH}_3\text{]}_x\) \((x = 2, 3, 4, 5)\), in which the “b” repeat unit is identical to the five-membered ring formed in a tail-to-tail cyclopolymerization of disopropylidipropargylmalonolate, and methylene groups are capping the ends. For example, a “degenerate” metathesis reaction between the “monomer”, \(\text{[CH}_2\text{][b][CH}_3\text{]}_2\), and 2 equiv of \(\text{Mo(NAr)}'(\text{CHCM}_2\text{Ph})(\text{ORF}_6)_2\) (\(\text{Ar}' = 2,6\)-Me\(_2\text{C}_6\text{H}_3\)) gives \(\text{[Mo][CHCM}_2\text{Ph][Mo]}\) and 2 equiv of the aldehyde, \(\text{[CH}_2\text{][b][O]}\), then gives the “trimer”, \(\text{[CH}_2\text{][b][CH}_3\text{]}_3\). Treatment of \(\text{[CH}_2\text{][b][CH}_3\text{]}_2\) with 2 equiv of \(\text{[Mo][CHCM}_2\text{Ph]}\) gives \(\text{[Mo][b][Mo]}\), which upon treatment with 2 equiv of \(\text{[CH}_2\text{][b][O]}\) gives the “pentamer”, \(\text{[CH}_2\text{][b][CH}_3\text{]}_5\), which contains 11 double bonds in conjugation in a molecule in which the repeat units are connected by \(\text{C}==\text{C}\) bonds. The oligomers are not always obtained in high yield in pure form because \(\text{(inter alia)}\) \(\text{C}==\text{C}\) metathesis reactions compete with the Mo-Wittig reaction of the aldehyde (e.g., to give \(\text{[CH}_2\text{][b][CH}_3\text{]}_2\) also in the synthesis of \(\text{[CH}_2\text{][b][CH}_3\text{]}_3\)). These complications could be minimized by employing adducts (L)[Mo][b] Mo-Wittig reaction of the aldehyde (e.g., to give \(\text{[CH}_2\text{][b][CH}_2\text{]}\) also in the synthesis of \(\text{[CH}_2\text{][b][CH}_2\text{]}\)).

Introduction

Studies of conjugated polymers have been motivated in large part by the semiconducting or photophysical properties of the polymers, which make them useful in displays and lasers, as photovoltaics, and as nonlinear optical materials. Conjugated polymers, which make them useful in displays and lasers, are capping the ends. For example, a “degenerate” metathesis reaction between the “monomer”, \(\text{[CH}_2\text{][b][CH}_3\text{]}_2\), and 2 equiv of \(\text{Mo(NAr)}'(\text{CHCM}_2\text{Ph})(\text{ORF}_6)_2\) (\(\text{Ar}' = 2,6\)-Me\(_2\text{C}_6\text{H}_3\)) gives \([\text{Mo][CHCM}_2\text{Ph][Mo]}\) and 2 equiv of the aldehyde, \(\text{[CH}_2\text{][b][O]}\), then gives the “trimer”, \(\text{[CH}_2\text{][b][CH}_3\text{]}_3\). Treatment of \(\text{[CH}_2\text{][b][CH}_3\text{]}_2\) with 2 equiv of \(\text{[Mo][CHCM}_2\text{Ph]}\) gives \(\text{[Mo][b][Mo]}\), which upon treatment with 2 equiv of \(\text{[CH}_2\text{][b][O]}\) gives the “pentamer”, \(\text{[CH}_2\text{][b][CH}_3\text{]}_5\), which contains 11 double bonds in conjugation in a molecule in which the repeat units are connected by \(\text{C}==\text{C}\) bonds. The oligomers are not always obtained in high yield in pure form because \(\text{(inter alia)}\) \(\text{C}==\text{C}\) metathesis reactions compete with the Mo-Wittig reaction of the aldehyde (e.g., to give \(\text{[CH}_2\text{][b][CH}_3\text{]}_2\) also in the synthesis of \(\text{[CH}_2\text{][b][CH}_3\text{]}_3\)). These complications could be minimized by employing adducts (L)[Mo][b] Mo-Wittig reaction of the aldehyde (e.g., to give \(\text{[CH}_2\text{][b][CH}_2\text{]}\) also in the synthesis of \(\text{[CH}_2\text{][b][CH}_2\text{]}\)).

Poly[1,6-heptadiynes] such as poly[dialkylidipropargylmalonates], which are formed in an alkylidene-catalyzed cyclopolymerization reaction, are highly conjugated, relatively soluble, and relatively stable in air.

* Corresponding author. E-mail: rrs@mit.edu.

that contain the very type of five-membered ring being formed in a cyclopolymerization reaction, i.e., 1 in eq 1, have been shown to initiate rapidly,\(^9\) which is a requirement in order to prepare polymers with a known and controllable chain length and a low polydispersity. It has been shown that 2 will react with the aldehyde, \([\text{Me}_2\text{C}][\text{a}][\text{O}]\) (eq 1), to yield the “dimer”, \([\text{Me}_2\text{C}][\text{a}][\text{CMe}_2]\), cleanly and in relatively high yield, in a “Mo-Wittig” reaction. (The Mo=O product of Wittig-like reactions of this type is not a stable species and is not shown in any equations here.) Related bimetallic Mo reagents such as \([\text{Mo}][\text{b}][\text{Mo}]\), which can be prepared as shown in eq 2 (\([\text{Mo}]\) is \(\text{Mo}[(\text{NAr}')(\text{ORf}_6)]\) and \(\text{Ar}' = 2,6-\text{Me}_2\text{C}_6\text{H}_3\)), have been shown to react similarly (eq 3), an approach that increases the chain length in two directions.\(^{10}\) (Isopropyl esters (b) were found to lead to more crystalline and more stable derivatives.\(^{10}\)) Finally, it was shown, and confirmed in an X-ray study, that bimetallic species could be prepared that contain more than one five-membered ring unit between Mo centers in a reaction related to that shown in eq 2, as shown in eq 4.\(^{10}\)

The results described above set the stage for a possible synthesis of a series of oligoenes with a specific length that contain \(=\text{CH}_2\) end groups instead of \(=\text{CMe}_2\) end groups. For example, we proposed that reaction of 2 equiv of \([\text{H}_2\text{C}][\text{b}][\text{O}]\) with \([\text{Mo}][\text{b}][\text{Mo}]\) would yield the “trimeric” 7-ene, \([\text{H}_2\text{C}][\text{b}_3][\text{CH}_2]\). Since \([\text{H}_2\text{C}][\text{b}_3][\text{CH}_2]\) contains methylene end groups, it could be employed to prepare another bimetallic reagent that contains three rings between the two Mo centers through a reaction analogous to that shown in eq 4, and the resulting bimetallic species should then yield the pentamer (11-ene) when treated with 2 equiv of \([\text{H}_2\text{C}][\text{b}][\text{O}]\). Related stepwise reactions would then produce the heptamer, nonamer, etc. An “even-membered” series of oligomers could be prepared beginning with \([\text{Mo}][\text{b}_2][\text{Mo}]\) (cf. eq 4). The key features of this new approach are that an oligoene produced in a given Wittig-like reaction can be employed to prepare the next bimetallic reagent and the chain can be grown in two directions. In this paper we demonstrate this new approach for the synthesis of oligoenes with a single structure and up to 11 double bonds.

**Results and Discussion**

**Reactions Involving the Bimetallic Species \([\text{Mo}][\text{b}][\text{Mo}]\).**

Attempts to synthesize the “trimer,” \([\text{H}_2\text{C}][\text{b}_3][\text{CH}_2]\), produced two products in low yield that could be separated by silica gel column chromatography and identified by \(^1\text{H}\) NMR spectroscopy.
as the expected “trimer,” \([\text{H}_2\text{C}]_3[\text{CH}_2]\) (in 11% yield), and the unexpected “dimer”, \([\text{H}_2\text{C}]_2[\text{CH}_2]\), in 22% yield (eq 6). The same ratio of dimer to trimer was observed when \([\text{Mo}]_2[\text{Mo}]\) was added to 5–10 equiv of \([\text{H}_2\text{C}]_2[\text{O}]\). The dimer and trimer can be recrystallized at −10 °C from diethyl ether and are relatively stable in solution in air. Their identities have been confirmed through X-ray structural studies (Figures 1 and 2; Table 1S11). Figures 1a and 2a show the overall structures, while Figures 1b and 2b reveal that the conjugated backbone of the central polyene chain is nearly planar in each. To our knowledge, these are the first X-ray studies of an oligomer of this general type, although an X-ray study of the bimetallic species shown in eq 4 has been reported,\(^{10}\) as mentioned earlier. Selected bond lengths within the polyene chain can be found in the figure captions.

We propose that \([\text{H}_2\text{C}]_3[\text{CH}_2]\) is formed via a “normal” Wittig-like reaction between \([\text{H}_2\text{C}]_2[\text{O}]\) and each end of \([\text{Mo}]_2[\text{Mo}]\), most likely with \([\text{Mo}]_2[\text{CH}_2]\) (eq 7) as an intermediate. Formation of \([\text{H}_2\text{C}]_2[\text{CH}_2]\) must result from competition between the desired Mo-Wittig reaction and metathesis of a terminal or possibly even internal (trans disubstituted) \(\text{C}==\text{C}\) bond within various \([\text{H}_2\text{C}]_2[\text{CH}_2]\) or \([\text{Mo}]_2[\text{CH}_2]\) species in the crude mixture. The low yields of dimer and trimer are consistent with formation of oligoenes longer than \([\text{H}_2\text{C}]_3[\text{CH}_2]\), along with ethylene, via homocoupling of terminal \(\text{C}==\text{C}\) bonds. It should be noted that we cannot exclude competition between the Wittig reaction and a metathesis reaction involving the terminal \(\text{C}==\text{C}\) bond within \([\text{H}_2\text{C}]_2[\text{O}]\), as shown in eqs 8 and 9.

(11) Crystallographic details can be found in tables submitted along with CIF files as part of the Supporting Information.
Some evidence for [Mo][b][O] could be found in a reaction between [Mo][b][Mo] and 1 equiv of [H2C][b][O] in CD2Cl2. According to proton NMR studies, after 30 min all [H2C][b][O] had been consumed, but some [Mo][b][Mo] was still present (14% of the Mo alkylidene species) and new alkylidene H resonances were observed that could be assigned to [Mo][b][CH2] (at 11.95 ppm, 46%), [Mo][b][CH2] (at 12.94 ppm), and [Mo][b2][CH2] (at 12.92 ppm) through a correlation of the alkylidene resonances with other resonances in the spectrum. A resonance that we assign to the aldehyde proton in [Mo][b][O] was observed at 9.31 ppm with an intensity the same as that for the 11.95 ppm alkylidene proton resonance. The dimer and trimer also were observed in an approximate 2:1 ratio. Addition of a second equivalent of [H2C][b][O] to this mixture led to the disappearance after 20 min of all alkylidene resonances except that at 11.95 ppm for [Mo][b][O] and to the same 2:1 ratio of [H2C][b2][CH2] to [H2C][b3][CH2]. Apparently [Mo][b][O] is relatively stable to further reactions under the conditions employed.

[Mo][b][CH2] and [Mo][b2][CH2] can be observed in the reaction between [Mo][b][Mo] and [H2C][b][CH2] in CD2Cl2 (eq 10). After 30 min [Mo][b][Mo] is still the major alkylidene species in the mixture (51% of observable Mo alkylidenes), but [Mo][b][CH2] (39%) and [Mo][b2][CH2] (10%) were also present. The resonances that we assigned to [Mo][b][O] above were not present in these experiments.

The reaction between [Mo][b][Mo] and [H2C][a][O] (“a” implies ethyl ester) yielded a mixture of [H2C][aba][CH2] (in 17% yield) and [H2C][ab][CH2] (in 19% yield; eq 11). This result rules out formation of [i-PrHC][aba][CH-i-Pr] and [i-PrHC][ab][CH-i-Pr], the only oligoene product, could be observed. After 1.5 h however, resonances that could be assigned to [i-PrHC][b][CH-i-Pr] were observed in the crude reaction mixture, consistent with [i-PrHC][b][CH-i-Pr] arising through secondary metathesis reactions between [Mo][b][CH2][i-Pr] and [i-PrHC][b][CH-i-Pr].

The reaction between [Mo][b][Mo] and [Me2C][b][O] (eq 3) gave only [Me2C][b3][CMe2] in 64% yield; that is, the Mo-Wittig reaction is even more favorable relative to C=C metathesis reactions when a trisubstituted olefin is present in the aldehyde. Note also that the reaction shown in eq 13 yielded only [i-PrHC][aba][CH-i-Pr] (in 71% yield), with no evidence for formation of [i-PrHC][ab][CH-i-Pr]. One could argue that the Mo-Wittig reaction is relatively more favored than C=C reactions when the smaller ethyl ester is present instead of an isopropyl ester.

Even [Me2C][b2][CMe2]10 will react slowly with [Mo][b][Mo] (in CD2Cl2) to give (after 3 h) resonances between 12.89 and 12.90 ppm (14% of the total alkylidenes) that can be ascribed to monometallic species, e.g., those shown in eq 14. These species can be formed through metathesis reactions involving the trisubstituted C=C bonds at the ends or the disubstituted C=C bonds in the middle of [Me2C][b2][CMe2]. The relatively slow metathesis reactions in these circumstances is presumably why the reaction between [Mo][b][Mo] and [Me2C][b][O] gave only [Me2C][b3][CMe2] in relatively good yield (64%), as noted above.
We conclude from these and many similar studies that the Mo-Wittig reaction is not as fast and selective as we had hoped; that is, terminal and possibly even internal double bonds are metathesized in a variety of circumstances. The flat polyene chain is relatively accessible sterically and also perhaps especially reactive in a metathesis reaction for electronic reasons.

We assume that the tetrasubstituted CMe2 or CMe3 bond in the five-membered ring is the least reactive by far for steric reasons. There is no evidence for cleavage of the C=C bond in the five-membered ring.

A bimetallic compound that contains a less electron-withdrawing alkoxide might be more selective for the Mo-Wittig reaction. A bimetallic species that contains trifluoro-tert-butoxide (OCMe2(CF3)3) or ORPr instead of OREt was prepared as shown in eq 15.12 NMR spectra suggested that it is a syn/syn isomer (the alkylidene has the syn configuration at each end, as shown) with an alkylidene resonance at 12.26 ppm. Reactions between [MoF3][b][MoF3] and [H2C][b2][CH2] and [H2C][b3][CH2], now in a ratio of 1:1, instead of 2:1.

Figure 3 shows the absorption spectra of the dimers and trimers that contain =CH2 and =CH(−Pr) end groups; the λmax values for these and analogous compounds that contain =CMe2 end groups10 are listed in Table 1. Transitions for the dimers and trimers that have =CH2 end groups consistently are found at shorter wavelengths than the analogous transitions in compounds that contain =CMe2 or =CH(−i-Pr) groups. As one might expect, λmax was the same for all dimers and trimers regardless of whether they contain ethyl esters or isopropyl esters.

Bimetallic Species That Contain More than One Five-Membered Ring. Long polyenes could be prepared more efficiently if Mo species could be prepared that contain more than one five-membered ring unit. Two equivalents of [Mo]-[CHCMe3] react with [H2C][b2][CH2] to yield [Mo][b2][Mo] in 97% yield (eq 16). Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into a THF solution of [Mo][b3][Mo] at −30 °C; these turned out to be crystals of a THF adduct, i.e., (THF)[Mo][b2][Mo](THF) (Figure 4 and Table 2S). A drawing is shown in Figure 4a, and a side view of the conjugated backbone is shown in Figure 4b. The geometry around the metal is approximately trigonal bipyramidal with each THF bound in an apical position.

Table 1. λmax (0−1 transition) and Molar Extinction Coefficients for Dimeric and Trimeric Compounds in CH2Cl2

<table>
<thead>
<tr>
<th>compound</th>
<th>λmax (nm)</th>
<th>ε/104 (cm−1 M−1)</th>
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<tr>
<td>[H2C][b2][CH2]</td>
<td>338</td>
<td>6.7</td>
</tr>
<tr>
<td>[H2C][b2][CH2]</td>
<td>338</td>
<td>4.3</td>
</tr>
<tr>
<td>[i-PrCH][b2][i-PrCH]</td>
<td>346</td>
<td>12.2</td>
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<tr>
<td>[Me2C][b2][CMe2]</td>
<td>356</td>
<td>N/A</td>
</tr>
<tr>
<td>[H2C][b3][CH2]</td>
<td>389</td>
<td>8.4</td>
</tr>
<tr>
<td>[H2C][aba][CH2]</td>
<td>389</td>
<td>6.3</td>
</tr>
<tr>
<td>[i-PrCH][b2][i-PrCH]</td>
<td>396</td>
<td>17.1</td>
</tr>
<tr>
<td>[i-PrCH][aba][i-PrCH]</td>
<td>396</td>
<td>1.2</td>
</tr>
<tr>
<td>[Me2C][b3][CMe2]</td>
<td>404</td>
<td>4.4</td>
</tr>
</tbody>
</table>

(12) Experimental details can be found in the Supporting Information.

Again a bis solvent adduct was obtained, although in this case it is a mixture of (ether)[Mo][b3][Mo](ether) and (ether)-[Mo][b3][Mo](ether) (Figure 5 and Table 2S; see the Experimental Section for a description of the structure and its solution). Figure 5 shows the overall structure of (ether)[Mo][b3][Mo](ether) along with a side view of the conjugated backbone. The geometry around the metal is approximately trigonal bipyramidal with each ether bound in an apical position trans to a syn alkylidene. [Mo][b3][Mo] was obtained in lower yield and lower purity when [Mo][CHCMe2Ph] was employed. It is believed that the initial metathesis product, Me2PhCCH, back-reacts with [Mo][b3][Mo] to yield [Mo][b3][CHCMe2Ph] and unstable [Mo][CH2] (eq 18). [Mo][b3][Mo] was found to be a mixture of syn/syn (∼63%), anti/anti (∼1%), and syn/anti (∼36%) isomers in CD2Cl2, according to proton NMR studies. The solubility differences between [Mo][b3][Mo] and [Mo][b2][Mo] (vide supra) are striking and surprising.

The polyene chains in the unsubstituted dimer and trimer can be compared with those in the “Mo-capped” relatives, including previously reported10 (THF)[MoAr][a2][MoAr](THF) ([MoAr] = Mo(NAr)(OR)2, where Ar = 2,6-diisopropylphenyl). The conjugated backbone is planar for [H2C][b2][CH2] and [H2C][b2][CH2], as well as for (THF)[Mo][b2][Mo](THF) and (THF)[MoAr][a2][MoAr](THF), but (Et2O)[Mo][b2][Mo](Et2O).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Quin][Mo][b][Mo][Quin] (08189) (heterochiral isomer only) and [THF][Mo][b2][Mo][THF] (08042)

<table>
<thead>
<tr>
<th></th>
<th>08189</th>
<th>08042</th>
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<tr>
<td>Mo(1)−N(1)</td>
<td>1.745(3)</td>
<td>1.710(4)</td>
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<tr>
<td>Mo(1)−C(1)</td>
<td>1.951(3)</td>
<td>1.926(5)</td>
</tr>
<tr>
<td>Mo(1)−O(1)</td>
<td>1.969(2)</td>
<td>1.950(4)</td>
</tr>
<tr>
<td>Mo(1)−N(2)</td>
<td>2.294(3)</td>
<td>2.363(3)</td>
</tr>
<tr>
<td>N(1)−Mo(1)−C(1)</td>
<td>99.60(13)</td>
<td>99.17(19)</td>
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<tr>
<td>N(1)−Mo(1)−O(1)</td>
<td>141.23(12)</td>
<td>115.67(19)</td>
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<td>89.16(12)</td>
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<td>99.41(12)</td>
<td>97.71(18)</td>
</tr>
<tr>
<td>O(1)−Mo(1)−C(1)</td>
<td>88.96(12)</td>
<td>170.65(17)</td>
</tr>
<tr>
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<td>85.87(11)</td>
<td>123.87(15)</td>
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<tr>
<td>O(1)−Mo(1)−N(2)</td>
<td>80.96(11)</td>
<td>78.45(14)</td>
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<td>O(2)−Mo(1)−N(2)</td>
<td>166.59(11)</td>
<td>77.09(14)</td>
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<tr>
<td>C(2)−Mo(1)−N(1)</td>
<td>127.1(2)</td>
<td>139.3(4)</td>
</tr>
<tr>
<td>C(11)−N(1)−Mo(1)</td>
<td>165.0(3)</td>
<td>171.2(5)</td>
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<tr>
<td>C(1)−C(2)</td>
<td>1.420(4)</td>
<td>1.421(6)</td>
</tr>
<tr>
<td>C(2)−C(6)</td>
<td>1.397(4)</td>
<td>1.367(6)</td>
</tr>
</tbody>
</table>

Again a bis solvent adduct was obtained, although in this case it is a mixture of (ether)[Mo][b3][Mo](ether) and (ether)-[Mo][b3][Mo](ether) (Figure 5 and Table 2S; see the Experimental Section for a description of the structure and its solution). Figure 5 shows the overall structure of (ether)[Mo][b3]-[Mo](ether) along with a side view of the conjugated backbone. The geometry around the metal is approximately trigonal bipyramidal with each ether bound in an apical position trans to a syn alkylidene. [Mo][b3][Mo] was obtained in lower yield and lower purity when [Mo][CHCMe2Ph] was employed. It is believed that the initial metathesis product, Me2PhCCH, back-reacts with [Mo][b3][Mo] to yield [Mo][b3][CHCMe2Ph] and unstable [Mo][CH2] (eq 18). [Mo][b3][Mo] was found to be a mixture of syn/syn (∼63%), anti/anti (∼1%), and syn/anti (∼36%) isomers in CD2Cl2, according to proton NMR studies. The solubility differences between [Mo][b3][Mo] and [Mo]-[b2][Mo] (vide supra) are striking and surprising.
takes on a more distorted, “wave-like” conformation. A wave-like conformation was also observed in the case of a bimetallic Ru compound, in which the two Ru centers were linked by an all-trans \((\text{CH})_{14}\) bridge. As one might expect, a strictly planar conformation is less likely to be found in the solid state as the conjugated chain becomes longer. The C–C bond lengths in all the bimetallic compounds are slightly shorter than in their unsubstituted analogues, but the C\text{d}C bond lengths and angles are similar in each.

As in the case of reactions between \([\text{Mo}][\text{b}][\text{Mo}]\) and \([\text{H}_2\text{C}][\text{b}][\text{O}]\), reactions of \([\text{Mo}][\text{b}_2][\text{Mo}]\) and \([\text{Mo}][\text{b}_3][\text{Mo}]\) with \([\text{H}_2\text{C}][\text{b}][\text{O}]\) yielded mixtures of oligoenes, according to NMR and UV–vis spectroscopies, as well as preliminary HPLC studies.

Trimethylphosphine and Quinuclidine Adducts of Bimetallic Species. We felt that it may be possible to discriminate more sharply between an Mo-Wittig reaction and a C\text{d}C metathesis reaction in 16e adducts, since the Mo-Wittig reaction might proceed through a six-coordinate species, whereas C\text{d}C metathesis is most likely to be possible only with 14e (base-free) species.

Addition of 2 equiv of PMe\text{3} to \([\text{Mo}][\text{b}][\text{Mo}]\) yielded the PMe\text{3} adduct \([\text{PMe3}][\text{Mo}][\text{b}][\text{Mo}][\text{PMe3}]\) (eq 19). According to \(^1\text{H}, ^1\text{C}, ^3\text{P}, \) and \(^{19}\text{F}\) NMR (CD\text{2}Cl\text{2}) spectra, \([\text{PMe3}][\text{Mo}][\text{b}][\text{Mo}][\text{PMe3}]\) exists as a mixture of one syn/syn (6%) and two anti/anti isomers (94%) (in a ratio 2:1). As many as six isomers (homochiral and heterochiral anti/anti, homochiral and heterochiral syn/syn, and finally two syn/anti isomers, which by definition cannot be heterochiral or homochiral) would be possible for a single type of adduct that is chiral at the metal center. Two possible anti/anti adducts, one heterochiral and one homochiral, in which PMe\text{3} binds trans to one alkoxide in a TBP adduct are shown in Figure 6. The heterochiral dimer has a plane of symmetry that passes through the C\text{b}2 carbon atom of the five-membered ring, while the homochiral dimer has a \(\text{C}_2\) axis through the C\text{b}2 carbon atom.

Addition of 2 equiv of quinuclidine to \([\text{Mo}][\text{b}][\text{Mo}]\) yielded the bisquinuclidine adduct \([\text{quin}][\text{Mo}][\text{b}][\text{Mo}][\text{quin}]\) (eq 20) in high yield. According to \(^1\text{H}, ^1\text{C}, \) and \(^{19}\text{F}\) NMR (C\text{6}D\text{6}) spectra, a mixture of at least six isomers is formed with alkylidene resonances in both the syn and anti region, the majority being anti species. In related monomeric compounds, quinuclidine was shown to attack not only the C\text{NO} but also the NOO and COO

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faces of M(NAr)(CHR)(ORF6)2 species. Therefore it is difficult to say from NMR results alone what is the nature of the various (quin)[Mo][b][Mo](quin) species observed in solution. Since (quin)[Mo][b][Mo](quin) and other quinuclidine adducts mentioned below do not pass elemental analyses, there is even a possibility that monoadducts, i.e., (quin)[Mo][b][Mo] species, may be present in the mixture.

Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into a C6D6 solution of (quin)[Mo][b][Mo](quin) at -30 °C. The structural study revealed that the crystal that was chosen does have the (quin)[Mo][b][Mo](quin) formula and contains co crystallized heterochiral anti/anti (87%) and homochiral anti/anti (13%) isomers with arrangements at Mo that are the same as those proposed for the bisPMe3 adduct (Figure 7; Tables 2 and 2S). The values for Mo(1)–C(1) (1.951(3) Å), Mo–C(1)–C(2) (127.1(2)°), Mo(1)–N(1) (1.745(3) Å), and Mo(1)–N(1)–C(11) (165.0(3)°) are not unusual. The heterochiral and homochiral anti/anti structures are only two of the several species found in solution, as noted above, and need not be the only component of the crystalline sample from which the crystal was chosen.

Addition of 2 equiv of PMe3 to [Mo][b2][Mo] led to formation of (PMe3)[Mo][b][b][Mo](PMe3) (eq 21). As observed for PMe3 adducts of monomeric alkylidenes,14 (PMe3)[Mo][b][b][Mo]–(PMe3) in CD2Cl2 initially was observed as a mixture of two syn/syn isomers (in a ratio 1:6:1), whose Hα resonances overlapped (δ 12.69, JPH 5.5, JCH 120). Over a period of 4 days, the compound isomerized to yield a mixture of two anti/anti isomers (δ 13.62, JPH 7.5, 13.61, JPH = 8.0, JCH = 146, in a ~1:1 ratio, 83%) and two syn/syn isomers (δ 12.72, JPH = 5.5; 12.69, JPH = 5.5, in a 1:2:1 ratio, 17%). Reaction of [Mo][b3][Mo] with 2 equiv of PMe3 led to formation of (PMe3)[Mo][b3][Mo](PMe3) (eq 22), which was observed as a mixture of syn/syn (major) and anti/anti (minor) isomers in C6D6, while reaction of [Mo][b3][Mo] with 2 equiv of quinuclidine yielded the corresponding quinuclidine adduct (eq 23).

Reactions of Adducts with [H2C][b][O]. Reaction of the mixture of (PMe3)[Mo][b][Mo](PMe3) isomers (10 mg) with 4 equiv of [H2C][b][O] in CD2Cl2 (1.5 mL) was monitored over time by 1H NMR spectroscopy. After 1 day, a new doublet resonance was observable at 13.63 ppm (JPH = 6.5 Hz, 15% of Mo-containing species), along with resonances for [H2C][b][b][CH2] and other Mo species, probably among them (PMe3).
was 0.5:1, and what we presume to be \((\text{PMe}_3)[\text{Mo}]_2[\text{CH}_3]\) was still observed. No \([\text{H}_2\text{C}][\text{b}][\text{CH}_3]\) was detected. The fact that the Mo-Wittig reactions involving trimethylphosphine adducts are extremely slow, along with the fact that no \([\text{H}_2\text{C}][\text{b}][\text{CH}_3]\) is detected, suggests that trimethylphosphine may not need to be lost from the metal in order for the complex to undergo the Mo-Wittig reaction and that \(\text{C} = \text{C}\) metathesis is effectively blocked.

Little reaction of \((\text{PMe}_3)[\text{Mo}]_2[\text{Mo}](\text{PMe}_3)\) with \([\text{H}_2\text{C}][\text{b}][\text{O}]\) was observed after 1 day. After 3 days, resonances that could be assigned to \([\text{H}_2\text{C}][\text{b}][\text{CH}_3]\) were observed, along with a new Mo-alkylidene resonance (presumably \((\text{PMe}_3)[\text{Mo}][\text{b}][\text{CH}_3]\), \(\delta = 13.64 \text{ ppm}, d, J_{\text{PH}} = 8 \)) overlapping with the alkylidene proton in the starting material. The new resonances increased in intensity over time. The ratio of unreacted \((\text{PMe}_3)[\text{Mo}][\text{b}][\text{Mo}](\text{PMe}_3)\) to \([\text{H}_2\text{C}][\text{b}][\text{CH}_3]\) was 4.8:1 after 3 days and 1.6:1 after 11 days. However, the reaction was only 50% complete even after 1 month under these conditions. The expected tetramer \([\text{H}_2\text{C}][\text{b}][\text{CH}_3]\) (\(\delta_{\text{max}} = 427 \text{ nm}\)) was isolated after 2 months; no \([\text{H}_2\text{C}][\text{b}][\text{CH}_3]\) was observed.

Reactions of \((\text{PMe}_3)[\text{Mo}][\text{b}][\text{Mo}](\text{PMe}_3)\) with \([\text{H}_2\text{C}][\text{b}][\text{O}]\) were monitored over time, and the same behavior was observed as in the case of \((\text{PMe}_3)[\text{Mo}][\text{b}][\text{Mo}](\text{PMe}_3)\). The expected pentamer \([\text{H}_2\text{C}][\text{b}][\text{CH}_3]\) (\(\delta_{\text{max}} = 455 \text{ nm}\)) was isolated from the product mixture after 1 month. Clearly \((\text{PMe}_3)[\text{Mo}][\text{b}][\text{Mo}](\text{PMe}_3)\) is not significantly more reactive than \((\text{PMe}_3)[\text{Mo}][\text{b}][\text{Mo}](\text{PMe}_3)\). Although this approach may not be suited to preparative chemistry, the purity of the oligoenes products appeared to be high relative to the purity of the products isolated from reactions of \([\text{Mo}][\text{b}][\text{Mo}](\text{quin})\) (\(n = 2, 3\)) with \([\text{H}_2\text{C}][\text{b}][\text{O}]\), according to UV−vis spectroscopy at room temperature.

A reaction between 2 equiv of \([\text{H}_2\text{C}][\text{b}][\text{O}]\) and the mixture of \((\text{quin})[\text{Mo}][\text{b}][\text{Mo}](\text{quin})\) species was monitored over time. After 30 min resonances only for \([\text{H}_2\text{C}][\text{b}][\text{CH}_3]\) were observed along with a new Mo-alkylidene resonance at 13.85 ppm (11% of Mo-containing species). After 1 day no Mo alkylidene resonances were observed and the only observed oligoene was \([\text{H}_2\text{C}][\text{b}][\text{CH}_3]\). The trimer could be prepared from \((\text{quin})[\text{Mo}][\text{b}][\text{Mo}](\text{quin})\) on a synthetic scale and purified by silica gel column chromatography in 63% isolated yield, a considerable improvement over the reaction shown in eq 6. Whether quinuclidine must dissociate from at least one Mo center in \((\text{quin})[\text{Mo}][\text{b}][\text{Mo}](\text{quin})\) to give \((\text{quin})[\text{Mo}][\text{b}][\text{Mo}]\) before \([\text{H}_2\text{C}][\text{b}][\text{O}]\) can react (with the 14e Mo center in \((\text{quin})[\text{Mo}][\text{b}][\text{Mo}]) is not known. The probability that quinuclidine dissociates from both ends before \([\text{H}_2\text{C}][\text{b}][\text{O}]\) reacts with either 14e Mo center is likely to be small. Clearly quinuclidine adducts are more reactive than trimethylphosphine adducts and yield only \([\text{H}_2\text{C}][\text{b}][\text{CH}_3]\) in a more reasonable time frame. It is not known whether quinuclidine remains bound to Mo or not.

Reaction of \((\text{quin})[\text{Mo}][\text{b}][\text{Mo}](\text{quin})\) with \([\text{H}_2\text{C}][\text{b}][\text{O}]\) yielded the pentamer, although it was contaminated with shorter oligoenes according to NMR and UV−vis spectroscopies. Evidently \(\text{C} = \text{C}\) metathesis reactions again compete with Mo-Wittig reactions as the distance between the two metal centers increases. Therefore it seems likely that the relatively clean synthesis of \([\text{H}_2\text{C}][\text{b}][\text{CH}_3]\) in the reaction between \((\text{quin})[\text{Mo}][\text{b}][\text{Mo}](\text{quin})\) and \([\text{H}_2\text{C}][\text{b}][\text{O}]\) is fortuitous. Therefore we must turn to other approaches in order to extend this method to the synthesis of polyenes longer than those reported here.

**Conclusions**

We have described a method of preparing oligoenes that are fragments of polymers obtained by ring-closing metathesis polymerization of dialkyl dipropargylmalonates to give polyenes that contain all five-membered rings. Oligomers with a single structure have been synthesized through alternating Wittig-like reactions of bimetallic Mo-alkylidene compounds with aldehydes followed by metathesis reactions between unsubstituted oligoenes thus synthesized with Mo(NAr′)(CHMe3R)(ORf6)2 (R = Me, Ph). In the Wittig-like reactions with unsaturated aldehydes complications arise because reactions between \(\text{C} = \text{C}\) bonds and Mo−C bonds compete with reactions between \(\text{C} = \text{O}\) bonds and Mo−C bonds. These complications could be minimized through the use of quinuclidine or (less practically) trimethylphosphine adducts as reagents. Although the approach described here employs Mo alkylidenes as stoichiometric reagents, no other method of preparing oligoenes of this type (e.g., phosphorus ylide approaches) has been reported. Also, since spectroscopic investigations are a major goal of this work, it is not necessary to prepare large quantities of pure oligoenes. Finally, we recognize that HPLC is likely to be the method of choice for analyzing and purifying oligoenes for spectroscopic purposes. Spectroscopic studies on pure oligoenes of this type containing up to 23 double bonds will be reported in the next paper in this series.

**Experimental Section**

**General Comments.** All air- and moisture-sensitive materials were manipulated in oven-dried (200 °C) glassware under an 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 prior to use (for diethyl ether, pentane, THF, and methylene chloride), then stored over 4 Å Linde-type molecular sieves. NMR solvents (CD6D, CD2Cl2, and THF-d8) were stored over 4 Å Linde-type molecular sieves. NMR spectra were recorded on Varian 500 or Varian 300 spectrometers. Chemical shifts for 1H and 13C spectra were referenced to the residual 1H and 13C resonances of the deuterated solvent (H: CD6D, δ 7.16; CD2Cl2, δ 5.32; CDCl3, δ 7.27; 13C: CD6D, δ 128.39; CD2Cl2, δ 54.00; CDCl3, δ 67.57; CD3Cl, δ 77.23) and are reported as parts per million relative to tetramethylsilane. 19F NMR spectra were referenced externally to fluorobenzene (δ −113.15 ppm upfield of CFCl3). UV−vis spectra were recorded using a Hewlett-Packard 8452A diode array spectrophotometer at approximately 22 °C. High-resolution mass spectrometry (EI and ESI) measurements were performed at the MIT Department of Chemistry Instrument Facility. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ, Columbia Analytical Services, Tucson, AZ, or Midwest Microlab LLC, Indianapolis, IN.

Mo(N(2,6-Me2C6H3)CHMe3R)(ORf6)2 (R = Ph, Me),17 [Mo][b][Mo],10 [H2C][a][O],15 [H2C][b][O],10 [H2C][b][CH2],10 [MeC]-

18) (a) Trost, B. M.; Older, C. M. Organometallics 2002, 21, 2544.
4.92 ( sept, J = 6, 2H, CH, CO₂(i-Pr)), 4.89 (sept, 4H, J = 6, CH, CO₂(i-Pr)), 3.66 (4H, CH₂), 3.36 (4H, CH₂), 3.30 (4H, CH₂), 2.41 (12H, Me, NAr⁺), 1.43 (12H, CMe₂(CF₃)₂), 1.26 (J = 6, 12H, Me, CO₂(i-Pr)), 1.12 (J = 6, 12H, Me, CO₂(i-Pr)), 1.04 (J = 6, 12H, Me, CO₂(i-Pr)). ¹H NMR (CD₂Cl₂) δ 13.21 (Mo=CHR, 2H), 6.83 (d, J = 15, 2H, CH=CHR), 6.80–6.72 (m, 6H, Ar), 6.50 (d, J = 15, 2H, CH=CHR), 5.09 (sept, J = 6, 2H, CH, CO₂(i-Pr)), 4.90 (sept, 4H, J = 6, CH, CO₂(i-Pr)) 3.86 (4H, CH₂), 3.77 (4H, CH₂), 3.56 (4H, CH₂), 2.27 (12H, Me, NAr⁺), 1.37 (12H, CMe₂(CF₃)₂). ¹¹³C NMR (CD₂Cl₂) δ 280.0 (Mo=CHR), 171.5 (C=O, CO₂(i-Pr)), 157.5, 146.2, 138.3, 130.9, 125.8, 126.2, 124.4, 124.3 (q, J CF = 282, CF₂), 124.0 (q, J CF = 286, CF₂), 123.2, 69.8 (OCH₃), 69.6 (OCH₂Me), 57.3 (quat), 57.1 (quat), 46.3 (CH₃), 41.3 (CH₃), 40.2 (CH₂), 21.70 (Me, CO₂(i-Pr)), 21.68 (Me, CO₂(i-Pr)), 21.63 (Me, CO₂(i-Pr)), 19.6, 19.3; ¹⁹F NMR (CD₂Cl₂) δ −78.2 (q, CF₂), −78.4 (q, CF₂). Anal. Calcd. For C₇₇H₈₀F₂₈N₂O₁₄P₂: C, 47.9; H, 4.66, N, 1.44. Found: C, 47.23; H, 4.70, N, 1.31.

**Synthesis of (PMe₃)[Mo][b][Mo][PMe₃]**. To a stirred solution of [Mo][b][Mo] (142 mg, 0.1 mmol) in Et₂O (10 mL) was added PMe₃ (30 µL, 0.3 mmol) via a microsyringe syringe. No color change was observed. The mixture was stirred overnight. The solvent was removed in vacuo, and the residue was triturated in pentane (5 mL) for 1 h, then filtered through a frit, and dried, yielding 137 mg (87% yield) of a deep orange powder of (PMe₃)[Mo][b][Mo][PMe₃]. In CD₂Cl₂, the compound exists as a mixture of one syn/syn (δ 12.35, Jₚ₋ₚ = 5, 6%) and two anti/anti isomers (94%, in ~2:1 ratio). The major anti/anti isomer appears to be heterochiral (PMe₃)[Mo][b][Mo][PMe₃] isomers: 1H NMR spectra are reported for a mixture of the two anti/anti isomers unless otherwise indicated.

¹H NMR (CD₂Cl₂) δ 13.24 (d, Jₚ₋ₚ = 6.5, 2H, Mo=CHR, homo), 13.21 (d, Jₚ₋ₚ = 6.5, 2H, Mo=CHR, anti/anti isomer, hetero), 7.17–7.11 (m, 4H, Ar), 7.10–7.07 (m, 2H, Ar), 5.11 (sept, J = 6, 1H, CH, i-Pr, hetero), 5.03 (sept, J = 6, 2H, CH, i-Pr, homo), 4.92 (sept, J = 6, 1H, CH, i-Pr, hetero), 4.11 (d, J = 19, 2H, homo), 3.84 (d, J = 19, 2H, hetero), 3.78 (J = 19, 2H, hetero), 3.59 (d, J = 19, 2H, homo), 2.74 (6H, CH₃, 2,6-Me₂C₆H₄), 2.46 (6H, CH₃, 2,6-Me₂C₆H₄), 1.90 (6H, OR₃, homo), 1.88 (6H, OR₃, hetero), 1.28–1.22 (overlapping m, 30H, CH₃, PMe₃, and CO₂(i-Pr), 1.19 (broad, 6H, OR₃); ¹³¹C NMR (CD₂Cl₂) δ 260.3 (Mo=CHR), 172.8, 171.6, 170.9, 154.6, 147.1, 139.2, 134.32, 134.28, 129.5, 129.4, 128.8, 128.7 (Jₚ = 26, C=CH), 128.4 (Jₚ = 27, C=C), 125.1 (q = 287, OCM(CF₃)₂), 69.9, 69.7, 69.5, 57.2, 57.0, 44.63, 44.55, 21.78, 21.76, 21.71, 21.6, 19.68, 19.65, 19.57, 19.52, 19.0, 18.9, 14.7 (d, J CF = 25, PMe₃), 14.5 (d, J CF = 26, PMe₃). ¹¹³C NMR (CD₂Cl₂) δ 6.65 (Mo=CHR, homo), 6.64 (Mo=CHR, anti/anti isomer, hetero), 6.64 (Mo=CHR, anti/anti isomer, homo), 6.41 (2H, CH=CHR), 5.11–4.99 (m, 4H, CH, i-Pr), 4.02–3.90 (m, 2H, CH₂), 3.80–3.66 (m, 4H, CH₂), 3.57–3.46 (m, 2H, CH₂), 3.43–3.22 (m, 4H, CH₂), 2.74 (6H, 2,6-Me₂C₆H₄, minor), 2.56 (12H, 2,6-Me₂C₆H₄, major), 2.47 (6H, 2,6-Me₂C₆H₄), 1.88 (broad, 6H, CMe(CF₃)₂, minor), 1.86 (broad, 6H, CMe(CF₃)₂, major), 1.32–1.21 (overlapping m, 40H, CH₃, i-Pr, PMe₃, CMe(CF₃)₂). ¹³¹C NMR (CD₂Cl₂) δ 6.65 (Mo=CHR, homo), 6.64 (Mo=CHR, anti/anti isomer, hetero), 6.64 (Mo=CHR, anti/anti isomer, homo), 6.41 (2H, CH=CHR), 5.11–4.99 (m, 4H, CH, i-Pr), 4.02–3.90 (m, 2H, CH₂), 3.80–3.66 (m, 4H, CH₂), 3.57–3.46 (m, 2H, CH₂), 3.43–3.22 (m, 4H, CH₂), 2.74 (6H, 2,6-Me₂C₆H₄, minor), 2.56 (12H, 2,6-Me₂C₆H₄, major), 2.47 (6H, 2,6-Me₂C₆H₄), 1.88 (broad, 6H, CMe(CF₃)₂, minor), 1.86 (broad, 6H, CMe(CF₃)₂, major), 1.32–1.21 (overlapping m, 40H, CH₃, i-Pr, PMe₃, CMe(CF₃)₂). ¹³¹C NMR (CD₂Cl₂) δ 6.65 (Mo=CHR, homo), 6.64 (Mo=CHR, anti/anti isomer, hetero), 6.64 (Mo=CHR, anti/anti isomer, homo), 6.41 (2H, CH=CHR), 5.11–4.99 (m, 4H, CH, i-Pr), 4.02–3.90 (m, 2H, CH₂), 3.80–3.66 (m, 4H, CH₂), 3.57–3.46 (m, 2H, CH₂), 3.43–3.22 (m, 4H, CH₂), 2.74 (6H, 2,6-Me₂C₆H₄, minor), 2.56 (12H, 2,6-Me₂C₆H₄, major), 2.47 (6H, 2,6-Me₂C₆H₄), 1.88 (broad, 6H, CMe(CF₃)₂, minor), 1.86 (broad, 6H, CMe(CF₃)₂, major), 1.32–1.21 (overlapping m, 40H, CH₃, i-Pr, PMe₃, CMe(CF₃)₂).
The mixture was stirred overnight. The solvent was removed in vacuo, and the residue was triturated in pentane (5 mL) for 1 h, then filtered through a glass frit. Removal of the solvent in vacuo yielded 153 mg (93% yield) of (quin)[Mo][b][Mo](quin) as a brown powder. In C₆D₆, the compound exists as a complex mixture of syn and anti isomers, according to (seven) resonances in the alkylidene region.

Selected ¹H NMR (C₆D₆) δ 13.57 (15%), 13.44 (12%), 13.36 (32%), 13.28 (7%), 12.68 (17%), 12.47 (13%), 12.33 (4%); ¹³C NMR (C₆D₆) δ −76.5, −76.7, −76.8, −77.17, −77.22, −77.6, −77.8, −78.0, −78.3. Attempts to obtain suitable elemental analyses were unsuccessful.

Synthesis of (quin)[Mo][b][Mo](quin). Quinuclidine (6 mg, 0.05 mmol) was added to a stirred solution of [Mo][b][Mo] [47 mg, 0.027 mmol] in diethyl ether (10 mL). No color change was observed. The mixture was stirred overnight. The solvent was removed in vacuo, and the residue was triturated in pentane (5 mL) for 1 h, then filtered through a frit and dried in vacuo, yielding 47 mg (90% yield) of (quin)[Mo][b][Mo](quin), a red powder, as a mixture of syn and anti isomers according to the ¹H NMR (C₆D₆) spectrum.

Selected ¹H NMR (C₆D₆) resonances: δ 13.90 overlapping with 13.88 (24%), 13.17 overlapping with 13.16 (37%), 12.98 overlapping with 12.96 (39%); ¹³C NMR (C₆D₆) δ −76.8, −77.2, −77.5, −77.8, −78.1, −78.3, −79.4. Attempts to obtain suitable elemental analyses were unsuccessful.

Synthesis of H₂C[b][CH₂] from (quin)[Mo][b][Mo]. Solid (quin)[Mo][b][Mo] (180 mg, 0.11 mmol) was dissolved in 0.7 mL of CD₂Cl₂, transferred to a J. Young NMR tube, and monitored directly to molybdenum were taken from the difference Fourier circle diffractometer (for [Et₂O][Mo][b3][Mo][Et₂O]) performing Siemen Platform three-circle diffractometer or a Bruker D8 three-circle diffractometer (for [Et₂O][Mo][b3][Mo][Et₂O]) coupled to Siemens P4 four-circle diffractometer and measured with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) (or Cu Kα radiation (λ = 1.54178 Å) for the data of [Et₂O][Mo][b3][Mo][Et₂O]) performing q-ω-scans. All structures were solved by direct methods using SHELXTL and refined against F² on all data by full-matrix least-squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on any carbon atom that binds directly to molybdenum were taken from the difference Fourier synthesis and refined semireflexively with the help of distance restraints. All other 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).

H₂C[b][CH₂] crystallizes in the monoclinic space group P2₁ with half a molecule in the asymmetric unit; the second half is generated by the crystallographic inversion center. The complete conjugated olefinic core of the molecule (i.e., atoms C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(16) and their symmetry equivalents) is planar within experimental error (0.03 Å).

H₂C[b][CH₂] crystallizes in the monoclinic space group P2₁ with one target molecule and a disordered solvent molecule (diethyl ether) in the asymmetric unit. The 14 conjugated carbon atoms C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(16) and their symmetry equivalents are planar within experimental error (0.03 Å).

[THF][Mo][b][Mo][THF] crystallizes in the monoclinic space group P2₁/cm with half a molecule in the asymmetric unit; the second half is generated by the crystallographic inversion center. The molecule cocrysallizes with a mixture of THF and pentane solvent molecules sharing the same site and disordered over several positions. This results in noninteger values for the elements C, H,

and O in the empirical formula. Three of the four ligands bound to the metal atom are also disordered over two positions. These disorders were refined with the help of similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. In spite of relatively low overall relative data quality, all hydrogen atoms of the olefinic core were clearly visible in the difference Fourier map and H(1) could be taken from the list of residual electron density maxima as described above. The conjugated olefinic core of the molecule (i.e., atoms C(1), C(2), C(3), C(5), C(6), C(7) and their symmetry equivalents) is perfectly planar within experimental error (0.01 Å) with the ester group carrying atom C(4) and its symmetry equivalent 0.358(8) Å above the plane.

\([\text{Et}_2\text{O}]\{\text{Mo}\}[^b_3]\{\text{Mo}\}[^\text{Et}_2\text{O}]\) crystallizes in the triclinic space group \(P1\) with two target molecules and several disordered solvent molecules in the asymmetric unit. The two crystallographically independent molecules are almost identical. The only difference between them is that the trigonal-bipyramidal coordination spheres of the two Mo atoms in one molecule are completed by two diethyl ether molecules (bisetherate), while one of the two Mo atoms in the other molecule carries a thf molecule and the other Mo a mixture of thf and Et₂O (ca. 60% thf, 40% ether). In addition, one Mo center of the bisetherate is disordered over two positions (and so are all atoms of the ligands that bind to it). The trimeric linkers between the two metals of both independent molecules, as well as the other Mo atoms and all other ligands, are well ordered. The structure does contain several noncoordinated solvent molecules, which are highly disordered over several positions, and a mixture of thf and pentane. This fairly complex solvent disorder model involves the crystallographic inversion center and results in noninteger values for the elements C, H, and O in the empirical formula. The disorders were refined with the help of similarity restraints on 1−2 and 1−3 distances. Similarity restraints and rigid bond restraints for anisotropic displacement parameters were applied to all atoms. The 12 conjugated carbon atoms C(1), C(2), C(6), C(7), C(8), C(9), C(13), C(14), C(15), C(16), C(20), and C(21) form a perfect plane within 0.10 Å. The best plane through all atoms of the planar core (the atoms mentioned above plus C(3), C(4), C(10), C(12), C(17), and C(19)) deviates only marginally from the first plane and is perfect within 0.11 Å. The ester group carrying atoms C(4), C(11), and C(18) are slightly above or below this plane (C(4) deviates 0.477(6) Å, C(11) 0.066(8) Å, and C(18) 0.554(7) Å). The planarity of the core of the second independent molecule is identical within the experimental error.

\([\text{quin}]\{\text{Mo}\}[^b]\{\text{Mo}\}[^\text{quin}]\) crystallizes in the triclinic space group \(P1\) with one molecule in the asymmetric unit. The ligands attached to the two molybdenum atoms are heavily disordered. Some of those disorders could be resolved and were refined using similarity restraints as described above. It is interesting to note that one of the ligand disorders corresponds to a mixture of isomers: the two axial ligands on Mo(2) (one O-C₆H₄F₆ ligand and one N-C₇H₁₃ ligand) are swapped in about 13% of the unit cells, giving rise to a different conformation of the chiral face on Mo(2). Therefore the crystal structure at hand describes a mixture of the heterochiral isomer with the homochiral one. The ratio of the two isomers was refined freely and converged at 0.867(2), corresponding to 87% of the heterochiral isomer and 13% of the homochiral one in the crystal. Atoms C(1), C(2), C(3), C(5), C(6), and C(7) of the olefinic core form a perfect plane within experimental error (0.03 Å). The ester group carrying atom C(4) lies 0.426(6) Å above this plane.

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Supporting Information Available:
Experimental details for syntheses of aldehydes, OC(CF₃)Me₂ complexes, and other miscellaneous experiments, tables of crystallographic data and CIF files for \([\text{H}_2\text{C}][^b_2]\{\text{CH}_2\}\) (06196), \([\text{H}_2\text{C}][^b_2]\{\text{CH}_2\}\) (06201), \([\text{THF}]\{\text{Mo}\}[^b_3]\{\text{Mo}\}[^\text{THF}]\) (08042), \([\text{Et}_2\text{O}]\{\text{Mo}\}[^b_3]\{\text{Mo}\}[^\text{Et}_2\text{O}]\) (D8-08011), and \([\text{quin}]\{\text{Mo}\}[^b]\{\text{Mo}\}[^\text{quin}]\) (08189). This material is available free of charge via the Internet at http://pubs.acs.org. Data for the structures are also available to the public at http://www.reciprocalnet.org.

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