6202 *Organometallics* **2008,** *27,* 6202–6214

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

Received August 5, 2008

In this paper we demonstrate a method of synthesizing oligoenes of diisopropyldipropargylmalonate, [CH$_2$][b$_x$][CH$_2$] ($x = 2, 3, 4, 5$), in which the "b" repeat unit is identical to the five-membered ring formed in a tail-to-tail cyclopolymerization of diisopropyldipropargylmalonate, and methylene groups are capping the ends. For example, a "degenerate" metathesis reaction between the "monomer", [CH$_2$][b][CH$_2$], and 2 equiv of Mo(NAr′)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ ([Mo][CHCMe$_2$Ph] where Ar′ = 2,6-Me$_2$C$_6$H$_3$ and OR$_{F6}$ = OCMe(CF$_3$)$_2$) gives [Mo][b][Mo]. An "Mo-Wittig" reaction between [Mo][b][Mo] and 2 equiv of the aldehyde, [CH$_2$][b][O], then gives the "trimer", [CH$_2$][b$_3$][CH$_2$]. Treatment of [CH$_2$][b$_3$][CH$_2$] with 2 equiv of [Mo][CHCMe$_2$Ph] gives [Mo][b$_3$][Mo], which upon treatment with 2 equiv of [CH$_2$][b][O] gives the "pentamer", [CH$_2$][b$_5$][CH$_2$], which contains 11 double bonds in conjugation in a molecule in which the repeat units are connected by *trans* C=C bonds. The oligoenes are not always obtained in high yield in pure form because (*inter alia*) C=C metathesis reactions compete with the Mo-Wittig reaction of the aldehyde (e.g., to give [CH$_2$][b$_2$][CH$_2$] also in the synthesis of [CH$_2$][b$_3$][CH$_2$]). These complications could be minimized by employing adducts (L)[Mo][b$_x$][Mo](L), where L = PMe$_3$ or quinuclidine, instead of base-free [Mo][b$_x$][Mo] species in the Mo-Wittig reaction. X-ray structures are reported for [CH$_2$][b$_2$][CH$_2$], [CH$_2$][b$_3$][CH$_2$], (THF)[Mo][b$_2$][Mo](THF), (Et$_2$O)[Mo][b$_3$][Mo](Et$_2$O), and a mixture of homochiral and heterochiral [quin][Mo][b][Mo][quin].

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.[1] Conjugated polymers also are of fundamental interest as models for understanding the electronic and optical properties of one-dimensional, conjugated π-electron systems in general. Polyacetylene, the simplest π-conjugated organic polymer, is relatively sensitive to oxygen and insoluble in common organic solvents. In contrast, substituted polyacetylenes such as polyphenylacetylenes[2] or poly[1,6-heptadiynes][3] are often more soluble and stable to air than is polyacetylene itself. A wide variety of other conjugated polymers such as polyparaphenylenevinylenes, polyparaphenyleneethnylenes, polythiophenes, and polypyrroles continue to be explored today.[4]

Poly[1,6-heptadiynes] such as poly[dialkyldipropargylmalonates], which are formed in an alkylidene-catalyzed cyclopolymerization reaction, are highly conjugated, relatively soluble, and relatively stable in air.[3] They were first prepared using "classical" olefin metathesis catalysts, i.e., Mo or W halides or oxyhalides treated with some alkylating agent.[3] In 1992 it was shown that diethyldipropargylmalonate (DEDPM) and related derivatives could be cyclopolymerized with Mo-based olefin metathesis catalysts such as Mo(NAr)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$, OR$_{F6}$ = OCMe(CF$_3$)$_2$).[5] These studies confirmed that high oxidation state Mo alkylidenes are catalysts for cyclopolymerization reactions of this general type and that five-membered rings and six-membered rings are formed (most likely) through addition of the first triple bond to the alkylidene to give a metallacyclobutene with the olefinic substituent (the former terminal acetylene group) in either the α or the β position, respectively. Catalysts subsequently were designed that produce polymers containing all six-membered rings[6] or >95% five-membered rings.[7] Ruthenium catalysts that produce largely five-membered rings have also been developed.[8] Among Mo catalysts all six-membered rings are formed when especially crowded biscarboxylate initiators are employed, which for steric reasons force "β addition" of the terminal triple bond. Initiators

---

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

(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) (a) Masuda, T.; Abdul Karim, S. M.; Nomura, R. *J. Mol. Catal. A* **2000**, *160*, 125. (b) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1986**, *81*, 122. (c) Mizumoto, T.; Masuda, T.; Higashimura, T. *J. Polym. Sci. 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. (f) Masuda, T. *J. Poly. Sci. A: Polym. Chem.* **2007**, *45*, 165.

(3) (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) Buchmeiser, M. R. *Monatsh. Chem.* **2003**, *134*, 327. (d) Buchmeiser, M. R. *Adv. Polym. Sci.* **2005**, *176*, 89.

(4) Martin, R. E.; Diedrich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350.

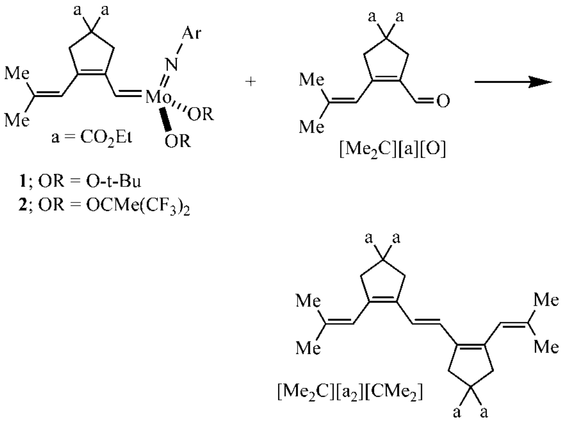
(5) (a) Fox, H. H.; Schrock, R. R. *Organometallics* **1992**, *11*, 2763. (b) Fox, H. H.; Wolf, M. O.; O'Dell, R.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827.

(6) (a) Schattenmann, F. J.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3295. (b) Schrock, R. R.; Tonzetich, Z. J.; Lichtscheidl, A. G.; Müller, P. *Organometallics* **2008**, *27*, 3986.

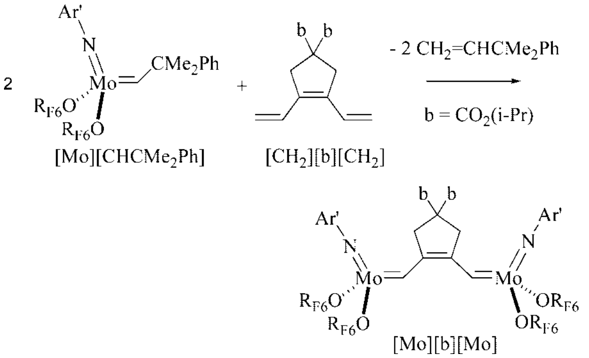
(7) (a) Anders, U.; Nuyken, O.; Buchmeiser, M. R.; Wurst, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 4044. (b) Anders, U.; Nuyken, O.; Buchmeiser, M. R.; Wurst, K. *Macromolecules* **2002**, *35*, 9029. (c) Anders, U.; Nuyken, O.; Buchmeiser, M. R. *J. Mol. Catal. A* **2004**, *213*, 89.

10.1021/om8007585 CCC: $40.75 © 2008 American Chemical Society
Publication on Web 10/31/2008

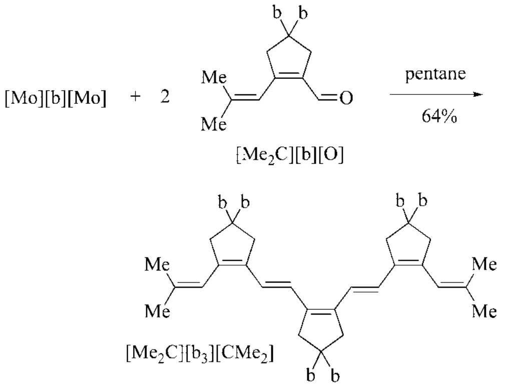
that contain the very type of five-membered ring being formed in a cyclopolymerization reaction, i.e., **1** in eq 1, have been shown to initiate rapidly,[9] which is a requirement in order to prepare polymers with a known and controllable chain length and a low polydispersity. It has been shown that **2** will react with the aldehyde, [Me_2C][a][O] (eq 1), to yield the "dimer", [Me_2C][a_2][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 [Mo][b][Mo], which can be prepared as shown in eq 2 ([Mo] is $Mo(NAr')(OR_{F6})_2$ and Ar′ = 2,6-$Me_2C_6H_3$), 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]



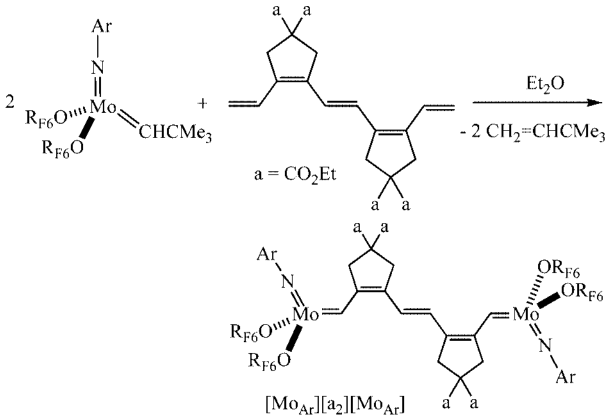
(1)



(2)

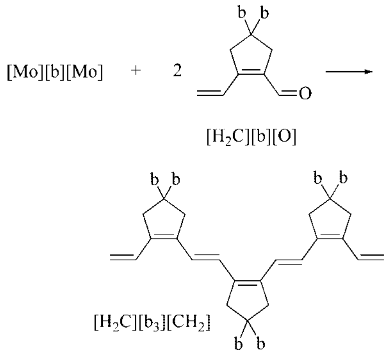


(3)



(4)

The results described above set the stage for a possible synthesis of a series of oligoenes with a specific length that contain =CH_2 end groups instead of =CMe_2 end groups. For example, we proposed that reaction of 2 equiv of [H_2C][b][O] (eq 5) with [Mo][b][Mo] would yield the "trimeric" 7-ene, [H_2C][b_3][CH_2]. Since [H_2C][b_3][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 [H_2C][b][O]. Related stepwise reactions would then produce the heptamer, nonamer, etc. An "even-membered" series of oligomers could be prepared beginning with [Mo][b_2][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.



(5)

Results and Discussion

Reactions Involving the Bimetallic Species [Mo][b][Mo]. Attempts to synthesize the "trimer," [H_2C][b_3][CH_2], produced two products in low yield that could be separated by silica gel column chromatography and identified by ^{1}H NMR spectroscopy

---

(8) (a) Krause, J. O.; Zarka, M. T.; Anders, U.; Weberskirch, R.; Nuyken, O.; Buchmeiser, M. R. *Angew. Chem.* **2003**, *115*, 6147. (b) Krause, J. O.; Nuyken, O.; Buchmeiser, M. R. *Chem.−Eur. J.* **2004**, *10*, 2029. (c) Krause, J. O.; Wang, D.; Anders, U.; Weberskirch, R.; Zarka, M. T.; Nuyken, O.; Jäger; C.; Haarer, D.; Buchmeiser, M. R. *Macromol. Symp.* **2004**, *217*, 179. (d) Halbach, T. S.; Krause, J. O.; Nuyken, O.; Buchmeiser, M. R. *Macromol. Rapid Commun.* **2005**, *26*, 784. (e) Vygodskii, Y. S.; Shaplov, A. S.; Lozinskaya, E. I.; Vlasov, P. S.; Malyshkina, I. A.; Gavrilova, N. D.; Kumar, P. S.; Buchmeiser, M. R. *Macromolecules* **2008**, *41*, 1919. (f) Mayershofer, M.; Nuyken, O.; Buchmeiser, M. R. *Macromolecules* **2006**, *39*, 3484.

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

(10) Czekelius, C.; Hafer, J.; Tonzetich, Z. J.; Schrock, R. R.; Christensen, R. L.; Müller, P. *J. Am. Chem. Soc.* **2006**, *128*, 16664.

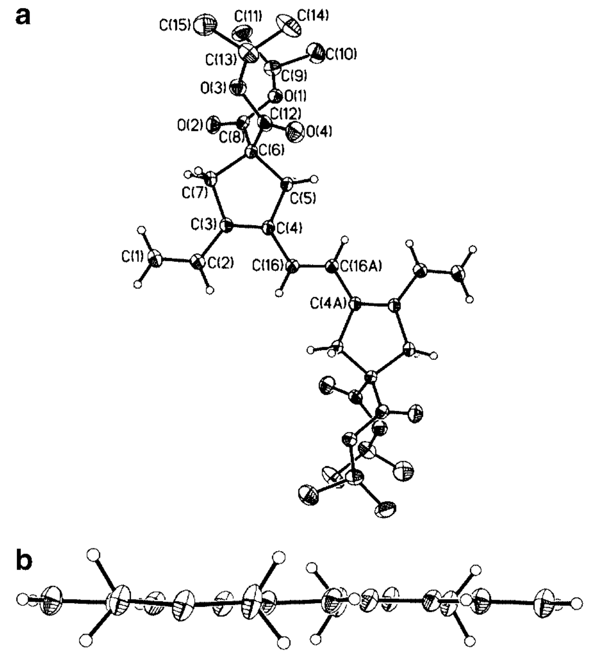


Figure 1. (a) Thermal ellipsoid drawing (50%) of the entire molecule of $[H_2C][b_2][CH_2]$. Selected C−C distances (Å): C(1)−C(2) = 1.3381(13), C(2)−C(3) = 1.4516(13), C(3)−C(4) = 1.3594(12), C(4)−C(16) = 1.4439(12), C(16)−C(16A) = 1.3558(17). (b) Side view of the main chain of $[H_2C][b_2][CH_2]$ (esters omitted).

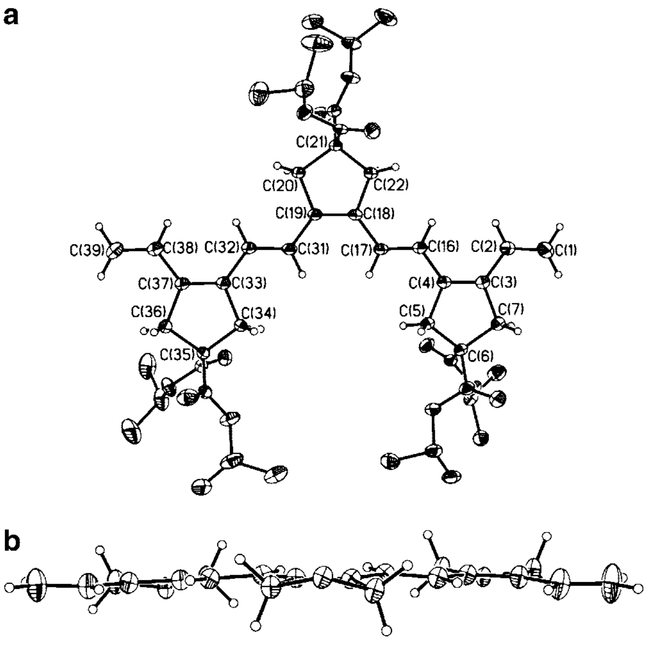
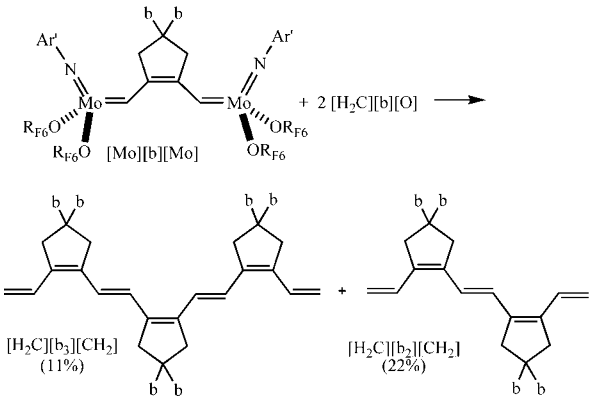


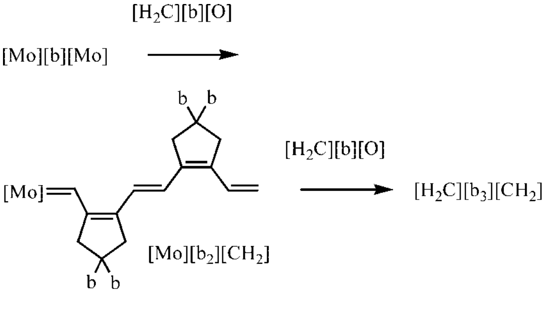
Figure 2. (a) Thermal ellipsoid drawing (50%) of the entire molecule of $[H_2C][b_3][CH_2]$. Selected distances (Å): C(1)−C(2) = 1.326(2), C(2)−C(3) = 1.453(2), C(3)−C(4) = 1.356(2), C(4)−C(16) = 1.4443(19), C(16)−C(17) = 1.347(2), C(17)−C(18) = 1.4408(18), C(18)−C(19) = 0.3617(19), C(19)−C(31) = 1.4428(19), C(31)−C(32) = 1.348(2), C(32)−C(33) = 1.4454(19), C(33)−C(37) = 1.355(2), C(37)−C(38) = 1.451(2), C(38)−C(39) = 1.322(2). (b) Side view of the main chain of $[H_2C][b_3][CH_2]$ (esters omitted).

as the expected "trimer," $[H_2C][b_3][CH_2]$ (in 11% yield), and the unexpected "dimer", $[H_2C][b_2][CH_2]$, in 22% yield (eq 6). The same ratio of dimer to trimer was observed when [Mo][b][Mo] was added *to* 5−10 equiv of $[H_2C][b][O]$. 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 1S[11]). 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.

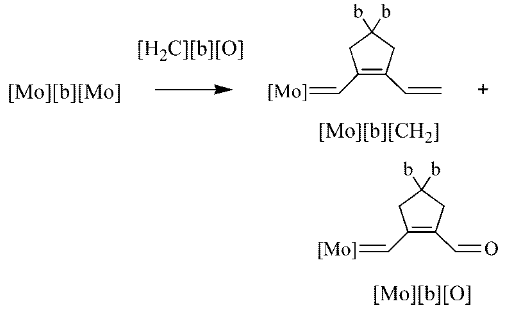


(6)

We propose that $[H_2C][b_3][CH_2]$ is formed via a "normal" Wittig-like reaction between $[H_2C][b][O]$ and each end of [Mo][b][Mo], most likely with $[Mo][b_2][CH_2]$ (eq 7) as an intermediate. Formation of $[H_2C][b_2][CH_2]$ must result from competition between the desired Mo-Wittig reaction and metathesis of a terminal or possibly even internal (*trans* disubstituted) C=C bond within various $[H_2C][b_x][CH_2]$ or $[Mo][b_x][CH_2]$ species in the crude mixture. The low yields of dimer and trimer are consistent with formation of oligoenes longer than $[H_2C][b_3][CH_2]$, along with ethylene, via homocoupling of terminal C=C bonds. It should be noted that we cannot exclude competition between the Wittig reaction and a metathesis reaction involving the terminal C=C bond *within* $[H_2C][b][O]$, as shown in eqs 8 and 9.



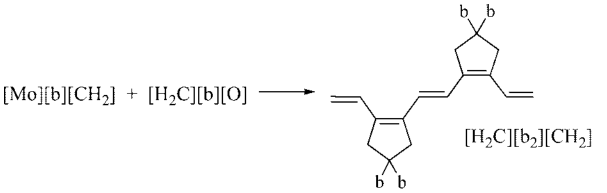
(7)



(8)

---

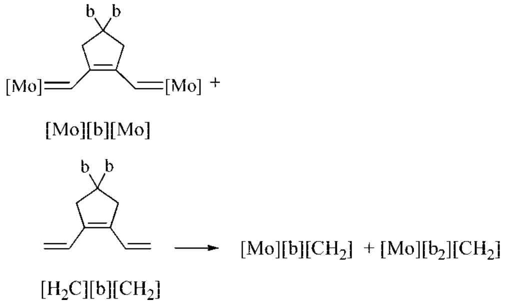
[11] Crystallographic details can be found in tables submitted along with CIF files as part of the Supporting Information.



(9)

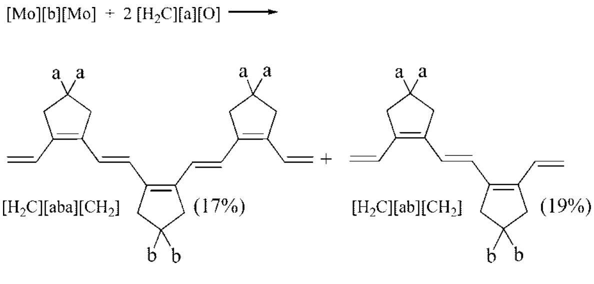
Some evidence for [Mo][b][O] could be found in a reaction between [Mo][b][Mo] and 1 equiv of [H$_2$C][b][O] in CD$_2$Cl$_2$. According to proton NMR studies, after 30 min all [H$_2$C][b][O] had been consumed, but some [Mo][b][Mo] was still present (14% of the Mo alkylidene species) and new alkylidene H$_\alpha$ resonances were observed that could be assigned to [Mo][b][O] (at 11.95 ppm, 46%), [Mo][b][CH$_2$] (at 12.94 ppm), and [Mo][b$_2$][CH$_2$] (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 [H$_2$C][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 [H$_2$C][b$_2$][CH$_2$] to [H$_2$C][b$_3$][CH$_2$]. Apparently [Mo][b][O] is relatively stable to further reactions under the conditions employed.

[Mo][b][CH$_2$] and [Mo][b$_2$][CH$_2$] can be observed in the reaction between [Mo][b][Mo] and [H$_2$C][b][CH$_2$] in CD$_2$Cl$_2$ (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][CH$_2$] (39%) and [Mo][b$_2$][CH$_2$] (10%) were also present. The resonances that we assigned to [Mo][b][O] above were not present in these experiments.



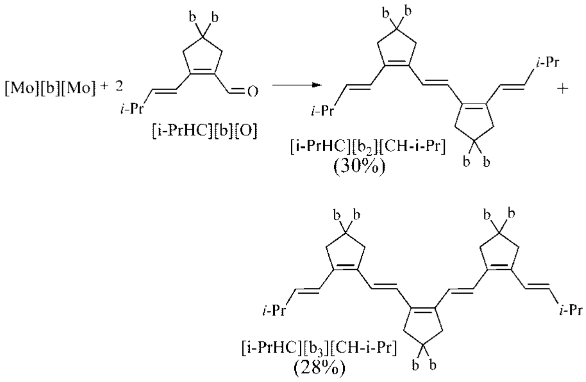
(10)

The reaction between [Mo][b][Mo] and [H$_2$C][a][O] ("a" implies ethyl ester) yielded a mixture of [H$_2$C][aba][CH$_2$] (in 17% yield) and [H$_2$C][ab][CH$_2$] (in 19% yield; eq 11). This result rules out formation of the dimer through alkylidene coupling in a bimolecular decomposition of [Mo][b][CH$_2$].



(11)

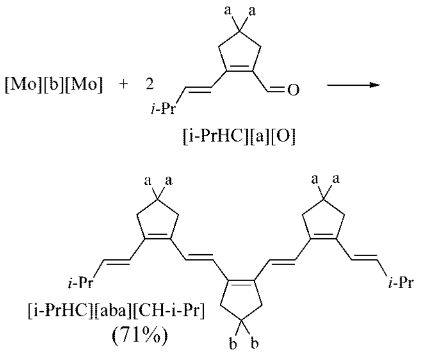
Reactions between [Mo][b][Mo] and [*i*-PrHC][b][O] gave [*i*-PrHC][b$_2$][CH-*i*-Pr] and [*i*-PrHC][b$_3$][CH-*i*-Pr] in approximately equal amounts (eq 12). They could be separated by silica gel column chromatography and identified through NMR studies. Since the yield of these two products is higher than the yield of [H$_2$C][b$_2$][CH$_2$] and [H$_2$C][b$_3$][CH$_2$], this result suggests that for steric reasons the Wittig reaction is more favorable relative to C=C reactions when the aldehyde contains the (*i*-Pr)CH=CH– end group.



(12)

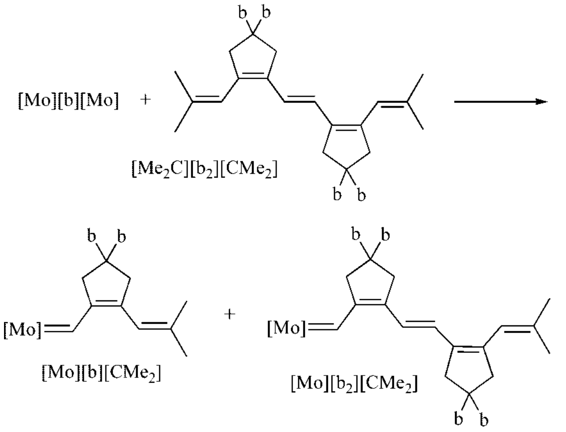
The reaction between [Mo][b][Mo] and 1 equiv of [*i*-PrHC][b][O] was monitored by proton NMR. After 30 min unreacted [Mo][b][Mo] was still present, but resonances that could be assigned to [Mo][b$_2$][CH-*i*-Pr] and [*i*-PrHC][b$_3$][CH-*i*-Pr], the only oligoene product, could be observed. After 1.5 h however, resonances that could be assigned to [*i*-PrHC][b$_2$][CH-*i*-Pr] were observed in the crude reaction mixture, consistent with [*i*-PrHC][b$_2$][CH-*i*-Pr] arising through secondary metathesis reactions between [Mo][b$_2$][CH-*i*-Pr] and [*i*-PrHC][b$_3$][CH-*i*-Pr].

The reaction between [Mo][b][Mo] and [Me$_2$C][b][O] (eq 3) gave only [Me$_2$C][b$_3$][CMe$_2$] in 64% yield; that is, the Mo-Wittig reaction is even more favorable relative to C=C metathesis reactions when a *tri*substituted 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.



(13)

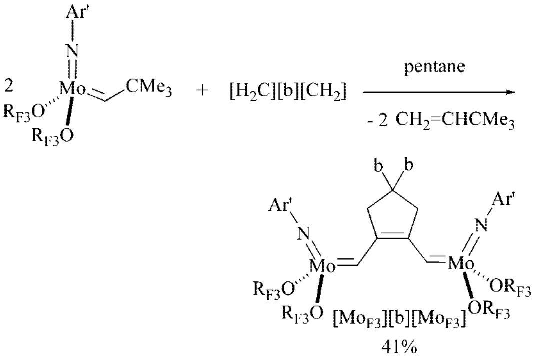
Even [Me$_2$C][b$_2$][CMe$_2$]^{10} will react slowly with [Mo][b][Mo] (in CD$_2$Cl$_2$) to give (after 3 h) resonances between 12.89 and 12.90 ppm (14% of the total alkylidenes) that can be ascribed to monometallic species, e.g., those shown in eq 14. These species can be formed through metathesis reactions involving the trisubstituted C=C bonds at the ends or the disubstituted C=C bonds in the middle of [Me$_2$C][b$_2$][CMe$_2$]. The relatively slow metathesis reactions in these circumstances is presumably why the reaction between [Mo][b][Mo] and [Me$_2$C][b][O] gave only [Me$_2$C][b$_3$][CMe$_2$] in relatively good yield (64%), as noted above.



(14)

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 C═C 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 ($OCMe_2(CF_3) = OR_{F3}$) instead of OR_{F6} 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 [Mo$_{F3}$][b][Mo$_{F3}$] and [H$_2$C][b][O] in CD_2Cl_2 again yielded both [H$_2$C][b$_2$][CH$_2$] and [H$_2$C][b$_3$][CH$_2$], now in a ratio of ~1:1, instead of 2:1.



(15)

Figure 3 shows the absorption spectra of the dimers and trimers that contain ═CH$_2$ and ═CH(*i*-Pr) end groups; the λ_{max} values for these and analogous compounds that contain ═CMe$_2$ end groups[10] are listed in Table 1. Transitions for the dimers and trimers that have ═CH$_2$ end groups consistently are found at shorter wavelengths than the analogous transitions in compounds that contain ═CMe$_2$ or ═CH(*i*-Pr) groups. As one might expect, λ_{max} 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][CHCMe$_3$] react with [H$_2$C][b$_2$][CH$_2$] to yield [Mo][b$_2$][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][b$_2$][Mo] at −30 °C; these turned out to be crystals of a THF adduct, i.e., (THF)[Mo][b$_2$][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 *trans* to a *syn* alkylidene. Binding of THF *trans* to the Mo═C bond has been observed for other dimeric species of this general type.[10,13] Selected bond lengths and angles can be found in Table 2. [Mo][b$_2$][Mo] is not readily soluble in pentane, benzene, or dichloromethane. A proton NMR spectrum in THF-d_8 showed alkylidene H$_\alpha$ resonances characteristic of *syn/syn* (63%, one H$_\alpha$ resonance), *anti/anti* (7%, one H$_\alpha$ resonance), and *syn/anti* (~30%, two one H$_\alpha$ resonances) isomers. (Proton NMR spectra typical of mixtures of this type are shown in ref 13.) Note that only the *syn/syn* isomer was observed in the solid state, but a mixture is observed in THF-d_8 solution.

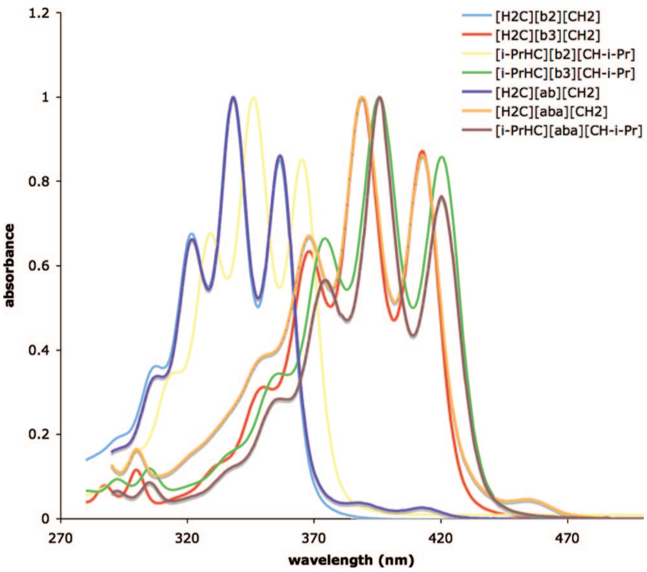


Figure 3. Absorption spectra of [H$_2$C][b$_2$][CH$_2$], [H$_2$C][b$_3$][CH$_2$], [*i*-PrCH][b$_2$][*i*-PrCH], [*i*-PrCH][b$_3$][*i*-PrCH], [H$_2$C][ab][CH$_2$], [H$_2$C][aba][CH$_2$], and [*i*-PrCH][aba][*i*-PrCH] in CH_2Cl_2 at room temperature.

Table 1. λ_{max} (0−1 transition) and Molar Extinction Coefficients for Dimeric and Trimeric Compounds in CH_2Cl_2

compound	λ_{max} (nm)	$\varepsilon/10^4$ (cm^{-1} M^{-1})
[H$_2$C][b$_2$][CH$_2$]	338	6.7
[H$_2$C][ab][CH$_2$]	338	4.3
[*i*-PrCH][b$_2$][*i*-PrCH]	346	12.2
[Me$_2$C][b$_2$][CMe$_2$]	356	N/A
[H$_2$C][b$_3$][CH$_2$]	389	8.4
[H$_2$C][aba][CH$_2$]	389	6.3
[*i*-PrCH][b$_3$][*i*-PrCH]	396	17.1
[*i*-PrCH][aba][*i*-PrCH]	396	1.2
[Me$_2$C][b$_3$][CMe$_2$]	404	4.4

The reaction between [H$_2$C][b$_3$][CH$_2$] and 2 equiv of [Mo][CHCMe$_3$] yielded [Mo][b$_3$][Mo] in 83% yield (eq 17). Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into a THF/ether solution of [Mo][b$_3$][Mo] at −30 °C.

---

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

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

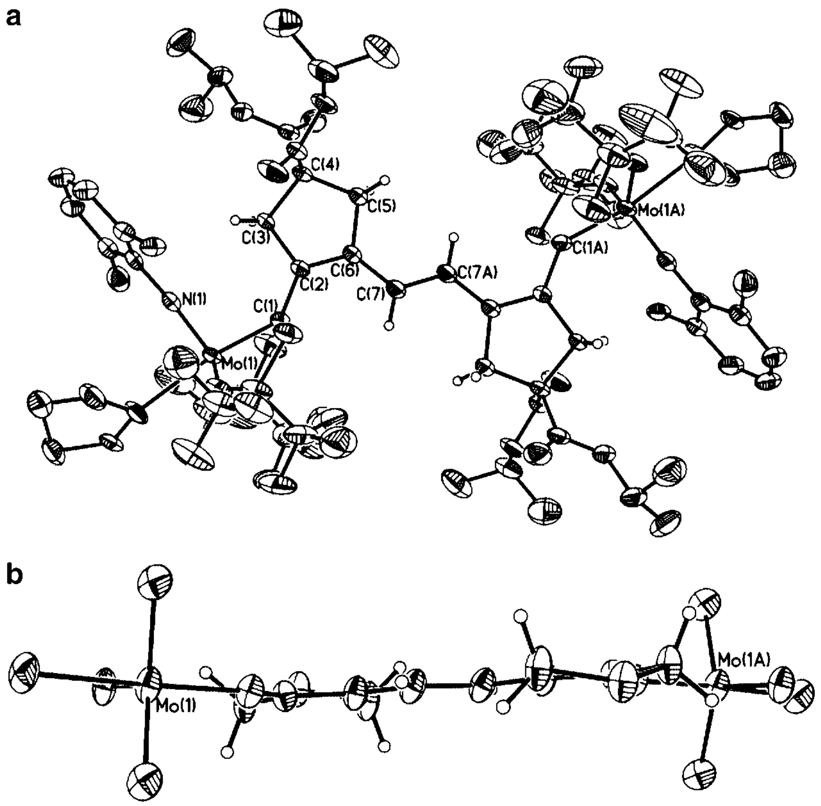
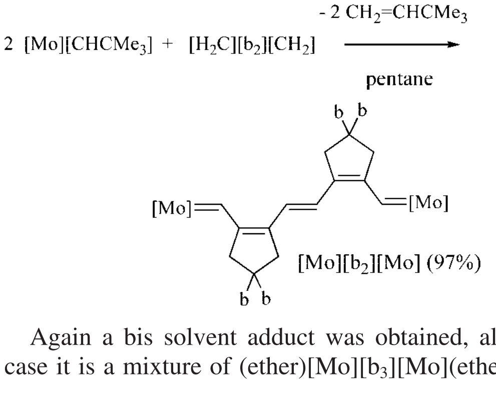


Figure 4. (a) Thermal ellipsoid drawing (50%) of (THF)[Mo][b$_2$][Mo](THF). Selected distances (Å) and angles (deg) are listed in Table 2. (b) Side view of the chain between Mo centers in (THF)[Mo][b$_2$][Mo](THF).

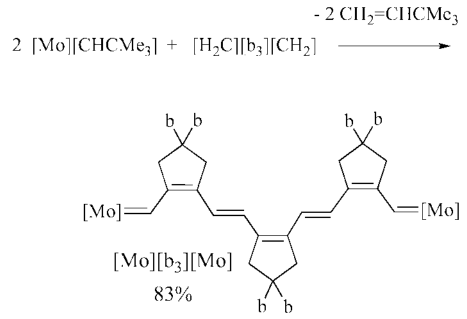
Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Quin][Mo][b][Mo][Quin] (08189) (heterochiral isomer only) and [THF][Mo][b$_2$][Mo][THF] (08042)

08189		08042	
Mo(1)−N(1)	1.745(3)	Mo(1)−N(1)	1.710(4)
Mo(1)−C(1)	1.951(3)	Mo(1)−C(1)	1.926(5)
Mo(1)−O(1)	1.969(2)	Mo(1)−O(1)	1.950(4)
Mo(1)−O(2)	2.020(2)	Mo(1)−O(2)	1.951(4)
Mo(1)−N(2)	2.294(3)	Mo(1)-O(1S)	2.363(3)
N(1)−Mo(1)−C(1)	99.60(13)	N(1)−Mo(1)−C(1)	99.17(19)
N(1)−Mo(1)−O(1)	141.23(12)	N(1)−Mo(1)−O(1)	115.67(19)
N(1)−Mo(1)−O(2)	99.65(12)	N(1)−Mo(1)−O(2)	114.05(19)
N(1)−Mo(1)−N(2)	89.16(12)	N(1)−Mo(1)−O(1S)	90.08(16)
C(1)−Mo(1)−O(1)	117.45(12)	C(1)−Mo(1)−O(1)	98.54(18)
C(1)−Mo(1)−O(2)	99.41(12)	C(1)−Mo(1)−O(2)	97.71(18)
C(1)−Mo(1)−N(2)	88.96(12)	C(1)−Mo(1)−O(1S)	170.65(17)
O(1)−Mo(1)−O(2)	85.87(11)	O(1)−Mo(1)−O(2)	123.87(15)
O(1)−Mo(1)−N(2)	80.96(11)	O(1)−Mo(1)−O(1S)	78.45(14)
O(2)−Mo(1)−N(2)	166.59(11)	O(2)−Mo(1)−O(1S)	77.09(14)
C(2)−C(1)−Mo(1)	127.1(2)	Mo(1)−C(1)−C(2)	139.3(4)
C(11)−N(1)−Mo(1)	165.0(3)	Mo(1)−N(1)−C(21)	171.2(5)
C(1)−C(2)	1.420(4)	C(1)−C(2)	1.421(6)
C(2)−C(6)	1.397(4)	C(2)−C(6)	1.367(6)
		C(6)−C(7)	1.426(7)
		C(7)−C(7A)	1.357(9)



(16)

Again a bis solvent adduct was obtained, although in this case it is a mixture of (ether)[Mo][b$_3$][Mo](ether) and (ether)-[Mo][b$_3$][Mo](THF) (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][b$_3$]-[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][b$_3$][Mo] was obtained in lower yield and lower purity when [Mo][CHCMe$_2$Ph] was employed. It is believed that the initial metathesis product, Me$_2$PhCCH=CH$_2$, back-reacts with [Mo][b$_3$][Mo] to yield [Mo][b$_3$][CHCMe$_2$Ph] and unstable [Mo][CH$_2$] (eq 18). [Mo][b$_3$][Mo] was found to be a mixture of *syn/syn* (~63%), *anti/anti* (~1%), and *syn/anti* (~36%) isomers in CD$_2$Cl$_2$, according to proton NMR studies. The solubility differences between [Mo][b$_3$][Mo] and [Mo]-[b$_2$][Mo] (*vide supra*) are striking and surprising.



(17)

The polyene chains in the unsubstituted dimer and trimer can be compared with those in the "Mo-capped" relatives, including previously reported[10] (THF)[Mo$_{Ar}$][a$_2$][Mo$_{Ar}$](THF) ([Mo$_{Ar}$] = Mo(NAr)(OR$_{F6}$)$_2$, where Ar = 2,6-diisopropylphenyl). The conjugated backbone is planar for [H$_2$C][b$_2$][CH$_2$] and [H$_2$C]-[b$_3$][CH$_2$], as well as for (THF)[Mo][b$_2$][Mo](THF) and (THF)[Mo$_{Ar}$][a$_2$][Mo$_{Ar}$](THF), but (Et$_2$O)[Mo][b$_3$][Mo](Et$_2$O)

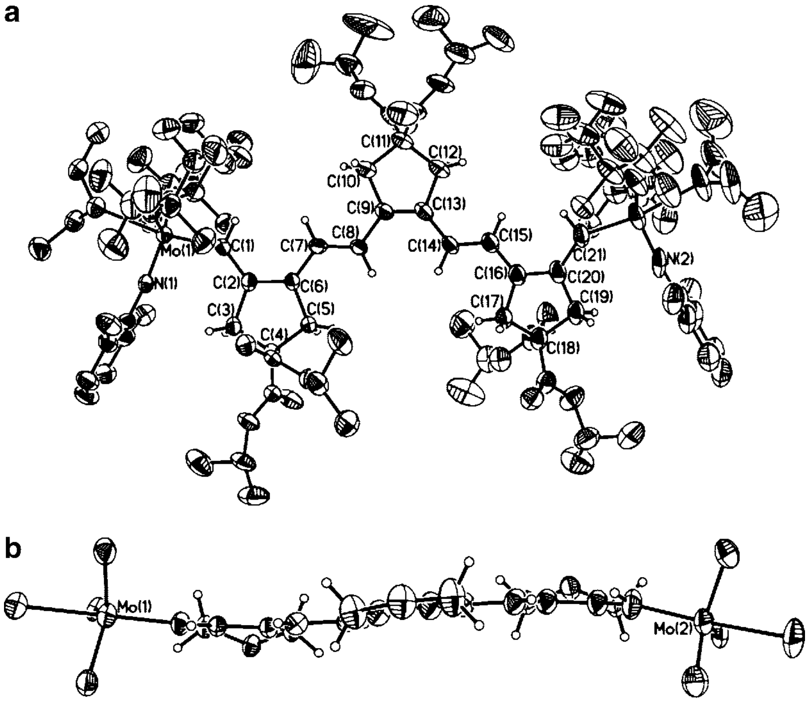
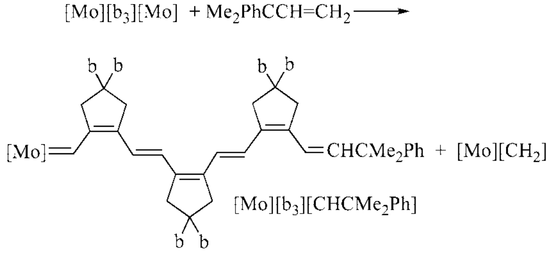


Figure 5. (a) Thermal ellipsoid drawing (50%) of $(Et_2O)[Mo][b_3][Mo](Et_2O)$. Distances (Å) in the chain between Mo centers: Mo(1)−C(1) = 1.939(5), C(1)−C(2) = 1.410(7), C(2)−C(6) = 1.394(7), C(6)−C(7) = 1.427(7), C(7)−C(8) = 1.351(7), C(8)−C(9) = 1.450(7), C(9)−C(13) = 1.349(8), C(13)−C(14) = 1.422(8), C(14)−C(15) = 1.356(8), C(15)−C(16) = 1.421(8), C(16)−C(20) = 1.366(8), C(20)−C(21) = 1.441(8), Mo(2)−C(21) = 1.946(6). (b) Side view of the main chain of $(Et_2O)[Mo][b_3][Mo](Et_2O)$.



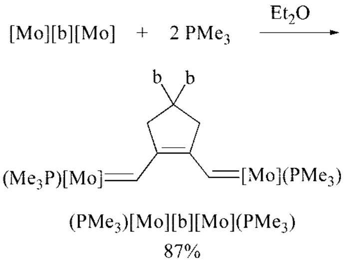
(18)

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* $(CH)_{14}$ bridge.[14] 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═C bond lengths and angles are similar in each.

As in the case of reactions between [Mo][b][Mo] and $[H_2C][b][O]$, reactions of $[Mo][b_2][Mo]$ and $[Mo][b_3][Mo]$ with $[H_2C][b][O]$ 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═C metathesis reaction in 16e adducts, since the Mo-Wittig reaction might proceed through a six-coordinate species, whereas C═C metathesis is most likely to be possible only with 14e (base-free) species.

Addition of 2 equiv of PMe_3 to [Mo][b][Mo] yielded the PMe_3 adduct $(PMe_3)[Mo][b][Mo](PMe_3)$ (eq 19). According to ^1H, ^{13}C, ^{31}P, and ^{19}F NMR (CD_2Cl_2) spectra, $(PMe_3)[Mo][b][Mo](PMe_3)$ 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.[15,16] Two possible *anti/anti* adducts, one heterochiral and one homochiral, in which PMe_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 Cb_2 carbon atom of the five-membered ring, while the homochiral dimer has a C_2 axis through the Cb_2 carbon atom.



(19)

Addition of 2 equiv of quinuclidine to [Mo][b][Mo] yielded the bisquinuclidine adduct (quin)[Mo][b][Mo](quin) (eq 20) in high yield. According to ^1H, ^{13}C, and ^{19}F NMR (C_6D_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 CNO but also the NOO and COO

---

(14) Yuan, P.; Wu, X.; Yu, G.; Du, D.; Liu, S. H. *J. Organomet. Chem.* **2007**, *692*, 3588.

(15) Gabert, A. J.; Schrock, R. R.; Müller, P. Chem. Asian J. **2008**, *3*, 1535.

(16) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832.

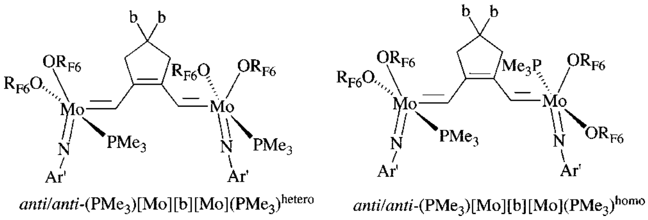
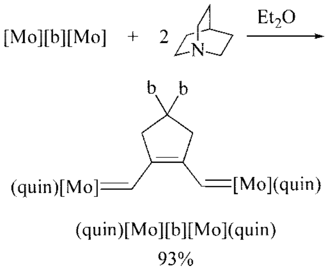


Figure 6. Possible heterochiral and homochiral forms of *anti/anti*-$[PMe_3][Mo][b][Mo][PMe_3]$.

faces of $M(NAr)(CHR)(OR_{F6})_2$ species.[14] 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.



(20)

Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into a C_6D_6 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 *cocrystallized* heterochiral *anti/anti* (87%) and homochiral *anti/anti* (13%) isomers with arrangements at Mo that are the same as those proposed for the bisPMe$_3$ 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 PMe_3 to $[Mo][b_2][Mo]$ led to formation of $(PMe_3)[Mo][b_2][Mo](PMe_3)$ (eq 21). As observed for PMe_3 adducts of monomeric alkylidenes,[14] $(PMe_3)[Mo][b_2][Mo]$-(PMe_3) in CD_2Cl_2 initially was observed as a mixture of two *syn/syn* isomers (in a ratio 1.6:1), whose H_α resonances overlapped (δ 12.69, $J_{PH} = 5.5$, $J_{CH} = 120$). Over a period of 4 days, the compound isomerized to yield a mixture of two *anti/anti* isomers (δ 13.62, $J_{PH} = 7.5$; 13.61, $J_{PH} = 8.0$, $J_{CH} = 146$, in a ~1:1 ratio, 83%) and two *syn/syn* isomers (δ 12.72, $J_{PH} = 5.5$; 12.69, $J_{PH} = 5.5$, in a 1.2:1 ratio, 17%). Reaction of $[Mo][b_3][Mo]$ with 2 equiv of PMe_3 led to formation of $(PMe_3)[Mo][b_3][Mo](PMe_3)$ (eq 22), which was observed as a mixture of *syn/syn* (major) and *anti/anti* (minor) isomers in C_6D_6, while reaction of $[Mo][b_3][Mo]$ with 2 equiv of quinuclidine yielded the corresponding quinuclidine adduct (eq 23).

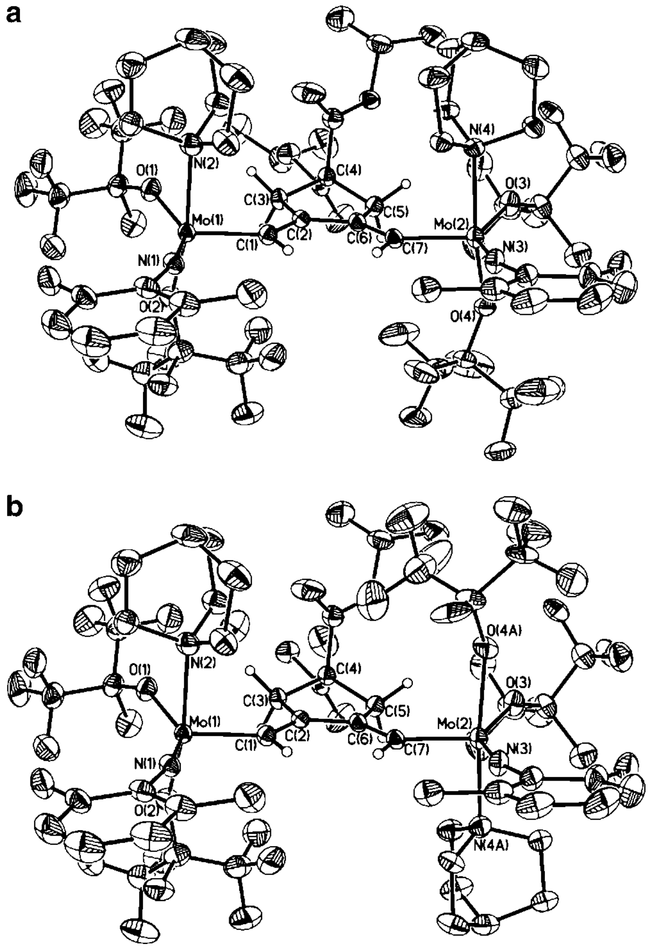
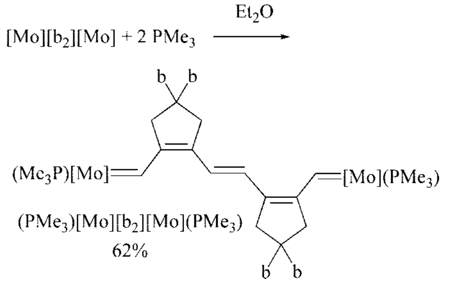
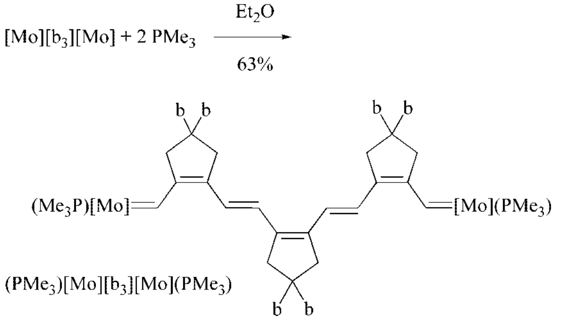


Figure 7. (a) Thermal ellipsoid drawing (50%) of heterochiral [quin][Mo][b][Mo][quin]. Selected distances (Å) and angles (deg) are listed in Table 2. (b) Thermal ellipsoid drawing (50%) of homochiral [quin][Mo][b][Mo][quin].

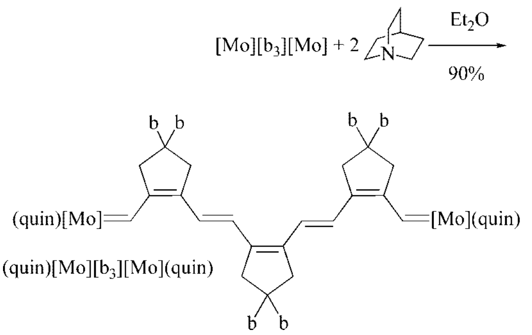


(21)



(22)

Reactions of Adducts with $[H_2C][b][O]$. Reaction of the mixture of $(PMe_3)[Mo][b][Mo](PMe_3)$ isomers (10 mg) with 4 equiv of $[H_2C][b][O]$ in CD_2Cl_2 (1.5 mL) was monitored over time by ^1H NMR spectroscopy. After 1 day, a new doublet resonance was observable at 13.63 ppm ($J_{PH} = 6.5$ Hz, 15% of Mo-containing species), along with resonances for $[H_2C][b_3]$-$[CH_2]$ and other Mo species, probably among them (PMe_3)-$[Mo][b_2][CH_2]$. The new resonances became more intense over time (the ratio of unreacted $(PMe_3)[Mo][b][Mo](PMe_3)$ to $[H_2C][b_3][CH_2]$ was 6.2:1 after 4 days and 0.9:1 after 1 month), but the reaction was not complete even after 7 weeks at 22 °C, when the ratio of $(PMe_3)[Mo][b][Mo](PMe_3)$ to $[H_2C][b_3][CH_2]$



(23)

was 0.5:1, and what we presume to be $(PMe_3)[Mo][b][CH_2]$ was still observed. No $[H_2C][b_2][CH_2]$ was detected. The fact that the Mo-Wittig reactions involving trimethylphosphine adducts are extremely slow, along with the fact that no $[H_2C][b_2][CH_2]$ 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 C═C metathesis is effectively blocked.

Little reaction of $(PMe_3)[Mo][b_2][Mo](PMe_3)$ with 2 equiv of $[H_2C][b][O]$ was observed after 1 day. After 3 days, resonances that could be assigned to $[H_2C][b_4][CH_2]$ were observed, along with a small new Mo-alkylidene resonance (presumably $(PMe_3)[Mo][b_3][CH_2]$, δ 13.64 ppm, d, $J_{PH} = 8$) overlapping with the alkylidene proton in the starting material. The new resonances increased in intensity over time. The ratio of unreacted $(PMe_3)[Mo][b_2][Mo](PMe_3)$ to $[H_2C][b_4][CH_2]$ 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 $[H_2C][b_4][CH_2]$ ($\lambda_{max} = 427$ nm) was isolated after 2 months; no $[H_2C][b_3][CH_2]$ was observed.

Reactions of $(PMe_3)[Mo][b_3][Mo](PMe_3)$ with $[H_2C][b][O]$ were monitored over time, and the same behavior was observed as in the case of $(PMe_3)[Mo][b_2][Mo](PMe_3)$. The expected pentamer $[H_2C][b_5][CH_2]$ ($\lambda_{max} = 455$ nm) was isolated from the product mixture after 1 month. Clearly $(PMe_3)[Mo][b_3][Mo](PMe_3)$ is not significantly more reactive than $(PMe_3)[Mo][b][Mo](PMe_3)$. Although this approach may not be suited to preparative chemistry, the purity of the oligoene products appeared to be high relative to the purity of the products isolated from reactions of $[Mo][b_n][Mo]$ ($n = 2, 3$) with $[H_2C][b][O]$, according to UV−vis spectroscopy at room temperature.

A reaction between 2 equiv of $[H_2C][b][O]$ and the mixture of (quin)[Mo][b][Mo](quin) species was monitored over time. After 30 min resonances only for $[H_2C][b_3][CH_2]$ 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 $[H_2C][b_3][CH_2]$. The trimer could be prepared from (quin)[Mo][b][Mo](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 (quin)[Mo][b][Mo](quin) to give (quin)[Mo][b][Mo] before $[H_2C][b][O]$ can react (with the 14e Mo center in (quin)[Mo][b][Mo]) is not known. The probability that quinuclidine dissociates from *both* ends before $[H_2C][b][O]$ reacts with either 14e Mo center is likely to be small. Clearly quinuclidine adducts are more reactive than trimethylphosphine adducts and yield only $[H_2C][b_3][CH_2]$ in a more reasonable time frame. It is not known whether quinuclidine remains bound to Mo or not.

Reaction of $(quin)[Mo][b_3][Mo](quin)$ with $[H_2C][b][O]$ yielded the pentamer, although it was contaminated with shorter oligoenes according to NMR and UV−vis spectroscopies. Evidently C═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 $[H_2C][b_3][CH_2]$ in the reaction between (quin)[Mo][b][Mo](quin) and $[H_2C][b][O]$ 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 $Mo(NAr')(CHCMe_2R)(OR_{F6})_2$ (R = Me, Ph). In the Wittig-like reactions with unsaturated aldehydes complications arise because reactions between C═C bonds and Mo═C bonds compete with reactions between C═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 (C_6D_6, CD_2Cl_2, and THF-d_8) 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 ^{13}C spectra were referenced to the residual $^1H/^{13}C$ resonances of the deuterated solvent (^1H: C_6D_6, δ 7.16; CD_2Cl_2, δ 5.32; THF-d_8, δ 3.58, CD_3Cl, δ 7.27; ^{13}C: C_6D_6, δ 128.39; CD_2Cl_2, δ 54.00; THF-d_8, δ 67.57, CD_3Cl, δ 77.23) 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 (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.

$Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2R)(OR_{F6})_2$ (R = Ph, Me),[17] [Mo][b][Mo],[10] [H2C][a][O],[10] $[H_2C][b][O]$,[10] $[H_2C][b][CH_2]$,[10] $[Me_2C]$-

---

[17] Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185.

[b$_2$][CMe$_2$],[10] and RuCp(NCMe)$_3$PF$_6$[18] were prepared as described in the literature.

Reaction of [Mo][b][Mo] with [H$_2$C][b][O] to give [H$_2$C][b$_2$][CH$_2$] and [H$_2$C][b$_3$][CH$_2$]. A solution of [H$_2$C][b][O] (415 mg, 1.41 mmol) in diethyl ether (30 mL) was added to a stirred solution of [Mo][b][Mo] (1.0 g, 0.7 mmol) in diethyl ether (20 mL). No color change was observed. After 3 h, the solvent was removed *in vacuo* and an aliquot of the brick-red residue was dissolved in 0.7 mL of CD_2Cl_2 and transferred to a J. Young NMR tube. No unreacted [Mo][b][Mo] or [H$_2$C][b][O] could be detected in the ^{1}H NMR spectrum. The entire product mixture was chromatographed on a silica gel column (45 cm height, 2 cm diameter). A 1:3 mixture of diethyl ether and hexane produced two fractions. According to ^{1}H NMR spectroscopy, the first fraction ($R_f \approx 0.4$) consisted of pale green-yellow [H$_2$C][b$_2$][CH$_2$], while the second fraction ($R_f \approx 0.3$) consisted of canary yellow [H$_2$C][b$_3$][CH$_2$].

After removing the solvent *in vacuo* from both fractions, [H$_2$C][b$_2$][CH$_2$] was recrystallized from diethyl ether (overnight at −10 °C) to yield 84 mg (22%) of pale green-yellow crystals suitable for X-ray crystallography. Crude [H$_2$C][b$_3$][CH$_2$] was dissolved in a small amount of diethyl ether and transferred to a small vial, which was placed in a bigger vial containing pentane. The big vial was tightly capped and slow diffusion of pentane into the ether solution of [H$_2$C][b$_3$][CH$_2$] at −10 °C overnight yielded 64 mg (11%) of yellow needle-shaped crystals suitable for X-ray crystallography.

Data for [H$_2$C][b$_2$][CH$_2$]: ^{1}H NMR (CD_2Cl_2) δ 6.89 (dd, J = 17, 11, 2H, CH$_2$=C*H*R), 6.63 (2H, RC*H*=C*H*R), 5.234 (d, J = 17, 2H, HC*H*=CHR), 5.225 (d, J = 11, 2H, HC*H*=CHR), 5.02 (sept, J = 6, 4H, CH, *i*-Pr), 3.27 (4H, CH$_2$), 3.22 (4H, CH$_2$), 1.23 (d, J = 6, 24H, Me, *i*-Pr); ^{1}H NMR (C_6D_6) δ 6.64 (2H, RC*H*=C*H*R), 6.56 (dd, J = 17, 11, 2H, CH$_2$=C*H*R), 5.09 (d, J = 17, 2H, HC*H*=CHR), 5.02 (sept, J = 6.5, 4H, CH, *i*-Pr), 4.97 (d, J = 11, 2H, HC*H*=CHR), 3.60 (4H, CH$_2$), 3.56 (4H, CH$_2$), 1.00 (d, J = 6.5, 24H, Me, *i*-Pr); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 171.7 (C=O), 137.0, 136.2, 129.9, 123.5, 116.2, 69.7 (O*C*HMe$_2$), 57.3 (quat), 41.5 (CH$_2$), 41.3 (CH$_2$), 21.8 (Me); HRMS (EI) *m/z* calcd for $C_{21}H_{44}O_8$ (M$^+$) *m/z* 556.3036, found 556.3052; UV/vis λ_{max} = 338 nm with $\varepsilon = 6.7 \times 10^4$ cm^{-1} M^{-1} in CH_2Cl_2. Anal. Calcd for $C_{32}H_{44}O_8$: C, 69.04; H, 7.97. Found: C, 68.95; H, 8.01.

Data for [H$_2$C][b$_3$][CH$_2$]: ^{1}H NMR (CD_2Cl_2) δ 6.90 (dd, J = 17, 11, 2H, CH$_2$=C*H*R), 6.67 (4H RC*H*=C*H*R), 5.242 (d, J = 17, 2H, HC*H*=CHR), 5.233 (d, J = 11, 2H, *H*CH=CHR), 5.03 (sept, J = 7, 4H, CH, *i*-Pr) overlapping with 5.02 (sept, J = 6, 2H, CH, *i*-Pr), 3.32 (4H, CH$_2$), 3.29 (4H, CH$_2$), 3.23 (4H, CH$_2$), 1.245 (d, J = 6, 12H, Me, *i*-Pr), 1.240 (d, J = 7, 24H, Me, *i*-Pr); ^{1}H NMR (C_6D_6) δ 6.72 (4H, RC*H*=C*H*R), 6.61 (dd, J = 17, 11, 2H, CH$_2$=C*H*R), 5.12−4.95 (overlapping m, 10H, HC*H*=CHR and CH, *i*-Pr), 3.68 (4H, CH$_2$), 3.55 (8H, CH$_2$), 1.03 (d, J = 6.5, 12H, Me, *i*-Pr), 0.99 (d, J = 6.5, 24H, Me, *i*-Pr); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 171.8 (C=O), 171.7 (C=O), 137.2, 137.1, 136.3, 129.9, 123.8, 123.3, 116.2, 69.8 (O*C*HMe$_2$), 69.7 (O*C*HMe$_2$), 57.4 (quat), 57.3 (quat), 41.7 (CH$_2$), 41.5 (CH $_2$), 41.4 (CH$_2$), 21.83 (Me), 21.82 (Me), 21.80 (Me); HRMS (ESI) *m/z* calcd for $C_{47}H_{64}NaO_{12}$ (M − Na$^+$) *m/z* 843.4290, found 843.4308; UV/vis λ_{max} = 389 nm with $\varepsilon = 8.4 \times 10^4$ cm $^{-1}$ M^{-1} in CH_2Cl_2.

Synthesis of [*i*-PrCH][b$_2$][*i*-PrCH] and [*i*-PrCH][b$_3$][*i*-PrCH]. A solution of [*i*-PrCH][b][O] (27 mg, 0.08 mmol; see Supporting Information) in CD_2Cl_2 (0.3 mL) was added to a stirred solution of [Mo][b][Mo] (56.8 mg, 0.04 mmol) in CD_2Cl_2 (0.2 mL). No color change was observed. The mixture was transferred to a J. Young NMR tube and monitored by ^{1}H and ^{19}F NMR (CD_2Cl_2) spectroscopy. After 30 min all [*i*-PrCH][b][O] was consumed and only a small amount of unreacted [Mo][b][Mo] was present. Solvent was removed *in vacuo*. The residue was chromatographed on silica gel using a mixture of diethyl ether and hexane (1:3) to yield two fractions. According to ^{1}H NMR spectra (in CD_2Cl_2) the first fraction (R_f = 0.6) consisted of pale yellow [*i*-PrCH][b$_2$][*i*-PrCH] (8 mg, 31%yield), while the second pale green-yellow fraction (R_f = 0.3) contained a mixture of [*i*-PrCH][b$_3$][*i*-PrCH] and 2,6-dimethylaniline. Recrystallization of the second fraction by slow diffusion of pentane into an ether solution of the mixture yielded 10 mg (28% yield) of pure yellow [*i*-PrCH][b$_3$][*i*-PrCH].

Data for [*i*-PrCH][b$_2$][*i*-PrCH]: ^{1}H NMR (CD_2Cl_2) δ 6.57 (2H, C*H*R=C*H*R), 6.51 (d, J = 15.6, 2H, R$_1$C*H*=CHR $_2$), 5.69 (dd, J = 15.6, 7.5, 2H, R$_1$CH=C*H*R$_2$), 5.01 (sept, J = 6.3, 4H, CH, *i*-Pr), 3.24 (4H, CH$_2$), 3.18 (4H, CH$_2$), 2.50−2.38 (m, 2H, CH, *i*-Pr), 1.23 (d, J = 6.3, 24H, Me, CO$_2$(*i*-Pr)), 0.06 (d, J = 6.6, 12H, Me, *i*-Pr); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 171.9 (C=O), 141.4, 136.4, 133.7, 122.8, 120.8, 69.6 (O*C*HMe$_2$), 57.3 (quat), 42.0 (CH$_2$), 41.4 (CH$_2$), 32.6 (CH, *i*-Pr), 22.9 (Me), 21.8 (Me); HRMS (ESI) *m/ z* calcd for $C_{38}H_{56}NaO_8$ (M − Na$^+$) *m/z* 663.3867, found 663.3888; UV/vis λ_{max} = 346 nm with $\varepsilon = 12.2 \times 10^4$ cm^{-1} M^{-1} in CH_2Cl_2.

Data for [*i*-PrCH][b$_3$][*i*-PrCH]: ^{1}H NMR ($CDCl_3$) δ 6.66−6.53 (m, 4H, RCH=CHR), 6.50 (d, J = 15.6, 2H, CH(*i*-Pr)=C*H*R), 5.69 (dd, J = 15.6, 7.2, 2H, CHR=C*H*(*i*-Pr)), 5.07 (sept, J = 6.3, 6H, CH, CO$_2$(*i*-Pr)), 3.32 (4H, CH$_2$), 3.31 (4H, CH$_2$), 3.23 (4H, CH$_2$), 2.55−2.37 (m, 2H, CH, *i*-Pr), 1.27 (d, J = 6.3, 36H, Me, CO$_2$(*i*-Pr)), 1.07 (d, J = 6.6, 12H, Me, *i*-Pr); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 171.8 (2C=O), 171.7 (C=O), 141.2, 136.8, 136.1, 133.4, 123.6, 122.1, 120.6, 69.5 (O*C*HMe$_2$), 69.3 (O*C*HMe$_2$), 57.22 (2 quat), 57.16 (quat), 41.9 (CH$_2$), 41.5 (CH$_2$), 41.2 (CH$_2$), 32.3 (CH, *i*-Pr), 22.9 (Me), 21.81 (Me), 21.79 (Me), 21.78 (Me); HRMS (ESI) *m/z* calcd for $C_{53}H_{76}NaO_{12}$ (M − Na$^+$) *m/z* 927.5229, found 927.5250; UV/vis λ_{max} = 396 nm with $\varepsilon = 17.1 \times 10^4$ cm^{-1} M^{-1} in CH_2Cl_2.

Synthesis of [Mo][b$_2$][Mo]. Solid [Mo][CHCMe$_3$] (140 mg, 0.22 mmol) was added to a stirred slurry of [H$_2$C][b$_2$][CH$_2$] (60 mg, 0.11 mmol) in pentane (10 mL). The mixture turned brown immediately. The mixture was stirred overnight, and an orange precipitate was filtered off, washed with pentane (3 × 0.5 mL), and dried *in vacuo*; yield 174 mg (97%) of dark orange [Mo][b$_2$][Mo]. The following NMR spectra are reported for the major isomer (*syn/syn*), unless otherwise indicated: ^{1}H NMR (THF-d_8) δ 13.81 (Mo=CHR, 7%), 13.78 (Mo=CHR, 15%), 13.01 (Mo=CHR, 11%) overlapping with 12.99 (J_{CH} = 125, Mo=CHR, *syn/syn*, 67%), 7.17−7.08 (m, 6H, Ar), 6.47 (d, J = 15, RC*H*=CHR, *syn/anti*), 6.43 (2H, C*H*R=C*H*R), 6.36 (d, J = 15, CHR=C*H*R, *syn/anti*) 4.88 (sept, J = 6, 4H, CH, CO$_2$(*i*-Pr)), 3.65 (4H, CH$_2$), 3.33 (4H, CH$_2$), 2.48 (12H, Me, NAr′), 1.28 (12H, CMe(CF$_3$)$_2$), 1.12 (d, J = 6, 12H, Me, CO$_2$(*i*-Pr)), 1.03 (d, J = 6, 12H, Me, CO$_2$(*i*-Pr)); ^{13}C{^{1}H} NMR (THF-d_8) δ 262.4 (Mo=CHR), 171.2 (C=O, CO$_2$(*i*-Pr)), 158.0, 148.9, 138.5, 129.8 129.0, 126.3, 125.2 (q, J_{C-F} = 284, CF$_3$), 123.5, 69.4 (O*C*HMe$_2$), 57.7 (quat), 46.9 (CH$_2$), 40.1 (CH$_2$), 21.8 (Me, CO$_2$(*i*-Pr)), 21.7 (Me, CO$_2$(*i*-Pr)), 19.5, 19.4; ^{19}F NMR (THF-d_8) δ −82.5 (q, CF$_3$), −82.9 (q, CF$_3$). Anal. Calcd for $C_{62}H_{70}F_{24}Mo_2N_2O_{12}$: C, 44.24; H, 4.19, N, 1.66. Found: C, 44.95; H, 4.27, N, 1.72.

Synthesis of [Mo][b$_3$][Mo]. Solid [Mo][CHCMe$_3$] (173 mg, 0.27 mmol) was added to a stirred solution of [H$_2$C][b$_3$][CH$_2$] (110 mg, 0.135 mmol) in diethyl ether (10 mL). After 2 h the solvent was removed from the brick-red solution *in vacuo*, and the residue was triturated in pentane (3 mL) overnight. The resulting precipitate was filtered off and washed with pentane (3 × 1 mL), and solvents were removed *in vacuo*; yield (214 mg (83% yield) of brick-red [Mo][b$_3$][Mo].

A similar reaction between [Mo][CHCMe$_2$Ph] (130 mg, 0.18 mmol) and [H$_2$C][b$_3$][CH$_2$] (75 mg, 0.09 mmol) in pentane (15 mL) yielded 127 mg (72% yield) of [Mo][b$_3$][Mo].

The following NMR spectra are reported for the major isomer of [Mo][b$_3$][Mo] (*syn/syn*), unless otherwise indicated: ^{1}H NMR (CD_2Cl_2) δ 13.58 (Mo=C*H*R) shoulder on 13.56 (Mo=C*H*R, total

---

(18) (a) Trost, B. M.; Older, C. M. *Organometallics* **2002**, *21*, 2544. (b) Kundig, E. P.; Monnier, F. R. *Adv. Synth. Catal.* **2004**, *346*, 901.

19%), 12.93 (Mo=C*H*R, 18%) overlapping with 12.91 (Mo=C*H*R, J_{CH} = 128, *syn/syn*, 63%), 7.50−7.09 (m, 6H, Ar), 6.54 (d, *J* = 15.5, 2H, C*H*R=CHR), 6.47 (d, *J* = 15.5, 2H, CHR=C*H*R), 5.07 (sept, *J* = 6, 2H, CH, CO$_2$(*i*-Pr)), 4.89 (sept, 4H, *J* = 6, CH, CO$_2$(*i*-Pr)), 3.66 (4H, CH$_2$), 3.36 (4H, CH$_2$), 3.30 (4H, CH$_2$), 2.41 (12H, Me, NAr′), 1.43 (12H, CMe(CF$_3$)$_2$), 1.26 (d, *J* = 6, 12H, Me, CO$_2$(*i*-Pr)), 1.12 (d, *J* = 6, 12H, Me, CO$_2$(*i*-Pr)), 1.04 (d, *J* = 6, 12H, Me, CO$_2$(*i*-Pr); ^{1}H NMR (C$_6$D$_6$) δ 13.21 (Mo=C*H*R, 2H), 6.83 (d, *J* = 15, 2H, C*H*R=CHR), 6.80−6.72 (m, 6H, Ar), 6.50 (d, *J* = 15, 2H, CHR=C*H*R), 5.09 (sept, *J* = 6, 2H, CH, CO$_2$(*i*-Pr)), 4.90 (sept, 4H, *J* = 6, CH, CO$_2$(*i*-Pr)), 3.86 (4H, CH$_2$), 3.77 (4H, CH$_2$), 3.56 (4H, CH$_2$), 2.27 (12H, Me, NAr′), 1.37 (12H, CMe(CF$_3$)$_2$), 1.00 (d, *J* = 6, 12H, Me, CO$_2$(*i*-Pr)), 0.89 (d, *J* = 6, 12H, Me, CO$_2$(*i*-Pr)), 0.86 (d, *J* = 6, 12H, Me, CO$_2$(*i*-Pr); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 280.0 (Mo=CHR), 171.5 (C=O, CO$_2$(*i*-Pr)), 171.3 (C=O, CO$_2$(*i*-Pr)), 157.5, 146.2, 138.3, 138.0, 129.5, 128.5, 126.2, 124.4, 124.3 (q, J$_{CF}$ = 282, CF$_3$), 124.0 (q, J_{CF} = 286, CF$_3$), 123.2, 69.8 (O*C*HMe$_2$), 69.6 (O*C*HMe$_2$), 57.3 (quat), 57.1 (quat), 46.3 (CH$_2$), 41.3 (CH$_2$), 40.2 (CH$_2$), 21.70 (Me, CO$_2$(*i*-Pr)), 21.68 (Me, CO$_2$(*i*-Pr)), 21.63 (Me, CO$_2$(*i*-Pr)), 19.6, 19.3; ^{19}F NMR (C$_6$D$_6$) δ −78.2 (q, CF$_3$), −78.4 (q, CF$_3$). Anal. Calcd for C$_{77}$H$_{90}$F$_{24}$Mo$_2$N$_2$O$_{16}$: C, 47.49; H, 4.66, N, 1.44. Found: C, 47.23; H, 4.70, N, 1.31.

Synthesis of (PMe$_3$)[Mo][b][Mo](PMe$_3$). To a stirred solution of [Mo][b][Mo] (142 mg, 0.1 mmol) in Et$_2$O (10 mL) was added PMe$_3$ (30 μL, 0.3 mmol) via a microliter 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 (PMe$_3$)[Mo][b][Mo](PMe$_3$). In CD$_2$Cl$_2$, the compound exists as a mixture of one *syn/syn* (δ 12.35, J_{PH} = 5, 6%) and two *anti/anti* isomers (94%, in ~2:1 ratio). The major *anti/anti* isomer appears to be heterochiral (PMe$_3$)[Mo][b][Mo](PMe$_3$)$^{\rm hetero}$ (60%), whereas the minor isomer is homochiral (PMe$_3$)[Mo][b][Mo](PMe$_3$)$^{\rm homo}$ (34%). The following NMR spectra are reported for a mixture of the two *anti/anti* isomers unless otherwise indicated.

^{1}H NMR (CD$_2$Cl$_2$) δ 13.24 (d, J_{PH} = 6.5, 2H, Mo=C*H*R, homo), 13.21 (d, J_{PH} = 6.5, J_{CH} = 139, 2H, Mo=C*H*R, *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_{PH} = 19, 2H, homo), 3.84 (d, J_{PH} = 19, 2H, hetero), 3.78 (d, J_{PH} = 19, 2H, hetero), 3.59 (d, J_{PH} = 19, 2H, homo), 2.74 (6H, CH$_3$, 2,6-*Me*$_2$C$_6$H$_2$), 2.46 (6H, CH$_3$, 2,6-*Me*$_2$C$_6$H$_2$), 1.90 (6H, OR$_{F6}$, hetero), 1.88 (6H, OR$_{F6}$, homo), 1.28−1.22 (overlapping m, 30H, CH$_3$, PMe$_3$ and CO$_2$*i*-Pr), 1.19 (broad, 6H, OR$_{F6}$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 260.3 (Mo=*C*HR), 172.8, 171.6, 170.9, 154.6, 147.1, 139.2, 134.32, 134.28, 129.5, 129.4, 128.8, 128.7 (J_{CP} = 26, C=C), 128.4 (J_{CP} = 27, C=C), 125.1 (q, *J* = 287, OCMe(*C*F$_3$)$_2$), 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_{CP} = 25, P*Me*$_3$), 14.5 (d, J_{CP} = 26, P*Me*$_3$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 3.5 (hetero), 3.4 (homo); ^{19}F NMR (CD$_2$Cl$_2$) δ −77.6, −78.1, −78.4, −78.7, −78.8. Anal. Calcd for C$_{53}$H$_{68}$F$_{24}$Mo$_2$N$_2$O$_8$P$_2$: C, 40.52; H, 4.36, N, 1.78. Found: C, 40.71; H, 4.35, N, 1.90.

Synthesis of (PMe$_3$)[Mo][b$_2$][Mo](PMe$_3$). To a stirred solution of [Mo][b$_2$][Mo] (40 mg, 0.023 mmol) in Et$_2$O (10 mL) was added PMe$_3$ (9 μL, 0.1 mmol) via a microliter 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. The solid was dried *in vacuo* to yield 26 mg (62% yield) of deep orange (PMe$_3$)[Mo][b$_2$][Mo](PMe$_3$).

In the ^{1}H NMR (CD$_2$Cl$_2$) spectrum, initially only one Mo=CHR signal was observed (δ 12.69, J_{PH} = 5.5, J_{CH} = 120), but the CH$_2$ region showed signals that would correspond to two different symmetric species, in a ratio 1.6:1. The ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) spectrum also showed two signals (δ 4.7 and 4.4 in a ~2:1 ratio). Over 4 days the above mixture isomerized into a mixture of two *syn/syn* (δ 12.72, J_{PH} = 5.5; 12.69, J_{PH} = 5.5, in a 1.2:1 ratio, 17%) and two *anti/anti* isomers (δ 13.62, J_{PH} = 7.5; 13.61, J_{PH} = 8.0, J_{CH} = 146, in a ~1:1 ratio, 83%). The following NMR spectra are reported for mixtures of isomers unless otherwise indicated.

Initial mixture of two *syn/syn* isomers in a 1.6:1 ratio: ^{1}H NMR (CD$_2$Cl$_2$) δ 12.69, J_{PH} = 5.5, J_{CH} = 120, Mo=C*H*R, overlapping *syn/syn* isomers), 7.08 (d, *J* = 7.5, 4H, Ar), 7.00 (t, *J* = 7.5, 2H, Ar), 6.41 (2H, CH=CH), 5.11−4.99 (m, 4H, CH, *i*-Pr), 4.04 (d, J_{PH} = 17, 2H, CH$_2$, major), 3.96 (d, J_{PH} = 17, 2H, CH$_2$, minor), 3.81 (d, J_{PH} = 17, 2H, CH$_2$, minor), 3.73 (d, J_{PH} = 17, 2H, CH$_2$, major), 3.62 (d, J_{PH} = 19) overlapping with 3.61 (d, J_{PH} = 19, 2H, CH$_2$, major+minor), 3.41 (d, J_{PH} = 19) overlapping with 3.40 (d, J_{PH} = 19, 2H, CH$_2$, major+minor), 2.56 (12H, 2,6-*Me*$_2$C$_6$H$_2$), 1.86 (broad, 6H, C*Me*(CF$_3$)$_2$), 1.31−1.21 (overlapping m, 48H, CH$_3$, *i*-Pr, P*Me*$_3$, C*Me*(CF$_3$)$_2$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 4.7, 4.4 (ratio ~2:1); ^{19}F NMR (CD$_2$Cl$_2$) δ −78.1, −78.4, −78.9, −79.5.

Final mixture of two *syn/syn* and two *anti/anti* isomers: ^{1}H NMR (CD$_2$Cl$_2$) δ 13.62 (J_{PH} = 7.5) overlapping with 13.61 (J_{PH} = 8.0, J_{CH} = 146, in a ~1:1 ratio, 83%), 12.72 (J_{PH} = 5.5, 9%), 12.69 (J_{PH} = 5.5, 8%), 7.16−6.99 (m, 6H, Ar), 6.41 (2H, CH=CH), 5.12−4.97 (m, 4H, CH, *i*-Pr), 3.82 (d, J_{PH} = 17.5, CH$_2$), 3.72 (d, J_{PH} = 17.5, CH$_2$), 3.71 (d, J_{PH} = 17.5, CH$_2$), 3.65 (d, J_{PH} = 17.5, CH$_2$), 3.64 (d, J_{PH} = 17.5, CH$_2$), 3.53 (d, J_{PH} = 17.5, CH$_2$), 3.44 (d, J_{PH} = 18, CH$_2$), 3.39 (d, J_{PH} = 18, CH$_2$), 3.38 (d, J_{PH} = 18, CH$_2$), 2.75 (2,6-*Me*$_2$C$_6$H$_2$, ~20%), 2.74 (2,6-*Me*$_2$C$_6$H$_2$, ~26%), 2.56 (2,6-*Me*$_2$C$_6$H$_2$, 8%), 2.47 (2,6-*Me*$_2$C$_6$H$_2$, 46%), 1.90 (OC*Me*(CF$_3$)$_2$), 1.89 (OC*Me*(CF$_3$)$_2$), 1.86 (OC*Me*(CF$_3$)$_2$), 1.30−1.22 (overlapping m, 48H, CH$_3$, *i*-Pr, P*Me*$_3$, C*Me*(CF$_3$)$_2$); selected ^{13}C{^{1}H} NMR resonances (CD$_2$Cl$_2$) δ 172.2, 171.9, 171.5, 171.3, 154.5, 139.2, 134.8, 128.6, 128.3, 69.9 (O*C*HMe$_2$), 69.82 (O*C*HMe$_2$), 69.78 (O*C*HMe$_2$), 69.75 (O*C*HMe$_2$), 57.6 (quat), 57.5 (quat), 45.5 (CH$_2$), 40.4 (CH$_2$), 21.90 (Me), 21.87 (Me), 21.8 (Me), 21.74 (Me), 21.67 (Me), 14.8 (d, J_{CP} = 26, P*Me*$_3$), 14.7 (d, J_{CP} = 26, P*Me*$_3$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 4.7, 4.6, 4.5 (ratio ~0.2:1:1); ^{19}F NMR (CD$_2$Cl$_2$) δ −79.8, −79.9, −80.3, −80.9. Anal. Calcd for C$_{68}$H$_{88}$F$_{24}$Mo$_2$N$_2$O$_{12}$P$_2$: C, 44.50; H, 4.83, N, 1.53. Found: C, 44.84; H, 4.68; N, 1.53.

Synthesis of (PMe$_3$)[Mo][b$_3$][Mo](PMe$_3$). To a stirred solution of [Mo][b$_3$][Mo] (30 mg, 0.015 mmol) in Et$_2$O (10 mL) was added PMe$_3$ (5 μL, 0.05 mmol) via a microliter 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 *in vacuo*, yielding 20 mg (63% yield) of a deep orange powder of (PMe$_3$)[Mo][b$_3$][Mo](PMe$_3$) as a mixture of 23% *anti/anti* and 77% *syn/syn* isomers according to the ^{1}H NMR (CD$_2$Cl$_2$) spectrum. The following NMR spectra are reported for the major isomer only unless otherwise indicated.

^{1}H NMR (CD$_2$Cl$_2$) δ 13.63 (J_{PH} = 8, 23%, minor), 12.71 (J_{PH} = 5.5, Mo=C*H*R, 77%, major), 7.08 (d, *J* = 7.5, 4H, Ar), 7.00 (t, *J* = 7.5, 2H, Ar), 6.65 (d, *J* = 15.5, 2H, CH=CH), 6.50 (d, *J* = 15.5, 2H, CH=CH), 5.11−4.99 (m, 6H, CH, *i*-Pr), 4.02−3.90 (m, 2H, CH$_2$), 3.80−3.66 (m, 4H, CH$_2$), 3.57−3.46 (m, 2H, CH$_2$), 3.43−3.22 (m, 4H, CH$_2$), 2.74 (6H, 2,6-*Me*$_2$C$_6$H$_2$, minor), 2.56 (12H, 2,6-*Me*$_2$C$_6$H$_2$, major), 2.47 (6H, 2,6-*Me*$_2$C$_6$H$_2$, minor), 1.88 (broad, 6H, C*Me*(CF$_3$)$_2$, minor), 1.86 (broad, 6H, C*Me*(CF$_3$)$_2$, major), 1.32−1.21 (overlapping m, 60H, CH$_3$, *i*-Pr, P*Me*$_3$, C*Me*(CF$_3$)$_2$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 4.9 (major), 4.7 (minor); ^{19}F NMR (CD$_2$Cl$_2$) δ −77.7, −78.0, −78.4, −79.1. Anal. Calcd for C$_{83}$H$_{108}$F$_{24}$Mo$_2$N$_2$O$_{16}$P$_2$: C, 47.48; H, 5.18, N, 1.33. Found: C, 47.38; H, 5.15; N, 1.31.

Synthesis of (quin)[Mo][b][Mo](quin). Quinuclidine (23 mg, 0.2 mmol) was added to a stirred solution of [Mo][b][Mo] (142 mg, 0.1 mmol) in Et$_2$O (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 glass frit. Removal of the solvent *in vacuo* yielded 153 mg (93% yield) of (quin)[Mo][b][Mo](quin) as a brown powder. In C_6D_6, the compound exists as a complex mixture of *syn* and *anti* isomers, according to (seven) resonances in the alkylidene region.

Selected ^{1}H NMR (C_6D_6) δ 13.57 (15%), 13.44 (12%), 13.36 (32%), 13.28 (7%), 12.68 (17%), 12.47 (13%), 12.33 (4%); ^{19}F NMR (C_6D_6) 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$_3$][Mo](quin). Quinuclidine (6 mg, 0.05 mmol) was added to a stirred solution of [Mo][b$_3$][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$_3$][Mo](quin), a red powder, as a mixture of *syn* and *anti* isomers according to the ^{1}H NMR (C_6D_6) spectrum.

Selected ^{1}H NMR (C_6D_6) resonances: δ 13.90 overlapping with 13.88 (24%), 13.17 overlapping with 13.16 (37%), 12.98 overlapping with 12.96 (39%); ^{19}F NMR (C_6D_6) −76.8, −77.2, −77.5, −77.8, −78.1, −78.3, −79.4. Attempts to obtain suitable elemental analyses were unsuccessful.

Synthesis of [H$_2$C][b$_3$][CH$_2$] from (quin)[Mo][b][Mo](quin). Solid (quin)[Mo][b][Mo](quin) (180 mg, 0.11 mmol) was added to a stirred solution of [H$_2$C][b][O] (65 mg, 0.22 mmol) in 10 mL of Et_2O. No color change was observed. The mixture was stirred overnight. The solvent was removed *in vacuo*, and the product mixture was passed through a silica gel colum using a mixture of ether and hexane (1:3) as eluent. The product was purified further through recrystallization from diethyl ether at 10 °C overnight to give 56 mg (63% yield) of spectroscopically pure (NMR and UV−vis) [H$_2$C][b$_3$][CH$_2$].

Synthesis of [H$_2$C][b$_4$][CH$_2$] from (PMe$_3$)[Mo][b$_2$][Mo](PMe$_3$). A mixture of solid (PMe$_3$)[Mo][b$_2$][Mo](PMe$_3$) (10 mg, 0.005 mmol) and [H$_2$C][b][O] (4 mg, 0.011 mmol) was dissolved in 0.7 mL of CD_2Cl_2, transferred to a J. Young NMR tube, and monitored over time by ^{1}H NMR spectroscopy. After 2 months, the only Mo-alkylidene resonance observed was (PMe$_3$)[Mo][b$_3$][CH$_2$] (δ 13.64, d, J_{PH} = 8), in a 0.7:1 ratio to [H$_2$C][b$_4$][CH$_2$]. The solvent was removed *in vacuo*, and the residue was washed with hexanes (3 × 2 mL) in air and dried *in vacuo*, yielding 5 mg (85% yield) of a dark orange powder. The product was further purified by passing it through an alumina plug using CH_2Cl_2 as eluent, to give 3 mg (51% yield) of a bright orange powder of spectroscopically pure [H$_2$C][b$_4$][CH$_2$].

^{1}H NMR (CD_2Cl_2) δ 6.90 (dd, J = 17, 11, 2H, $CH_2{=}CHR$), 6.71 (2H, =C*H*R), 6.68 (4H, =C*H*R), 5.24 (d, J = 17, 2H, HC*H*=CHR), 5.23 (d, J = 11, 2H, HC*H*=CHR), 5.08−4.95 (m, 8H, CH, *i*-Pr), 3.35 (4H, CH$_2$), 3.33 (4H, CH$_2$), 3.31 (4H, CH$_2$), 3.23 (4H, CH$_2$), 1.27−1.23 (m, 48H, Me, *i*-Pr); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 171.82 (C=O), 171.78 (C=O), 137.4, 137.29, 137.25, 136.3, 129.9, 123.9, 123.6, 123.3, 116.2 (=CH$_2$), 69.8 (O*C*HMe$_2$), 69.7 (O*C*HMe$_2$), 57.42 (quat), 57.41 (quat), 41.8 (CH$_2$), 41.7 (CH$_2$), 41.5 (CH$_2$), 41.4 (CH$_2$), 21.86 (Me), 21.85 (Me), 21.84 (Me), 21.82 (Me); HRMS (ESI) *m/z* calcd for $C_{62}H_{84}NaO_{16}$ (M − Na$^+$) *m/z* 1107.5652, found 1107.5645; UV/vis λ_{max} = 427 nm with ε = 9.1 × 10^4 cm^{-1} M^{-1} in CH_2Cl_2.

Synthesis of [H$_2$C][b$_5$][CH$_2$]. Solid [H$_2$C][b][O] (5 mg, 0.017 mmol) was added to solid (quin)[Mo][b$_3$][Mo](quin) (9 mg, 0.004 mmol). Benzene-*d*$_6$ (0.7 mL) was added, the mixture was transferred to a J. Young NMR tube, and the reaction was monitored over time by ^{1}H NMR (C_6D_6) spectroscopy. After 3 h, no Mo-alkylidene resonance was detected. The solvent was removed *in vacuo*, and pentane (1 mL) was added to the mixture. The precipitate was washed with pentane (3 × 1 mL) and dried *in vacuo* to give 9 mg of an orange powder. The washings were collected, and the solvent was removed *in vacuo* by rotary evaporation. According to ^{1}H NMR (C_6D_6) and UV−vis spectroscopies, the orange powder consisted of largely [H$_2$C][b$_5$][CH$_2$] (λ_{max} = 455 nm), whereas the washings contained largely [H$_2$C][b$_4$][CH$_2$].

Data for [H$_2$C][b$_5$][CH$_2$]: ^{1}H NMR (C_6D_6) δ 6.82 (d, J = 11, 4H, =C*H*R), 6.75 (d, J = 11, 4H, =C*H*R), 6.62 (dd, J = 17, 11, 2H, $CH_2{=}CHR$), 5.15−4.95 (overlapping m, 14H, CH, *i*-Pr and =C*H*$_2$), 3.68 (4H, CH$_2$), 3.64 (4H, CH$_2$), 3.61 (4H, CH$_2$), 3.58 (4H, CH$_2$), 3.56 (4H, CH$_2$), 1.06−0.98 (overlapping m, 60H, Me, *i*-Pr); ^{1}H NMR (CD_2Cl_2) δ 6.90 (dd, J = 17, 11, 2H, $CH_2{=}CHR$), 6.73 (4H, =C*H*R), 6.69 (4H, =C*H*R), 5.25 (d, J = 17, 2H, HC*H*=CHR), 5.24 (d, J = 11, 2H, HC*H*=CHR), 5.06−4.99 (m, 10H, CH, *i*-Pr), 3.37 (8H, CH$_2$), 3.33 (4H, CH$_2$), 3.31 (4H, CH$_2$), 3.24 (4H, CH$_2$), 1.27−1.23 (m, 60H, Me, *i*-Pr); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 171.8 (C=O), 171.83 (C=O), 171.79 (C=O), 137.6, 137.5, 137.32, 137.30, 136.4, 129.9, 123.9, 123.70, 123.66, 123.4, 116.2 (=CH$_2$), 69.79 (O*C*HMe$_2$), 69.77 (O*C*HMe$_2$), 69.71 (O*C*HMe$_2$), 69.70 (O*C*HMe$_2$), 57.54 (quat), 57.45 (quat), 57.43 (quat), 41.89 (CH$_2$), 41.85 (CH$_2$), 41.76 (CH$_2$), 41.5 (CH$_2$), 41.4 (CH$_2$), 21.88 (Me), 21.86 (Me), 21.85 (Me), 21.83 (Me); HRMS (ESI) *m/z* calcd for $C_{77}H_{104}NaO_{20}$ (M − Na$^+$) *m/z* 1371.7013, found 1371.7010; UV/vis λ_{max} = 455 nm with ε = 10.7 × 10^4 cm^{-1} M^{-1} in CH_2Cl_2.

X-ray Structural Studies. Diffraction data were collected on a Siemens Platform three-circle diffractometer or a Bruker D8 three-circle diffractometer (for [Et$_2$O][Mo][b$_3$][Mo][Et$_2$O]) coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) (or Cu Kα radiation (λ = 1.54178 Å) for the data of [Et$_2$O][Mo][b$_3$][Mo][Et$_2$O]) 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.[19] 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 semifreely 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).

[H$_2$C][b$_2$][CH$_2$] crystallizes in the triclinic space group $P\bar{1}$ 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).

[H$_2$C][b$_3$][CH$_2$] crystallizes in the triclinic space group $P\bar{1}$ 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(16), C(17), C(18), C(19), C(31), C(32), C(33), C(37), C(38), and C(39) lie in a plane within 0.09 Å. The best plane through all atoms of the planar core (the atoms mentioned above plus C(5), C(7), C(20), C(22), C(34), and C(36)) deviates only marginally from the first plane and is perfect within 0.10 Å. The ester group carrying atoms (C(6), C(21), and C35)) are slightly above or below this plane (C(6) deviates 0.3562(18) Å, C(21) 0.2681(16) Å, and C(35) 0.1628(17) Å).

[THF][Mo][b$_2$][Mo][THF] crystallizes in the monoclinic space group $P2_1/n$ with half a molecule in the asymmetric unit; the second half is generated by the crystallographic inversion center. The molecule cocrystallized 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,

---

(19) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

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.

$[Et_2O][Mo][b_3][Mo][Et_2O]$ crystallizes in the triclinic space group $P\bar{1}$ 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 Et_2O (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 C18)) 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.

[quin][Mo][b][Mo][quin] crystallizes in the triclinic space group $P\bar{1}$ 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 $O\text{-}C_4H_3F_6$ ligand and one $N\text{-}C_7H_{13}$ 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.

Acknowledgment. R.R.S. thanks the Department of Energy (DE-FG02-86ER13564) for research support.

Supporting Information Available:

Experimental details for syntheses of aldehydes, $OC(CF_3)Me_2$ complexes, and other miscellaneous experiments, tables of crystallographic data and CIF files for $[H_2C][b_2][CH_2]$ (06196), $[H_2C][b_3][CH_2]$ (06201), $[THF][Mo][b_2][Mo][THF]$ (08042), $[Et_2O][Mo][b_3][Mo][Et_2O]$ (D8-08011), and [quin][Mo][b][Mo][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.

OM8007585