Carboxylate-Based Molybdenum Alkylidene Catalysts: Synthesis, Characterization, and Use as Initiators for 1,6-Heptadiyne Cyclopolymerizations

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The carboxylate species Mo(NR)(CHCM2R′(O2CCPh3)2 (R = various aryl groups or 1-adamantyl; R′ = Ph or Me) have been synthesized by salt metathesis between Mo(NR)(CHCM2R′)(OTf)2(DME) (OTf = trifluoromethanesulfonate; DME = 1,2-dimethoxyethane) and sodium triphenylacetate. Other carboxylate compounds that have been prepared by this route include Mo(NAr)(CHCM2Ph)(O2CR′)2 (Ar = 2,6-i-Pr2C6H3; R′ = CPh2Me, Si(SiMe3)3) and Na[Mo(NAD)(CHCM2Ph)(O2CCPh3)2(PMe3) (Ar = 2,6-Me2C6H3)]. Terphenylcarboxylate species Mo(NR)(CHCM2Ph)(O2CTer)2 (Ter = 2,6-diphenyl-4-methylphenyl or 2,6-diphenyl-4-methoxyphenyl) or 2,6-diphenyl-4-methoxyphenyl) were prepared through protonolysis of Mo(NR)(CHCM2R′)-(Me2Pyrr) with TerCO2H, and one of them was characterized through X-ray crystallography. Trimethylphosphine adducts of selected triphenylacetate complexes have been isolated, and the X-ray crystal structure of Mo(NAr′′)2(CH-t-Bu)(O2CCPh3)2(PMe3) (Ar′′ = 2-t-BuC6H4) was obtained. Several of the triphenylacetate complexes are active initiators for the regioselective polymerization of diethyl dipropargylmalonate (DEPDM).

Introduction

Tungsten and molybdenum high oxidation state alkylidene complexes of the type M(NR)(CHR′)(OR′)2 (M = Mo or W; R, R′, and R′′ = various bulky alkyl or aryl groups)1 have proven useful for a variety of catalytic metathesis reactions. Examples include the living ring-opening metathesis polymerization (ROMP) of strained olefins,2 the polymerization of monoalkynes or dialkynes to yield polyynes,3 and the ring-closing metathesis (RCM) of dienes.1b-d,4 Molybdenum-based compounds are believed to be less sensitive to functionalities than tungsten-based species and therefore have been preferred.5 Unsubstituted tungsten complexes also in some cases have been found to be relatively stable toward loss of ethylene, whereas observable molybdacyclobutanes are rare;6 turnover frequencies with Mo catalysts therefore can be higher than with W catalysts in certain circumstances. One valuable asset of M(NR)(CHR′)(OR′)2 catalysts is their modularity. Variation of the NR and OR′′ ligands can lead to different reactivities and selectivities, often dramatically so, especially in stereoselective ROMP of strained olefins and asymmetric metathesis reactions. We have reported the synthesis of Mo(NR)(CHR′)(pyrrole)- (OR′′) species7 through addition of R′′OH to Mo(NR)(CHR′)- (pyrrole)2 species,8 where the pyrrole is the parent pyrrole (NC6H4 = Pyr) or 2,5-dimethylpyrrole (NC6Me2H2 = Me2-Pyr). The Mo(NR)(CHR′)(pyrrole)(OR′′) species are potentially even more highly variable as well as chiral at the metal center. Although enyne metatheses have not been successful with a wide variety of Mo(NR)(CHR′)(OR′′)2 catalysts, preliminary results suggest that some enyne metatheses are successful with Mo(NR)(CHR′)(Pyr)(OR′′) species.7

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An important feature of polymerization reactions involving terminal alkynes is the (presumably irreversible) addition of the alkyne to place the alkyne substituent in either a terminal alkynes is the (presumably irreversible) addition of the \( \text{Me}_{2}C \) to \( \text{N} \) in the metalacyclobutene intermediate, rearrangement of which yields either a disubstituted or monosubstituted alkylidene (Scheme 1). If both addition pathways are operative, the resulting polyenes will contain a mixture of five-membered rings (as a consequence of \( \alpha \)-addition) or six-membered rings (as a consequence of \( \beta \)-addition) as the repeat unit (eq 1).

Several \( \text{Mo}^{\text{III}} \) and \( \text{Ru}^{\text{II}} \) catalysts are known that are capable of producing polyenes that contain 95% five-membered rings, while we reported (in a preliminary fashion) the synthesis and polymerization behavior of some molybdenum imido alkylidene complexes that contain two carboxylate ligands that serve as initiators for the living polymerization of diethyl dipropargylmalonate to give polyenes that contain >98% six-membered rings. \( ^{11} \) In this paper we describe some further studies of biscarboxylate complexes. Carboxylate ligands smaller than \( \text{Ph}_{3} \text{CO} \) are ill-defined (possibly oligomeric) species that could not be isolated. Complexes \( 1\text{a} \sim 1\text{e} \) were prepared from bistriflate precursors through salt metathesis reactions with sodium tripentylacetate (eq 2; \( \text{Ar} = 2,6-i \text{-Pr}_{2}C_{6}H_{3}, \text{Ar}' = 2,6-\text{Me}_{2}C_{6}H_{3}, \text{Ad} = 1\text{-adamantyl}, \text{Ar}'' = 2-\text{-BuC}_{6}H_{4}, \text{Ar}^{\prime \prime} = 2,6-\text{Cl}_{2}C_{6}H_{3} \)). All triphenylacetate complexes, with the exception of \( 1\text{b} \), are soluble in common organic solvents other than alkanes. Chemical shifts for alkylidene \( \alpha \)-protons range from 13.76 to 13.91 ppm, while \( \alpha \)-carbon shifts range from 305.5 to 313.4 ppm. These relatively downfield chemical shifts are more consistent with five- or six-coordinate species than four-coordinate imido alkylidene species. \(^{11} \) All alkylidenes exist as syn isomers in solution, as judged by \( J_{\text{CH}} \) values that range from 117 to 125 Hz (see Experimental Section). \(^{12} \) The \( R \) groups in the imido ligands in \( 1\text{a}, 1\text{b}, \) and \( 1\text{e} \) freely rotate on the NMR time scale about the \( N=C \) bond at room temperature.

A single-crystal X-ray study of \( 1\text{d} \) revealed it to be a distorted six-coordinate 18-electron species in which both carboxylates are bound \( k^{2} \). \(^{11} \) However, both are bound somewhat asymmetrically, with \( \text{Mo-O} \) distances of 2.136 and 2.261 Å for one carboxylate and 2.090 and 2.336 Å for the other carboxylate. The longer \( \text{Mo-O} \) bonds are trans to the \( \text{Mo=O} \) (2.336 Å) or the \( \text{Mo=N} \) bond (2.261 Å). The carboxylates are technologically inequivalent in this structure, although all biscarboxylate complexes show time-averaged \( C_{3v} \) symmetry in solution at room temperature, consistent with a fluxional coordination geometry on the NMR time scale that may or may not involve intermediates that contain at least one \( \text{N}^{\text{I}} \) carboxylate.

Attempts to prepare several other biscarboxylate complexes did not lead to identifiable species. For example, numerous attempts to prepare pivalate (\( \text{O}_{2}\text{C-i-Bu} \)) complexes yielded products that displayed several alkylidene peaks in proton NMR spectra and that could not be purified through repeated recrystallization. The use of \( 3,5\text{-di-tert-butylbenzoate and 2,6-dimethylbenzoate (~O}_{2}\text{C} \text{(Ar)} \) led to the formation of anionic \( \text{ate} \) adamantylimido species in which three carboxylate ligands are bound to the metal. One of these was isolated and characterized (2, eq 3). In order to maintain an 18 e count at the metal, two of the carboxylates must be \( k^{2} \) in the \( \text{ate} \) complexes. Indeed, two carboxylates of one type (presumably \( k^{2} \)) and one of another (presumably \( k^{3} \)) are found in proton NMR spectra at room temperature. No THF is present in 2 according to NMR spectra; therefore the sodium ion is likely to be bound to an oxygen atom in one or more of the carboxylate ligands.

A diphenylmethylacetate (\( \text{Ph}_{2}\text{MeCCO} \)) complex could be prepared when the 2,6-diisopropylphenyl imido ligand (3, eq 4).

\[^{12} \text{Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. Organometallics 1991, 10, 1832.}\]


4) was employed. The NMR spectral features of 3 are nearly identical to those of 1a. Examination of the methyl groups of the carboxylate ligand by NMR spectroscopy at temperatures down to 193 K (in methylene chloride-\(d_2\)) revealed no evidence of inequivalent carboxylate ligands on the NMR time scale. Bisdiphenylmethylacetate complexes that contain smaller imido groups could not be isolated. For example, attempts to prepare Mo(NAr′′)(CH-t-Bu)(O2CCMePh2)2 (Ar′′ = t-BuC6H4) yielded an insoluble yellow powder that did not dissolve readily in dichloromethane and that could not be identified.

A complex containing two (TMS)3SiCO2- ligands was prepared through the reaction shown in eq 5. Analogous complexes containing the 2-tert-butylphenyl or 1-adamantyl imido ligands appeared to form readily and cleanly according to preliminary (1H NMR) studies, but only 4 was isolated and fully characterized. The C\_R and H\_R chemical shifts in 4 were in the range typical of the other carboxylate compounds discussed above.

**Synthesis of Bisbenzoate Complexes.** We find that “ate” complexes can be avoided and bisbenzoate complexes prepared if 2,6-terphenylcarboxylates\(^{13}\) are employed. The two chosen terphenylcarboxylates contain \(p\)-methyl or \(p\)-methoxy substituents in the phenyl ring bound in the 2 and 6 positions in the benzoate backbone, (O2CTerMe) and (O2CTerOMe), respectively. The chosen method of synthesis consisted of addition of 2 equiv of the acid to Mo(NR)(CHCMe2Ph)(Me2Pyr)2 (Me2Pyr = 2,5-dimethylpyrrolide; eq 6).\(^{8}\) The complexes can also be prepared via salt metathesis starting from the corresponding bistriflate precursor and 2 equiv of NaO2CTer. However, the more complicated workup involves recrystallization of the compounds because the initial product obtained from the reaction is relatively impure. In the case of complexes that contain the adamantylimido ligand (discussed below), the product of the salt metathesis reaction could not be obtained in a pure form suitable for further chemical and reactivity investigations. The resulting bisbenzoates, Mo(NAr′)(CHCMe2Ph)(O2CTerMe)2 (5a) and Mo(NAr′)(CHCMe2Ph)(O2CTerOMe)2 (5b) (eq 6), were isolated in yields between 50% and 60%. Similarly, bisbenzoate alkylidene complexes containing the adamantylimido group, Mo(NAd)(CHCMe2Ph)(O2CTerMe)2 (5c) and Mo(NAd)(CHCMe2Ph)(O2CTerOMe)2 (5d), were obtained in yields ranging between 40% and 70% (eq 6). The 1H NMR spectra of all compounds suggest that a mirror plane is present on the NMR time scale as a consequence of rapid carboxylate interconversion. Only a syn isomer is observed for each with \(\delta\)H\_R, \(\delta\)C\_R, and \(J\)\_CH values similar to other carboxylates described earlier. The resonances corresponding to the alkyl groups of the imido substituents, as well as to the alkyl groups of the carboxylate, are sharp, again consistent with a plane of symmetry being present on the NMR time scale.

Crystals of 5a were grown from a saturated methylene chloride solution layered with diethyl ether. The structure is shown in Figure 1. (See Table 1 for details.) The structure is best described as a distorted octahedron, with both carboxylate groups bound to the metal in a \(\kappa^2,\kappa^2\) fashion, similar to the bисcarboxylate described in the preliminary communication.\(^{11}\) The alkylidene is in the syn orientation. The most interesting features are again long Mo(1)–O(1) and Mo(1)–O(3) bond lengths (2.2867(16) and 2.3186(16) Å, respectively), i.e., those trans to the imido and alkylidene groups, respectively. In the solid state the two carboxylates are inequivalent, but equivalent

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dimensions: 598.0x792.0

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15a

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3989

Mo(NAr)(CHCMe2Ph)(O2CCPh3)2 (syn)

Fm molecules of pentane (disordered) per molecule of µ-chloride (33.9-


Table 1. Crystal Data and Structure Refinement Details for 1d·PMes and 5a*

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<tr>
<th></th>
<th>5a</th>
<th>1d·PMes b</th>
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<tr>
<td>empirical formula</td>
<td>C60H32MoNO4</td>
<td>C60H32Cl2MoNO4P</td>
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<tr>
<td>fw</td>
<td>1006.09</td>
<td>1157.14</td>
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<td>triclinic</td>
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<td>space group</td>
<td>PI</td>
<td>PI</td>
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<td>unit cell dimens</td>
<td>a = 12.194(6) Å</td>
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<td></td>
<td>b = 12.241(6) Å</td>
<td>b = 14.0067(4) Å</td>
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<tr>
<td></td>
<td>c = 20.290(11) Å</td>
<td>c = 17.7003(4) Å</td>
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<td>α = 88.7519(9)°</td>
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<td></td>
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<td></td>
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<td>γ = 88.9480(10)°</td>
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<td>3050.21(13) Å3</td>
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<td>Z</td>
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<td>2</td>
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<td>1.260 g/cm3</td>
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<td>0.376 mm-1</td>
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<td>F(000)</td>
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<td>−17 ≤ h ≤ 17, −19 ≤ k ≤ 19, −24 ≤ l ≤ 24</td>
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<tr>
<td>no. of refnls collected</td>
<td>48 967</td>
<td>68 763</td>
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<tr>
<td>no. of indep refns</td>
<td>13 298 [R(int) = 0.0371]</td>
<td>17 080 [R(int) = 0.0259]</td>
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<td>completeness to θ = 29.57°</td>
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<td>99.7%</td>
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<tr>
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<td>17 080/299/717</td>
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<td>1.039</td>
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<td>final R indices [I &gt; 2σ(I)]</td>
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<td>R1 = 0.0434, wR2 = 0.1074</td>
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<td>largest diff peak and hole</td>
<td>0.939 and −0.633 e·Å⁻³</td>
<td>2.425 and −1.172 e·Å⁻³</td>
</tr>
</tbody>
</table>

* For both structures the wavelength was 0.71073 Å, the temperature was 100(2) K, the absorption correction was semiempirical from equivalents, and the refinement method was full-matrix least-squares on F2. b The solid-state structure of 1d·PMes contains one molecule of CH2Cl2 and 1.5 molecules of pentane (disordered) per molecule of 1d·PMes.

Figure 2. Electronic absorption spectrum of Mo(NAr)(CHCMe2Ph)(O2CCPh3)2 (1a) at 23 °C in methylene chloride (33.9 μM).

in solution on the NMR time scale. The monomeric structure of 5a contrasts with the dimeric structure of [Mo(NAr)(CHCMe2Ph)(CF3CO2)(µ-CF3CO2)]2, in which one of the two trifluoroacetates bound to each Mo is bridging between two Mo centers.14

Observation of anti Isomers. The UV−vis spectrum of 1a is shown in Figure 2. The absorption maximum at 324 nm (ε ≈ 15 000 M⁻¹ cm⁻¹) is similar to what was found for Mo(NAr)(CH-t-Bu)(OR)2 complexes in which R = t-Bu, CMe2(CF3), or CMe(CF3)2.15 This absorption is ascribed to the M−Nπ moød→π° transition, in part because a photoinduced mixture of syn and anti isomers (eq 7) can be formed through irradiation of samples with 366 nm light in toluene. Rates of interconversion of syn and anti alkylidyne isomers in bisalkoxide complexes vary by several orders of magnitude, with the slowest rates being found for alkylidyne complexes that contain relatively electron-withdrawing alkoxides such as OCMe(CF3)2. Interconversion of syn and anti isomers appears to be most facile in a 14e species. For example, the base (e.g., PMes) in a 16e adduct of Mo(NAr)(CH-t-Bu)[OCMe(CF3)2]2 must be lost before syn and anti isomers can interconvert. A coordinating solvent such as THF will also hinder alkylidyne rotation to a significant degree in Mo(NR)(CHR′)(OR′)2 species on the basis of slower rates and negative values for the activation entropy for syn/anti interconversion in THF.15 Since syn and anti isomers can have dramatically different reactivities,16 the rate of interconversion of syn and anti isomers and the position of that equilibrium can have important consequences in terms of metathesis with such species.

Photolysis of a sample of 1a in toluene-d8 at 366 nm for 3 h at 22 °C yielded a mixture containing 16% of a new species in which δHμ = 13.93 ppm and JCH = 138 Hz, characteristic of an anti isomer. At 22 °C the anti isomer was found to convert to the syn isomer in a first-order manner with kabs = 1.5 × 10⁻⁶ s⁻¹ (t½ = 5.4 days). A sample of 1c irradiated in toluene-d8 at 366 nm for 2 h at 22 °C produced a mixture containing 28% of an anti species (δHμ = 13.99 ppm, δCH = 140 Hz) that reverted back to the syn isomer at 22 °C with kabs = 3.0 × 10⁻⁴ s⁻¹ (t½ = 5.4 days).


unchanged after 4 h at 22 °C produced a mixture containing 17% of an anti species (δHₐ = 13.90 ppm, JCH = 137 Hz) that reverted to the syn isomer at 0 °C with kₚ = 1.6 × 10⁻⁵ s⁻¹. At room temperature the reaction was too fast to measure accurately (t₁/₂ ≈ 3 min). Therefore at room temperature the relative rates of conversion of anti to syn isomers are 1d > 1c > 1a with t₁/₂ ranging from ~5 days (for 1d) to ~3 min (for 1c).

\[ k \text{anti} = k \text{syn} = k \text{eq} \]

Syn/anti isomerization reactions of bisbenzoate complexes were studied briefly for 5a and 5c. A sample of 5a in toluene-d₈ was photolyzed at 22 °C with 366 nm light for 2 h. The resulting mixture contained 7% of the anti species (δHₐ = 13.6 ppm, JCH = 137 Hz) and 93% of the syn species (δHₐ = 13.4 ppm, JCH = 126 Hz). The rate constant for the anti to syn conversion of 5a at 22 °C in toluene-d₈ was found to be \( 5 \times 10^{-4} \text{ s}^{-1} \). Photolysis of a solution of 5c in toluene-d₈ at room temperature for 2 h yielded a mixture of 9% anti (δHₐ = 13.9 ppm, JCH = 140 Hz) and 91% syn (δHₐ = 13.2 ppm, JCH = 124 Hz) isomers. However, unlike 5a, which proved to have a short half-life for conversion of anti to syn, 5c was virtually unchanged after 4 h at 22 °C. Only after 16 h at 22 °C did the amount of the anti species decrease to ~3% (30% of the initial amount).

Trimeylphosphine Adducts of Tribiphenylacetate Complexes. Base adducts of imido alkylidene complexes often can serve as models of the first adduct formed when a substrate approaches the metal center in a catalytic reaction. The 18-electron biscarboxylates are unlikely to bind a Lewis base if the carboxylates must equilibrate without generating a single species. Compound 1e reacts with PMe₃ to give a mixture of the desired adduct, 1ε·PMe₃ (~20%; δHₐ at 13.47 ppm in C₆D₆), and a side product that could not be separated from 1ε·PMe₃ through recrystallization. The side product contained a broad resonance at 10.44 characteristic of a NHAr²⁺ proton. Therefore the side product is believed to be Mo(NHArCl)(CH-t-Bu)(OCMe-(CF₃)₂)₂(PMe₃), which can be isolated as a syn isomer that slowly converts over a period of days in solution into the anti isomer (completely), a process that is believed to require loss of trimethylphosphine followed by (inherently slow) syn to anti rotation about the Mo=C bond in intermediate Mo(NHAr)(CH-t-Bu)(OCMe(CF₃)₂)₂. Addition of PMe₃ to 2 in CD₂Cl₂ yielded a precipitate of Na(O₂CCMePh₂) and 2·PMe₃ after several minutes, according to ¹H NMR experiments (eq 10). The ¹H NMR spectrum of 2·PMe₃ displayed a doublet allylidene resonance (J₁₂ = 6.0 Hz) and two singlet resonances of area six (each) for the methyl groups of the benzoate ligands, consistent with binding of a single PMe₃ to the metal and two different types of nonequilibrating carboxylate ligands. It should be noted that Lewis bases have been employed in the past to isolate adducts of alkylidene complexes that are unstable as 14e four-coordinate species.

Crystals of 1d·PMe₃ were grown from a saturated solution of 1d·PMe₃ in a 1:1 mixture of methylene chloride and pentane. A single-crystal X-ray study revealed the structure shown in Figure 3. (See Table 1 for crystallographic details.) The compound has pseudo-octahedral coordination geometry with the trimethylphosphine cis to mutually cis imido and syn allylidene ligands. A bidentate triphenylacetate ligand lies approximately in the N(1)−Mo(1)−C(1) plane with carboxylate oxygens bound trans to the imido and allylidene ligands (Mo(1)−O(3) = 2.2597(13) Å, Mo(1)−O(4) = 2.2873(13) Å). The Mo(1)−C(1)−C(2) angle (152.65(15)°) is relatively large,

\[ \text{Mo}(1)−\text{C}(1)−\text{C}(2) \]

2.2873(13), Mo(1)  
106.04(8), P(1)  
118.94(16), Mo(1)  
173.51(13), O(1)  
57.27(5), Mo(1)  
54.64(11), C(1)  
164.68(4), O(3)  
124.19(11).
Table 3. Relative Five- And Six-Membered Ring Content in Polymers Prepared in Toluene Employing 1d as the Initiator

<table>
<thead>
<tr>
<th>Sample</th>
<th>Five-membered rings</th>
<th>Six-membered rings</th>
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<tbody>
<tr>
<td>poly(DDPDM)</td>
<td>9.0</td>
<td>91.0</td>
</tr>
<tr>
<td>poly(DEDPM)</td>
<td>1.7</td>
<td>98.3</td>
</tr>
<tr>
<td>poly(BEDPM)</td>
<td>2.8</td>
<td>97.2</td>
</tr>
<tr>
<td>poly(DBDPM)</td>
<td>3.8</td>
<td>96.2</td>
</tr>
<tr>
<td>poly(EDPA)</td>
<td>31</td>
<td>69</td>
</tr>
</tbody>
</table>

* Determined through integration of the carbonyl region (165–172 ppm) and the quaternary carbon region (40–60 ppm) of the 125 MHz 13C NMR spectrum at 25 °C in CDCl3. † Determined through integration of the carbonyl carbon resonances at 174.5 ppm (six-membered ring) and 175.5 ppm (five-membered ring).

Scheme 2. Other Monomers Explored in This Study

Conclusions

The ability to prepare and isolate stable, well-defined, carbonylate complexes depends critically on the steric bulk of the carbonylate. Carboxylates that possess smaller substituents result in “ate” complexes or formation of ill-defined oligomeric species. Binding of the carbonylates in a κ2 fashion is favored, which yields a metal center that is unreactive toward olefins but in the right circumstances will react with terminal alkynes, possibly through an unsaturated (κ1, κ2 or κ3, κ2) intermediate.

The utility of the carbonylate species lies in their ability to selectively polymerize DEDPM to give a polymer that contains all six-membered rings. Unfortunately, however, smaller or larger ester groups in the dipropargylmalonate, as well as use of ethyldipropargylacetate, lead to polymers that do not contain exclusively six-membered rings. Terphenylcarboxylates provide almost too much steric protection at the metal center and also compromise the formation of six-membered rings. In the end it is somewhat surprising that polymer that contains only six-membered rings can form at all, since α,α′-disubstituted metalacyclobutene intermediates would appear less sterically crowded than α,α′-disubstituted metalacyclobutene intermediates, all else being equal. Therefore we have little hope that many examples will arise in which only six-membered rings are formed from 1,6-heptadiynes. In contrast, formation of 1,6-heptadiyne polymers that contain only five-membered rings through formation of α,α′-disubstituted metalacyclobutene intermediates seems to hold more promise. Such polymers also do not contain opportunities for E/Z isomerism and are relatively linear and rigid. We plan to focus on the synthesis of polymers that contain only five-membered rings in future studies.

Experimental Section

All manipulations were performed 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, then stored over 4 Å Linde-type molecular sieves. Benzene-d6 was dried over sodium/benzophenone ketyl and vacuum-distilled. Methylene chloride-d3 was dried over CaH2, vacuum distilled, and stored over 4 Å Linde-type molecular sieves. Chloroform-d2 was stored over 4 Å Linde-type molecular sieves. NMR spectra were recorded on Varian spectrometers operating at 300 or 500 MHz. Chemical shifts for 1H and 13C spectra were referenced to the residual 1H and 13C resonances of the deuterated solvent [1H: C6D6, δ 7.16; CDCl3, δ 7.26; CD2Cl2, δ 3.52; CD3Cl, δ 7.26; 13C: C6D6, δ 128.39; CD2Cl2, δ 45.00; CDCl3, δ 77.36] and are reported as parts per million relative to tetramethylsilane. 31P NMR spectra were referenced externally to 85% H3PO4 (δ 0.00 ppm). Gel permeation chromatography (GPC) employed two Jordi-Gel DVB mixed bed columns in series, a Wyatt Mini Dawn light scattering detector, and a Knauer refractometer using samples 0.5–0.6 w/v in THF. Alternatively, a GPC online viscometry setup consisted of two Jordi-Gel DVB mixed bed columns in series and a Viscotek differential refractometer/Viscometer H-500 using samples 0.1–0.2% w/v in THF. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd.) that ranged from 1206 to 1.03 × 106 g/mol. GPC data were analyzed using either Astrette 1.2 (Wyatt Technology) or Unical 4.03 (Viscotek Technology). UV–vis spectra were recorded on an Agilent 8453 diode array spectrometer. Elemental analyses were performed by H. Kolbe Microanalytical Laboratory, Mülheim an der Ruhr, Germany.

Mo(NR₂)(CHCMePh)(OTf)₂(DME) species, where R = 2,6-i-Pr₅C₆H₃ (Ar), 2,6-Me₅C₆H₃ (Ar′), 1-adamantyl (Ad), 2-i-Bu₅C₆H₃ (Ar″), and 2,6-Cl₂C₆H₃ (Ar‴), were prepared according to published

Monomers that contain all five-membered rings. More rapid propagation relative to initiation appears to result from the relatively “flatt” nature of a vinyl-substituted alkylidene in a propagating species (relative to a neopentylidene or neophyldiene initiator), regardless of whether a five- or a six-membered ring is found. Buchmeiser has also reported a monomer dependence found for six-membered versus five-membered rings being formed when 5c was employed (83%) and when 5d was employed (77% β product).

Three sterically different dialkyl dipropargylmalonates and one dipropargyl acetate (ethyldipropargylacetate or EDPA) were investigated in bulk polymerization reactions employing initiator 1b (Scheme 2). The three monomers are polymerized in toluene by 1d in good isolated yield (>90%). The relative ring content (five versus six) was determined by 13C NMR, and the results are listed in Table 3. Polymerization of dialkylmalonates that are smaller or larger than DEDPM was less selective, especially polymerization of dimethylpropargylmalonate. Polymerization of EDPA was virtually unselective, with a ratio of 69:31 being found for six-membered versus five-membered rings being found. Buchmeiser has also reported a monomer dependence of the five-membered ring content of 1,6-heptadiyne polymers prepared with high oxidation state catalysts. For poly(EDPA) the carbonyl carbon was found to be a better choice for determining ring content.
procedures. Syntheses of Mo(NAr)(CHMe3)(O2CCPh3), Mo(NAr)(CHMe3)(O2CCMe3)2, Mo(NAr′)(CH-t-Bu)(O2CCPh3), and Mo(NAd)(CHMe3)(O2CCPh3)2 have been reported in a preliminary fashion and are repeated below for convenience. Tetrahydrofuran (THF) and toluene were prepared as described in the literature. All carboxylate salts were prepared by crystallization from THF/pentane. PMe3 was purchased from Strem Chemicals and used as received. All other reagents were purchased from commercial vendors and used as received.

Mo(NAr)(CHMe3)(O2CCPh3)2 (1a). To a suspension of 0.369 g (0.466 mmol) of Mo(NAr)(CHMe3)(O2CCPh3)(OTf)(DME) in 25 mL of diethyl ether at −25 °C was added 0.350 g (0.915 mmol) of NaO2CCPh3. The mixture was allowed to warm to room temperature and stir for 60 min, during which time the solution became homogeneous. The volatiles were removed in vacuo, and the residue was extracted into 20 mL of methylene chloride. The extract was filtered through Celite, and the solution volume was reduced to ∼1–2 mL in vacuo. Several volumes of pentane were added, and the solution was allowed to stand at −25 °C for 24 h to yield yellow microcrystals (0.425 g, 88%): 1H NMR (CD2Cl2, 300 MHz) δ 13.91 (s, 1, MoCH2), 7.49−6.89 (m, 38, Ar), 3.78 (sept, 2, CHMe2), 1.50 (s, 6, CMe2Ph), 1.03 (d, 12, CHMe2); 13C NMR (75 MHz) δ 138.4 Hz). At 22 °C conversion of Mo(II) to Mo(III) was too fast to measure accurately.

To a solution of 0.500 g (0.635 mmol) of Mo(NAr)(CH-t-Bu)(O2CCPh3)(OTf)(DME) in 25 mL of diethyl ether was added 0.827 g (2.16 mmol) of NaO2CCPh3·THF as a solid in one portion. The solution was allowed to warm to room temperature and stir for 1 h, during which time a yellow precipitate formed. All volatiles were removed in vacuo, and the residue was extracted into 20 mL of methylene chloride.

The extract was filtered through Celite, and the solution volume was reduced to 2 mL in vacuo. The solution was layered with several volumes of pentane and set aside at −25 °C for 24 h. The complex crystallized as yellow microcrystals (0.751 g, 82%): 1H NMR (CD2Cl2, 300 MHz) δ 13.76 (s, 1, C3H8Me), 7.58 (m, 1, Ar), 7.35−7.17 (m, 33, Ar), 1.33 (s, 9, tert-Bu), 1.17 (s, 9, tert-Bu); 13C NMR (75 MHz) δ 131.4 Mo(Cs, 1JCH = 123 Hz), 191.9 (CO2), 154.6, 145.6, 143.0, 135.6, 131.0, 128.5, 128.2, 127.5, 127.1, 126.4, 69.4 (CO2), 50.9, 36.0, 31.5, 30.7. Anal. Calcd for CsH35MoNO5: C, 74.40; H, 6.02; N, 1.58. Found: C, 74.67; H, 5.86; N, 1.36.

To a suspension of 0.740 g (1.04 mmol) of Mo(CH-t-Bu)(O2CCPh3)(OTf)(DME) in 35 mL of diethyl ether was added 0.853 g (2.23 mmol) of NaO2CCPh3·THF as a solid in one portion. The resulting suspension was stirred at room temperature for 90 min, during which time the reaction became yellow and a precipitate formed. All volatiles were removed in vacuo, and the residue was extracted into 15 mL of methylene chloride. The extract was filtered through Celite, and all volatiles were removed in vacuo. The remaining residue was treated with pentane to give 0.640 g (68%) of a yellow crystalline powder. The crude material was pure by NMR but could be recrystallized from methylene chloride/pentane: 1H NMR (CD2Cl2, 500 MHz) δ 13.81 (s, 1, MoCH2), 7.31−7.11 (m, 39, Ar), 1.16 (s, 9, tert-Bu); 13C NMR (125 MHz) δ 315.8 Mo(C55H53MoNO4: C, 74.40; H, 6.02; N, 1.58. Found: C, 74.67; H, 5.86; N, 1.36.

The extract was filtered through Celite, and the solution volume was reduced to ∼1–2 mL in vacuo. The solution was layered with several volumes of pentane and set aside at −25 °C for 24 h. The complex crystallized as yellow microcrystals (0.751 g, 82%): 1H NMR (CD2Cl2, 300 MHz) δ 13.76 (s, 1, C3H8Me), 7.58 (m, 1, Ar), 7.35−7.17 (m, 33, Ar), 1.33 (s, 9, tert-Bu), 1.17 (s, 9, tert-Bu); 13C NMR (75 MHz) δ 131.4 Mo(Cs, 1JCH = 123 Hz), 191.9 (CO2), 154.6, 145.6, 143.0, 135.6, 131.0, 128.5, 128.2, 127.5, 127.1, 126.4, 69.4 (CO2), 50.9, 36.0, 31.5, 30.7. Anal. Calcd for CsH35MoNO5: C, 74.40; H, 6.02; N, 1.58. Found: C, 74.67; H, 5.86; N, 1.36.

The extract was filtered through Celite, and the solution volume was reduced to ∼1–2 mL in vacuo. The solution was layered with several volumes of pentane and set aside at −25 °C for 24 h. The complex crystallized as yellow microcrystals (0.751 g, 82%): 1H NMR (CD2Cl2, 300 MHz) δ 13.76 (s, 1, C3H8Me), 7.58 (m, 1, Ar), 7.35−7.17 (m, 33, Ar), 1.33 (s, 9, tert-Bu), 1.17 (s, 9, tert-Bu); 13C NMR (75 MHz) δ 131.4 Mo(Cs, 1JCH = 123 Hz), 191.9 (CO2), 154.6, 145.6, 143.0, 135.6, 131.0, 128.5, 128.2, 127.5, 127.1, 126.4, 69.4 (CO2), 50.9, 36.0, 31.5, 30.7. Anal. Calcd for CsH35MoNO5: C, 74.40; H, 6.02; N, 1.58. Found: C, 74.67; H, 5.86; N, 1.36.
MoCHMe2Ph, 0.835 (d, 12, CHMe2); 13C NMR (CD2Cl2) δ 309.0 (MoCHMe2Ph), 185.0 (CO2), 152.5, 150.3, 148.9, 143.0, 138.6, 136.8, 131.6, 130.3, 129.9, 129.3, 128.5, 128.3, 128.1, 126.2, 126.0, 122.9, 57.5, 31.3, 28.6, 23.4, 21.2. Anal. Calcd for C63H50MoNO5: C, 76.40; H, 6.31; N, 1.39. Found: C, 76.31; H, 6.32; N, 1.42.

A small sample (~30 mg) of the pure compound was dissolved in a saturated solution of methylene chloride, and diethyl ether was layered on top at RT to yield small crystals suitable for diffraction.

A sample of 5a irradiated in toluene-δ6 at 366 nm for 2 h at 22 °C produced a mixture containing 7% of the i-species (δHα = 13.6 ppm, JCH = 137 Hz). At 22 °C the rate constant for the conversion from the α and i species was found to be 5 × 10^-4 s^-1.

**Mo(NAr)(CHR)(Me2Pyr)2 (0.250 g, 0.420 mmol) and PMe3.** The mixture was stirred for 2 h, and all volatiles were removed in vacuo. The residue was treated with pentane, and the white solid was collected by filtration and dried in vacuo to afford 0.271 g (85%) of the product as a white powder:

1H NMR (CD2Cl2, 500 MHz) δ 13.17 (d, 1, MoCH3, JCHP = 6.0 Hz), 7.45 (d, 2, Ar), 7.34 (m, 5, Ar), 7.25-7.00 (m, 28, Ar), 2.15 (s, 3, CMe2Ph), 2.01 (m, 3, AdH), 1.91 (m, 5, AdH), 1.58 (m, 6, AdH), 1.37 (s, 3, CMe2Ph), 0.58 (d, 9, PMe3); 13C NMR (125 MHz) δ 30.7 (d, CMe2Ph, JCP = 120 Hz, JCP = 18.0 Hz), 186.1 (br, CO2), 176.4 (br, CO2), 148.7 (d, JCP = 3.0 Hz), 146.9 (br), 146.5, 144.8 (br), 131.5-131.4 (br m), 130.8, 128.8, 128.2-127.7 (br m), 127.9, 126.6, 126.5, 126.4 (br, 74.1 (NC), 70.5 (br, CCO2), 69.0 (br, CCO2), 51.1 (d, PMe3, JCP = 3.1 Hz), 44.6, 36.2, 32.9 (d, JCP = 3.0 Hz), 29.9, 29.6, 16.9 (d, PMe3, JCP = 28 Hz); 31P NMR (121 MHz) δ 2.99. Anal. Calcd for C63H50MoNO5C: 73.60; H, 6.74; N, 1.31. Found: C, 73.81; H, 6.58; N, 1.31.

Mo(Nd)(CHCMe2Ph)(O2CCMePh)2(PMe3) (1c-PMe3). To a −25 °C suspension of 0.315 g (0.355 mmol) of Mo(Nd)(CHCMe2Ph)(O2CCMePh)3 in 10 mL of methylene chloride was added 80 µL (0.80 mmol) of PMe3 via microsyringe. The mixture immediately became orange and was allowed to stir at room temperature for 2 h. All volatiles were removed in vacuo, and the residue was treated with pentane to give 0.291 g (85%) of an orange solid. Crystals suitable for X-ray diffraction were grown from a concentrated methylene chloride/pentane solution.

NMR and combustion analyses were consistent with the presence of one molecule of methylene chloride per Mo. 1H NMR (CD2Cl2, 300 MHz) δ 13.13 (d, 1, MoCH3, JCHP = 4.9 Hz), 7.92 (dd, 1, o-Ar′), 7.62-7.57 (m, 12, Ar), 7.16 (dd, 1, m-Ar′); 7.08-6.98 (m, 18, Ar), 6.91 (m, 1, m-o or o-Ar′), 6.84 (m, 1, m-o or o-Ar′); 1.38 (s, 9, R-bu), 1.27 (s, 9, t-bu), 0.63 (s, 9, PMe3); 13C NMR (75 MHz) δ 314.9 (d, MoCH3, JCP = 118 Hz, JCP = 19 Hz), 146.0, 132.2, 127.9, 126.7, 69.8, 49.7, 36.3, 32.7, 31.6, 16.2 (d, PMe3). Anal. Calcd for C63H50MoNO5C: 67.56; H, 6.15; N, 1.34. Found: C, 76.83; H, 6.10; N, 1.15.

**Mo(Nd)(CHCMe2Ph)(O2CCMePh)2(PMe3) (1b-PMe3).** Trimethylphosphine 25 µL (0.24 mmol) was added via microsyringe to a suspension of 0.159 g (0.173 mmol) of Mo(Nd)′-(CHCMe2Ph)(O2CCMePh)3 in 3 mL of methylene chloride. The solution immediately became homogeneous. After 5 min all volatiles were removed in vacuo, the residue was dissolved in 1 mL of methylene chloride, and the solution was layered with several volumes of pentane. Storage of the solution at −25 °C afforded 0.155 g (90%) of yellow crystals, which were dried in vacuo. Analytically pure material was obtained by recrystallization from methylene chloride/pentane. NMR and combustion analysis was consistent with the presence of two molecules of methylene chloride per Mo: 1H NMR (CD2Cl2, 500 MHz) δ 13.21 (d, 1, MoCH3, JCHP = 5.5 Hz), 7.44 (d, 1, o-CMe2Ph), 7.32 (d, 12, o-CPh2), 7.24 (t, 2, m-CMe2Ph), 7.10 (m, 19, m-MePPh2 + p-MePPh, 6.93 (m, 3, Ar′), 2.34 (s, 6, Ar′-Me), 1.88 (s, 3, CMe2Ph), 1.47 (s, 3, CMe2Ph), 0.59 (d, 9, PMe3); 13C (125 MHz) δ 311.2 (d, MoC3, JCP = 118 Hz, JCP = 19 Hz), 181.7 (br s, CO2), 153.5 (d, JCP = 3.1 Hz), 148.8 (d, JCP = 2.3 Hz), 145.5, 137.7 (d, JCP = 2.3 Hz), 131.4, 128.9, 128.3, 127.9, 126.7, 126.8, 69.8, 33.0, 29.4, 20.2, 15.6 (d, PMe3, JCP = 28 Hz). Anal. Calcd for C63H50MoNO5C: P, 64.79; H, 5.52; N, 1.20. Found: C, 65.15; H, 5.74; N, 1.16.

**Mo(Nd)(CHCMe2Ph)(O2CCMePh)2(PMe3) (1c-PMe3).** The product was identical to that for preparing 1a starting from 0.348 g (0.440 mmol) of Mo(Nd)(CHCMe2Ph)(OTf)2(DME) and 0.278 g (0.869 mmol) of NaO2CCMePh2·THF. The product was isolated as 0.287 g (77%)
of yellow microcrystals: 1H NMR (CD2Cl2, 300 MHz) δ 13.96 (s, 1, Mo=CH2), 7.49–6.90 (m, 28, Ar), 3.73 (sept, 2, CHMe2), 2.04 (s, 6, O2CCMe2Ph), 1.51 (s, 6, CMe2Ph), 1.05 (d, 12, CHMe2); 13C NMR (75 MHz) δ 308.5 (Mo=Ca), JCH = 121 Hz), 193.9 (CO2), 153.0, 150.5, 149.4, 145.3, 145.1, 129.3, 129.0, 128.8, 127.4, 126.6, 126.5, 123.5, 58.6 (CCO2), 56.6 (CMe2Ph), 31.2, 29.5, 27.0, 23.9. Anal. Calc’d for C52H55NO4Mo: C, 73.14; H, 6.49; N, 1.64. Found: C, 73.14; H, 6.37; N, 1.58.

Mo(NAr)2(CHCMe2Ph)(O2C(SiMe3)2)2 (4). To a −25 °C solution of 0.190 g (0.24 mmol) of Mo(NAr)(CHCMe2Ph)(OTf)2(DME) in 4 mL of THF was added 0.155 g (0.49 mmol) of NaO2C(SiMe3)2 as a solid in one portion. The solution was allowed to warm to room temperature and stir for 40 min. All volatiles were removed in vacuo, and the residue was extracted into pentane. The extract was filtered through Celite and the solution volume reduced to ~1 mL in vacuo. Storage of the solution at room temperature afforded 0.170 g of the product (72%) as yellow crystals: 1H NMR (CD2Cl2, 300 MHz) δ 13.82 (s, 1, Mo=CH2), 7.36 (d, 2, Ar), 7.25 (t, 2, Ar), 7.09 (t, 1, Ar), 6.99 (br, 3, Ar), 3.98 (sept, 2, CHMe2), 1.61 (s, 6, CMe2Ph), 1.30 (d, 12, CHMe2), 0.39 (s, 54, SiMe3); 13C NMR (75 MHz) δ 304.0 (Mo=Ca), 211.4 (CO2), 153.3, 151.5, 149.2, 128.9, 128.7, 126.8, 126.4, 123.6, 56.7 (CMe2Ph), 31.9, 29.0, 24.6, 1.7 (SiMe3). Anal. Calc’d for C52H55NO4Mo: C, 75.24; H, 6.49; N, 1.64. Found: C, 75.24; H, 6.37; N, 1.58.

Attempts to Prepare 1e·PMe3. To a suspension of 0.209 g (0.232 mmol) of Mo(N(C6H5)2CH3)(CH-t-Bu)(O2CCPh2) in toluene was added 50 mL (0.49 mmol) of PMe3 via syringe. Upon addition of PMe3, the suspension immediately became homogeneous and took on a deep red color. The mixture was stirred for 30 min at room temperature. All volatiles were removed in vacuo, and the residue was treated with pentane to afford 0.179 g (79%) of an orange powder. Examination of the material by 1H NMR showed it to be a 1:5 mixture of 1e·PMe3 and what we propose is Mo(NArCl)(CHCMe2Ph)(O2CCPh2)(PMe3). Repeated crystallization from toluene/pentane resulted in the same mixture of products: 1H NMR (C6D6, 500 MHz) δ 5.0 Hz), 10.44 (br s, 1, NArCl); 13C NMR (75 MHz) 1H2), 32.2 (ring-C), 14.0 (O2CCPh2); minor additional resonances for the polymer backbone proton and carbon atoms can be detected in polymers containing all six-membered rings. We attribute these minor resonances to cis/trans isomerism at the exocyclic double bond.

Description of X-ray Studies. Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), performing q- and o-scans. All structures were solved by direct methods using SHELXS and refined against F2 on all data by full-matrix least-squares with SHELXL-97.20 All non-hydrogen atoms were refined anisotropically. Coordinates for the hydrogen atoms on C6 and the alkylidene groups were taken from the difference Fourier synthesis and subsequently refined semifreely with the help of distance restraints. All other hydrogen atoms were included in 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). A disordered isopropyl group in the structure of 5a, as well as disordered solvent molecules (pentane and dichloromethane) in the structure of 1d·PMe3, 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. One of the pentane molecules in the structure of 1d·PMe3 is disordered about the crystallographic inversion center, which leads to a noninteger value for C in the empirical formula, as the asymmetric unit contains only half a pentane molecule. For details of data and refinement statistics see Table 1.