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

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The carboxylate species $Mo(NR)(CHCMe_2R')(O_2CCPh_3)_2$ (R = various aryl groups or 1-adamantyl; R′ = Ph or Me) have been synthesized by salt metathesis between $Mo(NR)(CHCMe_2R')(OTf)_2(DME)$ (OTf = trifluoromethanesulfonate; DME = 1,2-dimethoxyethane) and sodium triphenylacetate. Other carboxylate compounds that have been prepared by this route include $Mo(NAr)(CHCMe_2Ph)(O_2CR'')_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$; R″ = CPh_2Me, $Si(SiMe_3)_3$) and $Na[Mo(NAd)(CHCMe_2Ph)(O_2CAr')_3]$ (Ar′ = 2,6-$Me_2C_6H_3$). Terphenylcarboxylate species $Mo(NR)(CHCMe_2Ph)(O_2CTer)_2$ (Ter = 2,6-diphenyl-4-methylphenyl or 2,6-diphenyl-4-methoxyphenyl) were prepared through protonolysis of $Mo(NR)(CHCMe_2R')(Me_2Pyr)_2$ with $TerCO_2H$, 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 $Mo(NAr'')(CH\text{-}t\text{-}Bu)(O_2CCPh_3)_2(PMe_3)$ (Ar″ = 2-*t*-BuC_6H_4) 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 polyenes,[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 tungstacyclobutane 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 $Mo(NR)(CHR')(pyrrolide)(OR'')$ species[7] through addition of R″OH to $Mo(NR)(CHR')(pyrrolide)_2$ species,[8] where the pyrrolide is the parent pyrrolide (NC_4H_4 = Pyr) or 2,5-dimethylpyrrolide ($NC_4Me_2H_2$ = Me_2Pyr). The $Mo(NR)(CHR')(pyrrolide)(OR'')$ 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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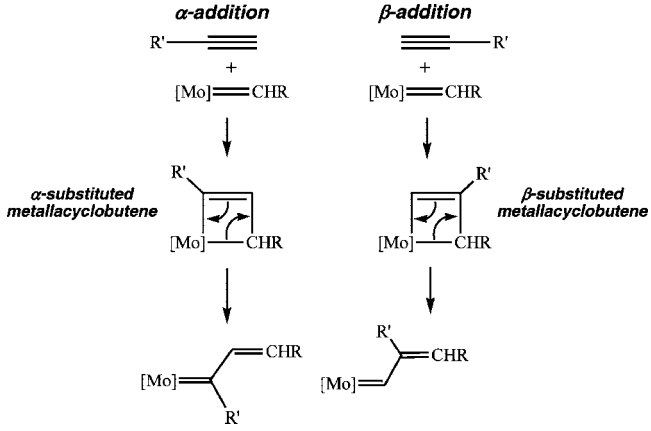
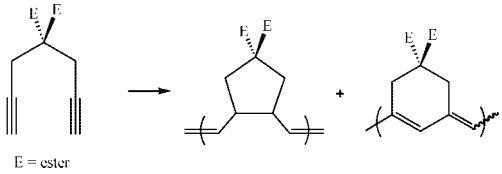
Scheme 1. α- and *β*-Addition Pathways in Terminal Alkyne Metathesis Polymerization



An important feature of polymerization reactions involving terminal alkynes is the (presumably irreversible) addition of the alkyne to place the alkyne substituent in either an α- or a *β*-position 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 α-addition) or six-membered rings (as a consequence of *β*-addition) as the repeat unit (eq 1). Several Mo[3e,9] and Ru[10] catalysts are known that are capable of producing polyenes that contain 95% five-membered rings,

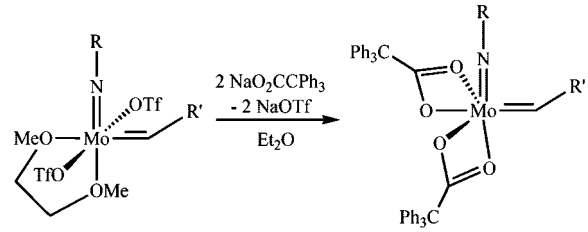


(1)

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 metathesis catalysts and 1,6-heptadiynes aimed at the synthesis of polymers that contain a high fraction of six-membered rings.

Results

Synthesis of Biscarboxylate Complexes. The sterically demanding triphenylacetate ligand was found to yield isolable biscarboxylate complexes. Carboxylate ligands smaller than triphenylacetate tended to give "ate" complexes (see below) or ill-defined (possibly oligomeric) species that could not be isolated. Complexes **1a**−**e** were prepared from bistriflate precursors through salt metathesis reactions with sodium triphenylacetate (eq 2; Ar = 2,6-*i*-$Pr_2C_6H_3$, Ar′ = 2,6-$Me_2C_6H_3$, Ad = 1-adamantyl, Ar″ = 2-*t*-BuC_6H_4, Ar^{Cl} = 2,6-$Cl_2C_6H_3$). All triphenylacetate complexes, with the exception of **1b**, are soluble in common organic solvents other than alkanes. Chemical shifts for alkylidene α-protons range from 13.76 to 13.91 ppm, while α-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.[1a] All alkylidenes exist as *syn* isomers in solution, as judged by J_{CH} values that range from 117 to 125 Hz (see Experimental Section).[12] The R groups in the imido ligands in **1a**, **1b**, and **1e** freely rotate on the NMR time scale about the N−C bond at room temperature.



(2)

1a: R = Ar, R' = CMe_2Ph
1b: R = Ar', R' = CMe_2Ph
1c: R = Ad, R' = CMe_2Ph
1d: R = Ar'', R' = *t*-Bu
1e: R = Ar^{Cl}, R' = *t*-Bu

A single-crystal X-ray study of **1d** revealed it to be a distorted six-coordinate 18-electron species in which both carboxylates are bound κ^2.[11] However, both are bound somewhat asymmetrically, with 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 Mo−O bonds are *trans* to the Mo=C (2.336 Å) or the Mo=N bond (2.261 Å). The carboxylates are technically inequivalent in this structure, although all biscarboxylate complexes show time-averaged C_s 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 κ^1 carboxylate.

Attempts to prepare several other carboxylate complexes did not lead to identifiable species. For example, numerous attempts to prepare pivalate (O_2C-*t*-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-di-*tert*-butylbenzoate and 2,6-dimethylbenzoate (O_2CAr') led to the formation of anionic "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 κ^1 in the "ate" complexes. Indeed, two carboxylates of one type (presumably κ^1) and one of another (presumably κ^2) 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 (Ph_2MeCCO_2) complex could be prepared when the 2,6-diisopropylphenyl imido ligand (**3**, eq

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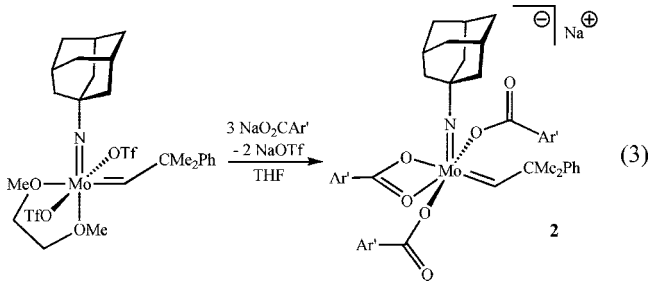
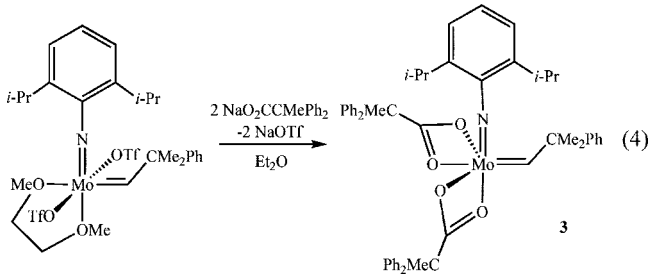


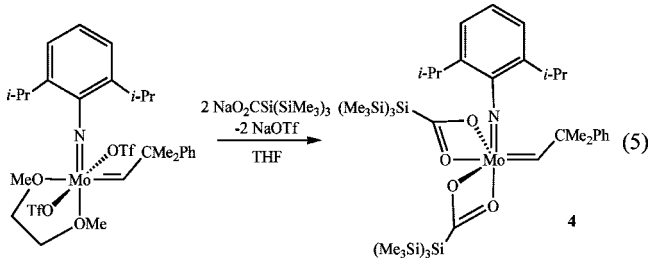
(3)

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)($O_2CCMePh_2$)$_2$ (Ar″ = 2-*t*-BuC_6H_4) yielded an insoluble yellow powder that did not dissolve readily in dichloromethane and that could not be identified.



(4)

A complex containing two $(TMS)_3SiCO_2^-$ 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 (^{1}H NMR) studies, but only **4** was isolated and fully characterized. The C_α and H_α chemical shifts in **4** were in the range typical of the other carboxylate compounds discussed above.



(5)

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, (O_2CTer_{Me}) and (O_2CTer_{OMe}), respectively. The chosen method of synthesis consisted of addition of 2 equiv of the acid to Mo(NR)($CHCMe_2Ph$)(Me_2Pyr)$_2$ (Me_2Pyr = 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 NaO_2CTer. However, the more complicated workup involves recrystallization of the compounds

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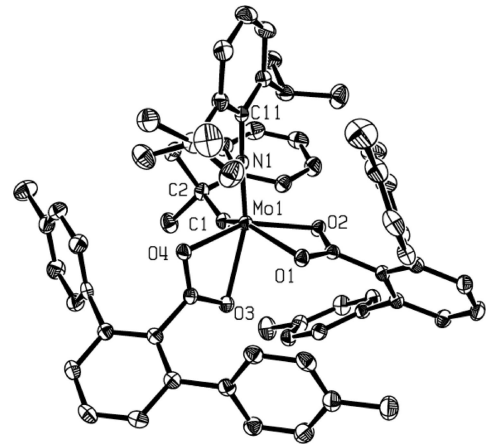
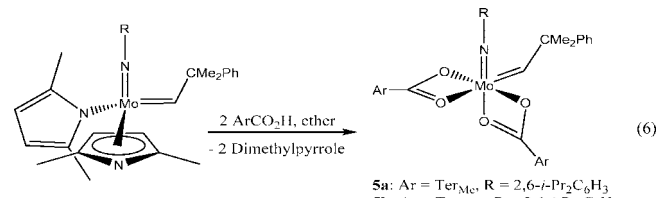


Figure 1. POV-ray (50% probability ellipsoids) of the solid-state structure of **5a**. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Mo(1)−N(1) = 1.7247(16), Mo(1)−C(1) = 1.902(2), Mo(1)−O(1) = 2.2867(16), Mo(1)−O(2) = 2.1160(14), Mo(1)−O(3) = 2.3186(16), Mo(1)−O(4) = 2.1252(14), Mo(1)−N(1)−C(11) = 174.15(13), Mo(1)−C(1)−C(2) = 145.18(14).

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)($CHCMe_2Ph$)(O_2CTer_{Me})$_2$ (**5a**) and Mo(NAr)($CHCMe_2Ph$)(O_2CTer_{OMe})$_2$ (**5b**) (eq 6), were isolated in yields between 50% and 60%. Similarly, bisbenzoate alkylidene complexes containing the adamantylimido group, Mo(NAd)($CHCMe_2Ph$)(O_2CTer_{Me})$_2$ (**5c**) and Mo(NAd)($CHCMe_2Ph$)(O_2CTer_{OMe})$_2$ (**5d**), were obtained in yields ranging between 40% and 70% (eq 6). The ^{1}H 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 δH_α, δC_α, 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.



(6)

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 κ^2,κ^2 fashion, similar to the biscarboxylate 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

Table 1. Crystal Data and Structure Refinement Details for 1d·PMe$_3$ and 5a[a]

	5a	1d·PMe$_3$[b]
empirical formula	$C_{64}H_{63}MoNO_4$	$C_{66.50}H_{82}Cl_2MoNO_4P$
fw	1006.09	1157.14
cryst size	0.25 × 0.20 × 0.10 mm^3	0.25 × 0.24 × 0.20 mm^3
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimens	a = 12.194(6) Å	a = 12.7389(3) Å
	b = 12.241(6) Å	b = 14.0067(4) Å
	c = 20.290(11) Å	c = 17.7003(4) Å
	α = 88.751(9)^o	α = 81.6190(10)°
	β = 76.586(9)^o	β = 77.5020(10)°
	γ = 66.079(9)^o	γ = 88.9480(10)°
volume	2684(2) Å^3	3050.21(13) Å^3
Z	2	2
density (calcd)	1.245 Mg/m^3	1.260 g/cm^3
absorp coeff	0.292 mm^{-1}	0.376 mm^{-1}
F(000)	1056	1222
θ range	1.04° to 28.28°	1.64° to 29.57°
index ranges	$-16 \le h \le 15$, $-16 \le k \le 16$, $-27 \le l \le 26$	$-17 \le h \le 17$, $-19 \le k \le 19$, $-24 \le l \le 24$
no. of reflns collected	48 967	68 763
no. of indep reflns	13 298 [R(int) = 0.0371]	17 080 [R(int) = 0.0259]
completeness to θ = 29.57°	99.8%	99.7%
max. and min. transmn	0.9713 and 0.9305	0.9286 and 0.9119
no. of data/restraints/params	13 298/100/665	17 080/299/717
goodness-of-fit on F^2	1.027	1.039
final R indices [$I > 2\sigma(I)$]	R1 = 0.0342, wR2 = 0.0804	R1 = 0.0390, wR2 = 0.1040
R indices (all data)	R1 = 0.0441, wR2 = 0.0860	R1 = 0.0434, wR2 = 0.1074
largest diff peak and hole	0.939 and −0.633 e·Å^{-3}	2.425 and −1.172 e·Å^{-3}

[a] 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 F^2. [b] The solid-state structure of **1d·PMe$_3$** contains one molecule of CH_2Cl_2 and 1.5 molecules of pentane (disordered) per molecule of **1d·PMe$_3$**.

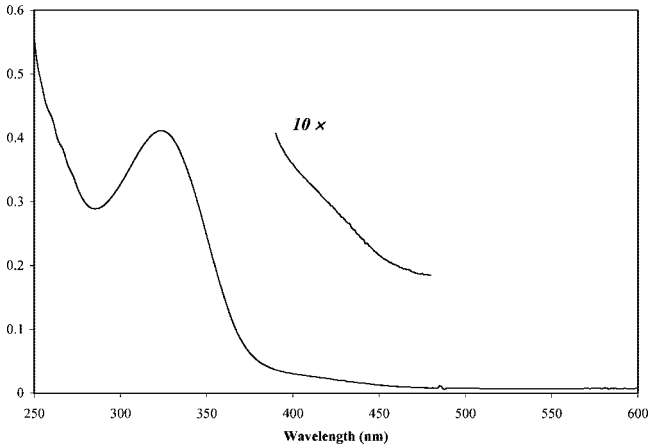
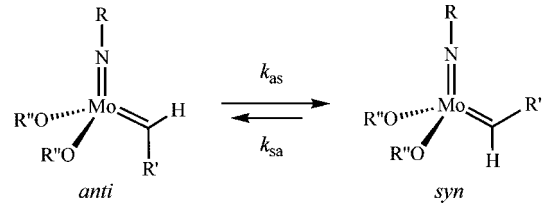


Figure 2. Electronic absorption spectrum of Mo(NAr)(CHCMe$_2$Ph)(O$_2$CCPh$_3$)$_2$ (**1a**) at 23 °C in methylene chloride (33.9 μM).

in solution on the NMR time scale. The monomeric sructure of **5a** contrasts with the dimeric structure of [Mo(NAr)(CHCMe$_2$Ph)(CF$_3$CO$_2$)(μ-CF$_3$CO$_2$)(ether)]$_2$, 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 ($\varepsilon \approx$ 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, CMe$_2$(CF$_3$), or CMe(CF$_3$)$_2$.[15] This absorption is ascribed to the M−N$_{imido}$ $\pi \rightarrow \pi^*$ transition, in part because a photostationary 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* alkylidene isomers in bisalkoxide complexes vary by several orders of magnitude, with the slowest rates being found for alkylidene complexes that contain relatively electron-withdrawing alkoxides such as OCMe(CF$_3$)$_2$. Interconversion of *syn* and *anti* isomers appears to be most facile in a 14*e* species. For example, the base (e.g., PMe$_3$) in a 16*e* adduct of Mo(NAr)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$ must be lost



(7)

before *syn* and *anti* isomers can interconvert. A coordinating solvent such as THF will also hinder alkylidene 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.

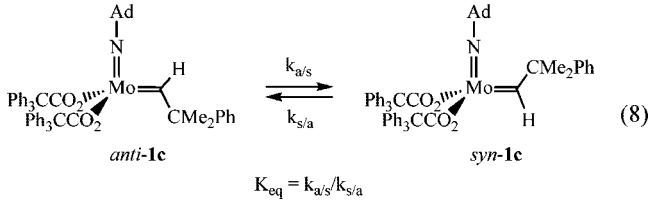
Photolysis of a sample of **1a** in toluene-d_8 at 366 nm for 3 h at 22 °C yielded a mixture containing 16% of a new species in which δH_α = 13.93 ppm and J_{CH} = 138 Hz, characteristic of an *anti* isomer. At 22 °C the *anti* isomer was found to convert to the *syn* isomer in a first-order manner with $k_{a/s} = 1.5 \times 10^{-6}$ s^{-1} ($t_{1/2}$ = 5.4 days). A sample of **1c** irradiated in toluene-d_8 at 366 nm for 2 h at 22 °C produced a mixture containing 28% of an *anti* species (δH_α = 13.99 ppm, J_{CH} = 140 Hz) that reverted back to the *syn* isomer at 22 °C with $k_{a/s} = 3.0 \times 10^{-4}$ s^{-1} ($t_{1/2}$

(14) Buchmeiser, M. R.; Wang, D.; Naumov, S.; Wurst, K. *J. Organomet. Chem.* **2006**, *691*, 5391.

(15) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.

(16) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 7588.

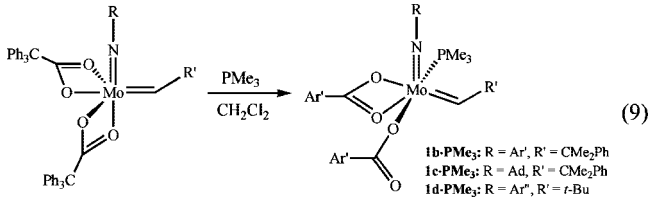
= 39 min). Finally, a sample of **1d** irradiated in toluene-d_8 at 366 nm for 2 h at 22 °C produced a mixture containing 17% of an *anti* species ($\delta H_\alpha = 13.90$ ppm, $J_{CH} = 137$ Hz) that reverted to the *syn* isomer at 0 °C with $k_{a/s} = 1.6 \times 10^{-5}$ s^{-1}. At room temperature conversion was too fast to measure accurately ($t_{1/2} \approx 3$ min). Therefore at room temperature the relative rates of conversion of *anti* to *syn* isomers are **1d** > **1c** > **1a** with $t_{1/2}$ ranging from ~5 days (for **1d**) to ~3 min (for **1c**).



(8)

Syn/anti isomerization reactions of bisbenzoate complexes were studied briefly for **5a** and **5c**. A sample of **5a** in toluene-d_8 was photolyzed at 22 °C with 366 nm light for 2 h. The resulting mixture contained 7% of the *anti* species ($\delta H_\alpha = 13.6$ ppm, $J_{CH} = 137$ Hz) and 93% of the *syn* species ($\delta H_\alpha = 13.4$ ppm, $J_{CH} = 126$ Hz). The rate constant for the *anti* to *syn* conversion of **5a** at 22 °C in toluene-d_8 was found to be 5×10^{-4} s^{-1}. Photolysis of a solution of **5c** in toluene-d_8 at room temperature for 2 h yielded a mixture of 9% *anti* ($\delta H_\alpha = 13.9$ ppm, $J_{CH} = 140$ Hz) and 91% *syn* ($\delta H_\alpha = 13.2$ ppm, $J_{CH} = 124$ 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).

Trimethylphosphine Adducts of Triphenylacetate 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.[12] Although the 18-electron biscarboxylates are unlikely to bind a Lewis base if the κ^2,κ^2 configuration is maintained, compounds **1b**−**d** do react readily with PMe_3 to give monoadducts (**1b·PMe$_3$**, **1c·PMe$_3$**, and**1d·PMe$_3$**, eq 9). Compound **1a** does not bind PMe_3 strongly enough to isolate the adduct, presumably because of the greater steric demands of the 2,6-diisopropylphenyl imido ligand.

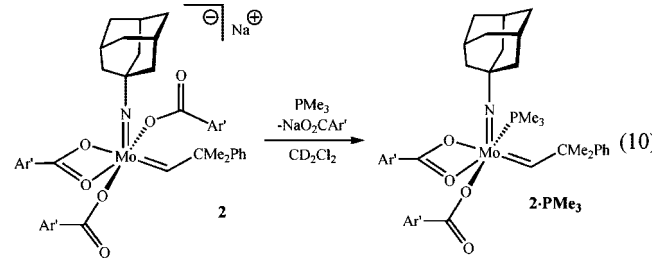


(9)

The phosphine adducts can be crystallized from methylene chloride upon addition of pentane. The alkylidene protons in **1b·PMe$_3$**−**1d·PMe$_3$** are coupled to phosphorus by 5−6 Hz, which is consistent with the phosphine not dissociating rapidly on the NMR time scale. Coupling constants of 5−6 Hz are analogous to those found in various phosphine adducts of imido alkylidene bisalkoxide complexes.[12] NMR spectra of **1c·PMe$_3$** and **1d·PMe$_3$** reveal that the carboxylates are inequivalent, consistent with one being κ^2 and the other being κ^1, as depicted in eq 9, and shown to be the case in the solid-state structure of **1d·PMe$_3$**. **1b·PMe$_3$** apparently has equivalent carboxylate ligands on the NMR time scale. The methyl groups of the neophylidene ligand are inequivalent in **1b·PMe$_3$**, which suggests that the carboxylates must equilibrate without generating a mirror plane that passes through the β-carbon of the alkylidene ligand.

Proton NMR spectra of freshly crystallized **1b·PMe$_3$**, **1c·PMe$_3$**, and **1d·PMe$_3$** show only the *syn* isomer. However, over a period of several days *anti* isomers appear. For example, when a solution of freshly prepared *syn*-**1d·PMe$_3$** was kept at −35 °C for a period of 2 days and the crystals were collected, NMR spectroscopy in C_6D_6 showed them to be a mixture of 41% of the *anti* isomer ($\delta H_\alpha = 13.8$ ppm, $J_{CH} = 135$ Hz) and 59% of the *syn* isomer ($\delta H_\alpha = 13.1$ ppm, $J_{CH} = 116$ Hz). After this solution was left at room temperature for 5 days, the mixture consisted of 64% of the *anti* species and 36% of the *syn* species. No further change was observed after 3 weeks; therefore the two appear to be at equilibrium at this point. This general behavior is analogous to that of Mo(NAr)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$), 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(NAr)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$.[12]

Compound **1e** reacts with PMe_3 to give a mixture of the desired adduct, **1e·PMe$_3$** (<20%; δH_α at 13.47 ppm in C_6D_6), and a side product that could not be separated from **1e·PMe$_3$** through recrystallization. The side product contained a broad resonance at 10.44 characteristic of a N*H*Ar^{Cl} proton. Therefore the side product is believed to be Mo(NHArCl)(C-*t*-Bu)(Ph$_3$CO$_2$)$_2$(PMe$_3$); full characterization was not pursued. Formation of an amido alkylidyne tautomer has been observed before in 2,6-dichlorophenylimido alkylidene complexes.[17] Addition of PMe_3 to **2** in CD_2Cl_2 yielded a precipitate of Na(O$_2$CCMePh$_2$) and **2·PMe$_3$** after several minutes, according to ^{1}H NMR experiments (eq 10). The ^{1}H NMR spectrum of **2·PMe$_3$** displayed a doublet alkylidene resonance ($J_{HP} = 6.0$ Hz) and two singlet resonances of area six (each) for the methyl groups



(10)

of the benzoate ligands, consistent with binding of a single PMe_3 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 14*e* four-coordinate species.[3b]

Crystals of **1d·PMe$_3$** were grown from a saturated solution of **1d·PMe$_3$** 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* alkylidene 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 alkylidene 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,

(17) Schrock, R. R.; Jamieson, J. Y.; Araujo, J. P.; Bonitatebus, P. J. J.; Sinha, A.; Lopez, L. P. H. *J. Organomet. Chem.* **2003**, *684*, 56.

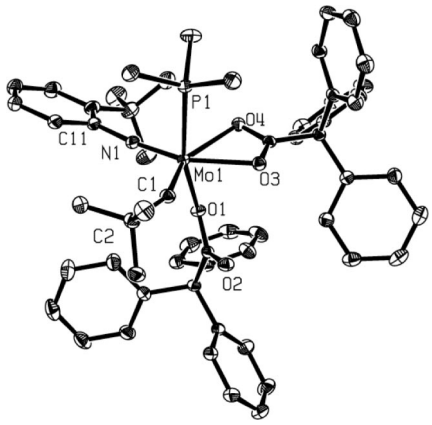


Figure 3. POV-ray (50% probability ellipsoids) of the solid-state structure of **1d·PMe$_3$**. Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Mo(1)−C(1) = 1.9107(18), Mo(1)−N(1) = 1.7402(15), Mo(1)−O(1) = 2.0822(13), Mo(1)−O(3) = 2.2597(13), Mo(1)−O(4) = 2.2873(13), Mo(1)−P(1) = 2.4967(5), N(1)−Mo(1)−C(1) = 106.04(8), P(1)−Mo(1)−O(1) = 164.68(4), O(3)−Mo(1)−O(4) = 57.27(5), Mo(1)−C(1)−C(2) = 152.65(15), Mo(1)−N(1)−C(11) = 173.51(13), O(1)−C(21)−O(2) = 124.63(16), O(3)−C(41)−O(4) = 118.94(16), Mo(1)−O(1)−C(21) = 124.19(11).

which is typical of sterically crowded *syn* alkylidene complexes, even though the 2-*tert*-butylphenyl group in the imido ligand is turned so that the *tert*-butyl group points away from the substituent in the *syn* alkylidene. The monodentate carboxylate ligand has a relatively short Mo(1)−O(1) bond length (2.0822(13) Å) compared to the Mo−O bond lengths in the bidentate ligand (Mo(1)−O(3) = 2.2597(13) Å, Mo(1)−O(4) = 2.2873(13) Å), as one might expect. Overall the structure is reminiscent of the structure of a typical adduct of a bisalkoxide species such as Mo(NAr)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$).[12] One can imagine that if a terminal alkyne were to bind to the metal in the same position as the trimethylphosphine, the steric influence of the *tert*-butyl group in the imido substituent combined with that of the bidentate triphenylacetate ligand could direct the terminal alkyne substituent (if large enough) to point in a direction that would yield the β-substituted metallacyclobutene intermediate (Scheme 1).

Cyclopolymerization of 1,6-Heptadiynes. None of the species reported here react readily with olefins, even ethylene or norbornene. However, several are competent, if slow, catalysts for the cyclopolymerization of diethyl dipropargylmalonate (DEDPM). Compound **1a** is an impractically slow initiator, presumably because of the steric demands of the diisopropylphenylimido ligand. Data for polymerization of DEDPM by **1c** and **1d** are listed in Table 2. Catalysts **1c** and **1d** produce polymers that contain >98% six-membered rings, according to ^{13}C NMR spectra, which reveal resonances for quaternary carbons in five-membered rings at 57−58 ppm and in six-membered rings at 54−55 ppm.[3d] ^{13}C NMR spectra are much more convenient to obtain, even in the absence of any relaxation agent such as Cr(acac)$_3$, when the quaternary carbon is ^{13}C-labeled. Typical spectra of polymers that contain only six-membered rings are shown in Figure 4. Compounds **1b** and **1e** are also initiators for the cyclopolymerization of DEDPM, but do not show any advantages over initiators **1c** and **1d**. Polymers prepared with initiators **1b** and **1e** contained only ~90% six-membered rings, according to ^{13}C NMR studies. All polymers prepared with initiators **1b**−**e** that contain up to 125 equiv of DEDPM are soluble in toluene, dichloromethane, and THF, but sparingly soluble in pentane and diethyl ether.

Table 2. Selected Polymerization Data for Poly-DEDPM Prepared with 1c an 1d in Toluene

catalyst	DEDPM equivalents	M_n theory	M_n calcd[†]	PDI (M_w/M_n)	yield (%)
1c	20	4948	43 060	1.63	91
1c	45	10 856	58 000	2.09	92
1c	65	15 582	103 900	1.62	91
1c	90	21 489	109 600	1.74	82
1c	125	29 760	122 700	1.80	75
1d	20	4948	13 590	1.26	91
1d	40	9673	40 280	1.13	92
1d	60	14 398	45 690	1.13	91
1d	80	19 124	72 440	1.15	89
1d	120	28 574	99 470	1.15	92

[†] Determined by GPC online viscometry versus polystyrene.

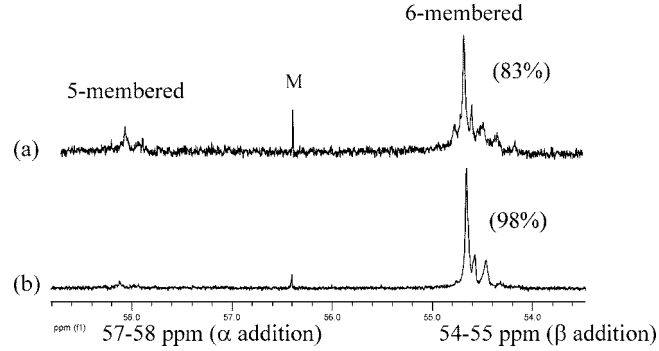
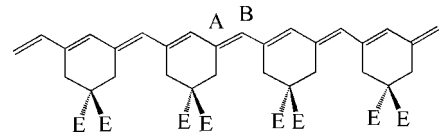


Figure 4. ^{13}C NMR spectra of polymers prepared from (quaternary ^{13}C-labeled) DEDPM (M) using initiators **5c** (a) and **1c** (b).

Polymers that contain exclusively five-membered rings[9c] are relatively insoluble in THF, but soluble in relatively polar solvents such as CH_2Cl_2, $CHCl_3$, and 1,2-dichloroethane. Unlike polymers that contain all five-membered rings, those that contain all six-membered rings do not appear to be a single structure, since *E*/*Z* isomers in the exocyclic double bond (A/B in the partial chain drawn below) are possible. We propose that *E*/*Z* isomerism is the source of the fine structure on the resonances between 54 and 55 ppm in Figure 4b.



Poly(DEDPM) prepared with **1c** showed molecular weight values (determined by GPC viscometry versus polystyrene) greater than expected based on the number of equivalents of monomer added (Table 2). Polydispersity values for polymers prepared with **1c** were found to range between 1.6 and 2.1. We ascribe the high molecular weight values to poor initiation relative to propagation since a calculation[18] of the ratio of the rate constant of propagation (k_p) to the rate constant of initiation (k_i) gave a value of 210 for **1c** in methylene chloride-d_2. In contrast, poly(DEDPM) prepared with **1d** had both molecular weights and polydispersities characteristic of a polymerization with a relatively low value for k_p/k_i (Table 3), and a calculation[18] produced a value for $k_p/k_i = 9$. We have shown that initiators can be prepared that lead to low values of k_p/k_i (even <1) and therefore low polydispersities for polydialkyldipropargylma-

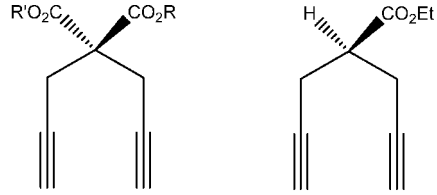
(18) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.

Table 3. Relative Five- And Six-Membered Ring Content in Polymers Prepared in Toluene Employing 1d as the Initiator

sample	five-membered rings	six-membered rings
poly(DMDPM)[a]	9.0	91.0
poly(DEDPM)[a]	1.7	98.3
poly(BEDPM)[a]	2.8	97.2
poly(DBDPM)[a]	3.8	96.2
poly(EDPA)[b]	31	69

[a] Determined through integration of the carbonyl region (165−172 ppm) and the quaternary carbon region (40−60 ppm) of the 125 MHz ^{13}C NMR spectrum at 25 °C in $CDCl_3$. [b] 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



R = Me, R' = Me; DMDPM
R = Et, R' = *t*-Bu; BEDPM
R = *t*-Bu, R' = *t*-Bu; DBDPM

EDPA

lonates that contain all five-membered rings.[9c] More rapid propagation relative to initiation appears to result from the relatively "flat" nature of a vinyl-substituted alkylidene in a propagating species (relative to a neopentylidene or neophylidene initiator), regardless of whether a five- or a six-membered ring is formed. Attempts to prepare biscarboxylate derivatives of bishexafluoro-*tert*-butoxide complexes containing alkylidene ligands that resemble the growing polymer chain failed, even though we have shown that di-*tert*-butoxide analogues can be prepared from bishexafluoro-*tert*-butoxide complexes in this manner.[9c]

DEDPM could be cyclopolymerized with initiators **5a**−**5d**, although more slowly than with initiators of type **1**. Polymerization of 10 equiv of ^{13}DEDPM (in which the quaternary carbon is ^{13}C-labeled) per equivalent of **5a** or **5b** produced polymer (∼80%) only after ∼1 week at room temperature. The amount of β product was ∼70% overall when either **5a** or **5b** was employed. Similarly, when 20 equiv of ^{13}DEDPM was added to **5c** or **5d**, the reactions were still slower than with initiators of type **1**. For example, after 74 h 86% of the starting material was consumed when **5c** was employed (83% β product) and 60% 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 **1d** (Scheme 2). The three malonates are polymerized in toluene by **1d** in good isolated yield (>90%). The relative ring content (five versus six) was determined by ^{13}C 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 dimethyldipropargylmalonate. 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.[3j] For poly(EDPA) the carbonyl carbon was found to be a better choice for determining ring content.

Conclusions

The ability to prepare and isolate stable, well-defined, carboxylate complexes depends critically on the steric bulk of the carboxylate. Carboxylates that possess smaller substituents result in "ate" complexes or formation of ill-defined oligomeric species. Binding of the carboxylates in a κ^2 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 (κ^1, κ^1 or κ^1, κ^2) intermediate.

The utility of the carboxylate 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,β-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 metallacyclobutene intermediates seems to hold more promise.[3e,9b] 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-d_6 was dried over sodium/benzophenone ketyl and vacuum-distilled. Methylene chloride-d_2 was dried over CaH_2, vacuum distilled, and stored over 4 Å Linde-type molecular sieves. Chloroform-d_1 was 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 ^{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; $CDCl_3$, δ 7.26; ^{13}C: C_6D_6, δ 128.39; CD_2Cl_2, δ 54.00; $CDCl_3$, δ 77.36) and are reported as parts per million relative to tetramethylsilane. ^{31}P NMR spectra were referenced externally to 85% H_3PO_4 (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 1.03×10^6 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(NR)(CHCMe$_2$Ph)(OTf)$_2$(DME) species, where R = 2,6-*i*-Pr$_2$C$_6$H$_3$ (Ar), 2,6-Me$_2$C$_6$H$_3$ (Ar′), 1-adamantyl (Ad), 2-*t*-BuC$_6$H$_4$ (Ar″), and 2,6-Cl$_2$C$_6$H$_3$ (Ar^{Cl}), were prepared according to published

procedures.[19] Syntheses of Mo(NAr)(CHCMe$_2$Ph)(O$_2$CCPh$_3$)$_2$, Mo(NAr)(CHCMe$_2$Ph)(O$_2$CCMePh$_2$)$_2$, Mo(NAr″)(CH-*t*-Bu)(O$_2$CCPh$_3$)$_2$, and Mo(NAd)(CHCMe$_2$Ph)(O$_2$CCPh$_3$)$_2$ have been reported in a preliminary fashion[11] and are repeated below for convenience. Ter$_{Me}$CO$_2$H and Ter$_{OMe}$CO$_2$H were prepared as described in the literature.[13] All carboxylate salts were prepared by addition of NaH to a THF solution of the corresponding acid (Aldrich) followed by crystallization from THF/pentane. PMe$_3$ was purchased from Strem Chemicals and used as received. All other reagents were purchased from commercial vendors and used as received.

Mo(NAr)(CHCMe$_2$Ph)(O$_2$CCPh$_3$)$_2$ (1a). To a suspension of 0.369 g (0.466 mmol) of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) in 25 mL of diethyl ether at −25 °C was added 0.350 g (0.915 mmol) of NaO$_2$CCPh$_3$·THF as a solid in one portion. 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 set aside at −25 °C for 24 h to yield yellow microcrystals (0.425 g, 88%): ^{1}H NMR (C$_6$D$_6$, 300 MHz) δ 13.91 (s, 1, MoC*H*α), 7.49−6.89 (m, 38, Ar), 3.78 (sept, 2, C*H*Me$_2$), 1.50 (s, 6, C*Me*$_2$Ph), 1.03 (d, 12, CH*Me*$_2$); ^{13}C NMR (75 MHz) δ 308.9 (Mo*C*α, J_{CH} = 122 Hz), 192.5 (*C*O$_2$), 153.1, 150.4, 149.6, 143.5, 131.5, 129.1, 128.8, 128.4, 127.6, 126.7, 126.5, 123.6, 69.7 (*C*CO$_2$), 56.8 (*C*Me$_2$Ph), 31.2, 29.4, 24.0. Anal. Calcd for C$_{62}$H$_{59}$NO$_4$Mo: C, 76.14; H, 6.08; N, 1.43. Found: C, 76.22; H, 6.15; N, 1.37.

In a sample irradiated in toluene-d_8 at 366 nm for 3 h at 22 °C a mixture containing 16% *anti* was formed (δH$_\alpha$ = 13.93 ppm, J_{CH} = 138.4 Hz). At 22 °C conversion of *anti* to *syn* was found to take place in a first-order manner with $k_{a/s} = 1.5 \times 10^{-6}$ s^{-1}.

Mo(NAr′)(CHCMe$_2$Ph)(O$_2$CCPh$_3$)$_2$ (1b). To a −25 °C suspension of 0.525 g (0.714 mmol) of Mo(NAr′)(CHCMe$_2$Ph)(OTf)$_2$(DME) in 40 mL of diethyl ether was added 0.560 g (1.47 mmol) of NaO$_2$CCPh$_3$·THF as a solid in one portion. The mixture was allowed to warm to room temperature and stir for 1 h. During this time, the mixture changed from yellow to orange and became homogeneous. The volatiles were removed *in vacuo*, and the residue was extracted into 60 mL of methylene chloride. The extract was filtered through Celite and the solution volume reduced *in vacuo* to ∼10 mL. Several volumes of pentane were added, resulting in precipitation of a yellow solid. The solid was collected by filtration and dried *in vacuo* to give 0.460 g (70%) of a yellow powder. Analytically pure material could be obtained by recrystallization from hot methylene chloride. Due to the insolubility of the complex in common solvents, a satisfactory ^{13}C NMR spectrum could not be obtained: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) δ 13.83 (br s, MoC*H*α), 7.29−6.96 (m, 38, Ar), 2.16 (s, 6, N-2,6-*Me*$_2$C$_6$H$_3$), 1.50 (s, 6, C*Me*$_2$Ph). Anal. Calcd for C$_{58}$H$_{51}$MoNO$_4$: C, 75.56; H, 5.58; N, 1.52. Found: C, 75.38; H, 5.65; N, 1.46.

Mo(NAd)(CHCMe$_2$Ph)(O$_2$CCPh$_3$)$_2$ (1c). Portions of NaO$_2$CCPh$_3$·THF (0.446 g, 1.44 mmol) were added as a solid over a period of 10 min to a −25 °C solution of 0.500 g (0.635 mmol) of Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$(DME) in 30 mL of diethyl ether. The solution darkened with each addition of the carboxylate salt. Once addition was complete, the reaction was allowed to stir at room temperature for 60 min. All volatiles were removed *in vacuo*, and the residue was extracted into methylene chloride. The extract was filtered through Celite, and the volatiles were removed *in vacuo*. The crude residue was treated with toluene and pentane to afford 0.451 g (72%) of the compound as an off-white powder. The material was purified by recrystallization from methylene chloride/pentane: ^{1}H NMR (C$_6$D$_6$, 300 MHz) δ 13.89 (s, 1, MoC*H*α), 7.51−7.47 (m, 12, Ar), 7.25 (dd, 2, Ar), 7.13−7.00 (m, 21, Ar), 1.86 (d, 6, Ad-C*H*$_2$), 1.71 (br, 3, Ad-C*H*), 1.59 (s, 6, C*Me*$_2$Ph), 1.29 (t, 6, Ad-C*H*$_2$); ^{13}C NMR (75 MHz) δ 305.5 (Mo*C*α, J_{CH} = 117 Hz), 191.7 (*C*O$_2$), 150.8, 143.5, 141.4, 131.1, 127.1, 126.0, 75.4 (N*C*), 69.6 (*C*CO$_2$), 51.8, 43.5, 35.8, 31.6, 29.5. Anal. Calcd for C$_{60}$H$_{57}$NMoO$_4$: C, 75.69; H, 6.03; N, 1.47. Found: C, 75.92; H, 6.28; N, 1.35.

A sample of **1c** irradiated in toluene-d_8 at 366 nm for 2 h at 22 °C produced a mixture containing 28% *anti* (δH$_\alpha$ = 13.99 ppm, J_{CH} = 140.0 Hz). At 22 °C conversion of *anti* to *syn* was found to take place in a first-order manner with $k_{a/s} = 3.0 \times 10^{-4}$ s^{-1}.

Mo(NAr′)(CH-*t*-Bu)(O$_2$CCPh$_3$)$_2$ (1d). To a −25 °C solution of Mo(NAr′)(CH-*t*-Bu)(OTf)$_2$(DME) (0.719 g, 1.03 mmol) in 25 mL of diethyl ether was added 0.827 g (2.16 mmol) of NaO$_2$CCPh$_3$·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 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%): ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) δ 13.76 (s, 1, J_{CH} = 120.5 Hz, MoC*H*α), 7.58 (m, 1, Ar), 7.35−7.17 (m, 33, Ar), 1.33 (s, 9, *t*-Bu), 1.17 (s, 9, *t*-Bu); ^{13}C NMR (75 MHz) δ 313.4 (Mo*C*α, J_{CH} = 123 Hz), 191.9 (*C*O$_2$), 154.6, 145.6, 143.0, 135.6, 131.0, 128.5, 128.2, 127.5, 127.1, 126.4, 69.4 (*C*CO$_2$), 50.9, 36.0, 31.5, 30.7. Anal. Calcd for C$_{55}$H$_{53}$MoNO$_4$: C, 74.40; H, 6.02; N, 1.58. Found: C, 74.67; H, 5.86; N, 1.36.

A sample of **1d** irradiated in toluene-d_8 at 366 nm for 2 h at 22 °C produced a mixture containing 17% *anti* (δH$_\alpha$ = 13.90 ppm, J_{CH} = 136.9 Hz). At 0 °C conversion of *anti* to *syn* was found to take place in a first-order manner with $k_{a/s} = 1.6 \times 10^{-5}$ s^{-1}; at room temperature conversion was too fast to measure accurately ($t_{1/2} \approx 3$ min).

Mo(NAr^{Cl})(CH-*t*-Bu)(O$_2$CCPh$_3$)$_2$ (1e). To a suspension of 0.740 g (1.04 mmol) of Mo(CH-*t*-Bu)(NAr^{Cl})(OTf)$_2$(DME) in 35 mL of diethyl ether was added 0.853 g (2.23 mmol) of NaO$_2$CCPh$_3$·(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. The 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: ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz) δ 13.81 (s, 1, MoC*H*α), 7.31−7.11 (m, 39, Ar), 1.16 (s, 9, *t*-Bu); ^{13}C NMR (125 MHz) δ 315.8 (Mo*C*α, J_{CH} = 121 Hz,), 192.1 (*C*O$_2$), 150.5, 142.8, 134.5, 131.0, 128.7, 128.7, 128.2, 127.6, 69.4 (*C*CO$_2$), 49.9, 30.8. Anal. Calcd for C$_{51}$H$_{43}$Cl$_2$MoNO$_4$: C, 68.00; H, 4.81; N, 1.56. Found: C, 67.68; H, 4.85; N, 1.48.

Mo(NAr)(CHCMe$_2$Ph)(O$_2$CTer$_{Me}$)$_2$ (5a). Mo(NAr)(CHR)(Me$_2$Pyr)$_2$ (0.295 g, 0.495mmol) was dissolved in a minimal amount of diethyl ether, and the solution was placed at −35 °C for 1 h. Ter$_{Me}$CO$_2$H (0.299 g, 0.989 mmol) was dissolved in a minimal amount of ether, and the solution was placed at −35 °C for 1 h. At the end of the cooling period, the solution containing the carboxylic acid was added to the other dropwise. The reaction was stirred at RT for 30 min. The volatiles were removed and the sample was triturated with pentane for 1 h until an orange powder precipitated. The powder was isolated by filtration. It was redissolved in diethyl ether and placed at −35 °C for 12 h to yield 0.279 g (56%) of pure orange product upon filtration: ^{1}H NMR (CD$_2$Cl$_2$) δ 13.13 (s, 1, MoC*H*CMe$_2$Ph, J_{CH} = 124.8 Hz), 7.60−6.80 (m, 30, aromatics), 3.17 (m, 2, C*H*Me$_2$), 2.19 (s, 12, R^{ptolyl} *Me*), 1.30 (s, 6,

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MoCHC*Me*$_2$Ph), 0.835 (d, 12, CH*Me*$_2$); ^{13}C NMR (CD_2Cl_2) δ 309 (Mo*C*HCMe$_2$Ph), 185 (*C*O$_2$), 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, 55.7, 31.3, 28.6, 23.4, 21.2. Anal. Calcd for $C_{65}H_{65}MoNO_4$: 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-d_8 at 366 nm for 2 h at 22 °C produced a mixture containing 7% of the *anti* species (δH_α = 13.6 ppm, J_{CH} = 137 Hz). At 22 °C the rate constant for the conversion from *anti* to *syn* isomers was found to be 5×10^{-4} s^{-1}.

Mo(NAr)(CHCMe$_2$Ph)(O$_2$CTer$_{OMe}$)$_2$ (5b). 5b was prepared as for **5a** from Mo(NAr)(CHR)(Me$_2$Pyr)$_2$ (0.250 g, 0.420 mmol) and Ter$_{OMe}$CO$_2$H (0.281 g (0.839 mmol). The volatiles were removed from the reaction mixture, and the sample was triturated with pentane for 1 h until an orange powder was obtained. The powder was isolated by filtration and recrystallized from ether at −35 °C to yield 0.248 g (55%) of pure product: ^{1}H NMR (CD_2Cl_2) δ 13.14 (s, 1, MoC*H*CMe$_2$Ph, J_{CH} = 123.28 Hz), 7.8−6.4 (m, 30, aromatics), 3.59 (s, 12, TerO*Me*), 3.24 (m, 2, C*H*Me$_2$Ph), 1.29 (s, 6, MoCHC*Me*$_2$), 0.85 (d, 12, CH*Me*$_2$); ^{13}C NMR (CD_2Cl_2) δ 307.0 (Mo*C*HCMe$_2$Ph), 185.3 (*C*O$_2$), 159.1, 142.7, 133.7, 130.3, 129.8, 128.3, 126.1, 122.9, 114.4, 113.6, 105.8, 55.2, 28.6, 23.4, 14.1, 12.8. Anal. Calcd for $C_{65}H_{65}MoNO_8$: C, 71.83; H, 5.93; N, 1.31. Found: C, 71.80; H, 5.86; N, 1.33.

Mo(NAd)(CHCMe$_2$Ph)(O$_2$CTer$_{Me}$)$_2$ (5c). Prepared as for **5a** from Mo(NAd)(CHR)(Me$_2$Pyr)$_2$ (0.288 g. 0.509 mmol) and Ter$_{Me}$CO$_2$H (308 mg, 1.020 μmol). After complete addition of the carboxylic acid, the off-white product precipitated out and was collected by filtration, washed twice with diethyl ether, and dried *in vacuo*; yield 330 mg (66%): ^{1}H NMR ($CDCl_3$) δ 13.04 (s, 1, MoC*H*CMe$_2$Ph, J_{CH} = 123.88 Hz), 7.42 (t, 2, terphenyl), 7.33−7.14 (m, 17, aromatics), 6.90 (d, 8, terphenyl), 2.18 (s, 12, *p-tolylMe*), 1.93 (s br, 3, *CH* Ad), 1.64 (s br, 6, *CH* Ad), 1.49 (s, 6, *CH Ad*); ^{13}C NMR ($CDCl_3$) δ 307.3, 185.7 (*C*O$_2$), 150.7, 141.9, 138.4, 136.6, 132.9, 129.9, 129.3, 129.2, 128.9, 128.4, 126.6, 126.0, 51.4, 43.3, 35.9, 31.4, 29.5, 21.3. Anal. Calcd for $C_{62}H_{61}MoNO_4$: C, 75.98; H, 6.27; N, 1.43. Found: C, 75.88; H, 6.35; N, 1.41.

Mo(NAd)(CHCMe$_2$Ph)(O$_2$CTer$_{OMe}$)$_2$ (5d). Prepared as for **5a** from Mo(NAd)(CHR)(Me$_2$Pyr)$_2$ (0.250 g, 0.442mmol) and Ter$_{OMe}$CO$_2$H (0.296 g, 0.884mmol). The volatiles were removed, and the sample was triturated with pentane for a few minutes. The white powder was isolated and dried by vacuum filtration; yield 0.200 g (43%) product: ^{1}H NMR ($CDCl_3$) δ 13.09 (s, 1, MoC*H*CMe$_2$Ph, J_{CH} = 123.40 Hz), 7.46 (t, 2, terphenyl), 7.32−7.14 (m, 12, aromatics), 6.63 (d, 8, terphenyl), 3.58 (s, 12, TerO*Me*), 1.89 (s br, 3, *CH Ad*), 1.60 (s, 6, *CH Ad*), 1.49 (s, 6, *CH Ad*); ^{13}C NMR ($CDCl_3$) δ 306.4, 185.8 (*C*O$_2$), 159.0, 150.4, 141.6, 133.6, 132.8, 130.1, 129.9, 129.2, 128.5, 128.4, 126.6, 126.1, 55.2, 51.3, 43.5, 35.9, 31.3, 29.5. Anal. Calcd for $C_{62}H_{61}MoNO_8$: C, 71.32; H, 5.89; N, 1.34. Found: C, 71.31; H, 5.95; N, 1.36.

Mo(NAr′)(CHCMe$_2$Ph)(O$_2$CCPh$_3$)$_2$(PMe$_3$) (1b·PMe$_3$). Trimethylphosphine 25 μL (0.24 mmol) was added via microsyringe to a suspension of 0.159 g (0.173 mmol) of Mo(NAr′)(CHCMe$_2$Ph)(O$_2$CCPh$_3$)$_2$ 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 combusion analysis was consistent with the presence of two molecules of methylene chloride per Mo: ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 13.21 (d, 1, MoC*H*α, J_{HP} = 5.5 Hz), 7.44 (d, 1, *o*-CMe$_2$*Ph*), 7.32 (d, 12, *o*-C*Ph*$_3$), 7.24 (t, 2, *m*-CMe$_2$Ph), 7.10 (m, 19, *m*/*p*-C*Ph*$_3$ + *p*-CMe$_2$*Ph*), 6.93 (m, 3, Ar′), 2.34 (s, 6, Ar′-*Me*), 1.88 (s, 3, C*Me*$_2$Ph), 1.47 (s, 3, C*Me*$_2$Ph), 0.59 (d, 9, P*Me*$_3$); ^{13}C (125 MHz) δ 311.2 (d, Mo*C*α, J_{CH} = 118 Hz, J_{CP} = 19 Hz), 181.17 (br s, *C*O$_2$), 153.5 (d, J_{CP} = 3.1 Hz), 148.8 (d, J_{CP} = 2.3 Hz), 145.5, 137.7 (d, J_{CP} = 2.3 Hz), 131.4, 128.9, 128.3, 127.9, 127.6, 126.8, 126.7, 126.6, 69.8, 33.0, 29.4, 20.2, 15.6 (d, P*Me*$_3$, J_{CP} = 28 Hz). Anal. Calcd for $C_{63}H_{64}Cl_4MoNO_4P$: C, 64.79; H, 5.52; N, 1.20. Found: C, 65.15; H, 5.74; N, 1.16.

Mo(NAd)(CHCMe$_2$Ph)(O$_2$CCPh$_3$)$_2$(PMe$_3$) (1c·PMe$_3$). To a −25 °C suspension of 0.293 g (0.308 mmol) of Mo(NAd)(CHCMe$_2$Ph)(O$_2$CCPh$_3$)$_2$ in 15 mL of toluene was added 35 μL (0.34 mmol) of PMe$_3$. 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: ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 13.17 (d, 1, MoC*H*α, J_{HP} = 6.0 Hz), 7.45 (d, 2, Ar), 7.34 (m, 5, Ar), 7.25−7.00 (m, 28, Ar), 2.15 (s, 3, C*Me*$_2$Ph), 2.01 (m, 3, Ad*H*), 1.91 (m, 6, Ad*H*), 1.58 (m, 6, Ad*H*), 1.37 (s, 3, C*Me*$_2$Ph), 0.58 (d, 9, P*Me*$_3$); ^{13}C NMR (125 MHz) δ 310.7 (d, Mo*C*α, J_{CH} = 120 Hz, J_{CP} = 18.0 Hz), 186.1 (br, *C*O$_2$), 176.4 (br, *C*O$_2$), 148.7 (d, J_{CP} = 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 (N*C*), 70.5 (br, *C*CO$_2$), 69.0 (br, *C*CO$_2$), 51.1 (d, *C*Me$_2$Ph, J_{CP} = 3.1 Hz), 44.6, 36.2, 32.9 (d, J_{CP} = 3.0 Hz), 29.9, 29.6, 16.9 (d, P*Me*$_3$, J_{CP} = 28 Hz); ^{31}P NMR (121 MHz) δ 2.99. Anal. Calcd for $C_{63}H_{66}MoNO_4P$: C, 73.60; H, 6.47; N, 1.36. Found: C, 73.81; H, 6.58; N, 1.31.

Mo(N-2-*t*-BuC$_6$H$_4$)(CH-*t*-Bu)(O$_2$CCPh$_3$)$_2$(PMe$_3$) (1d·PMe$_3$). To a solution of 0.315 g (0.355 mmol) of Mo(NAr″)(CH-*t*-Bu)(O$_2$CCPh$_3$)$_2$ in 10 mL of methylene chloride was added 80 μL (0.80 mmol) of PMe$_3$ 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: ^{1}H NMR (C_6D_6, 300 MHz) δ 13.13 (d, 1, MoC*H*α, J_{HP} = 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*- or *o*-Ar″), 6.84 (m, 1, *m*- or *o*-Ar″), 1.38 (s, 9, *t*-Bu), 1.27 (s, 9, *t*-Bu), 0.63 (d, 9, P*Me*$_3$); ^{13}C NMR (75 MHz) δ 314.9 (d, Mo*C*α, J_{CH} = 118 Hz, J_{CP} = 19 Hz), 146.0, 132.2, 127.9, 126.7, 69.8, 49.7, 36.3, 32.7, 31.6, 16.2 (d, P*Me*$_3$). Anal. Calcd for $C_{59}H_{64}Cl_2MoNO_4P$: C, 67.56; H, 6.15; N, 1.34. Found: C, 67.83; H, 6.10; N, 1.15.

Na[Mo(NAd)(CHCMe$_2$Ph)(O$_2$CAr′)$_3$] (2). To a −25 °C solution of Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$(DME) (0.423 g, 0.553 mmol) in 30 mL of THF was added 0.456 g (1.87 mmol) of NaO$_2$CAr′·THF as a solid in one portion. The mixture was allowed to stir at room temperature for 90 min, during which time it remained homogeneous. 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 reduced to ~1 mL *in vacuo*. The concentrated solution was layered with several volumes of pentane and set aside at −25 °C overnight. The compound precipitated as an off-white crystalline solid (0.310 g, 66%): ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 13.98 (br s, 1, MoC*H*α), 7.32 (d, 2, Ar), 7.14 (m, 6, Ar), 6.91 (m, 6, Ar), 2.25 (s, 12, Ar′-*Me*), 2.09 (s, 6, Ar′-*Me*), 1.97 (br s, 9, Ad-C*H* + Ad-C*H*$_2$), 1.62 (s, 6, C*Me*$_2$Ph), 1.51 (s, 6, Ad-C*H*$_2$); ^{13}C NMR (125 MHz) δ 310.4 (br, Mo*C*α), 179.8 (*C*O$_2$), 177.0 (*C*O$_2$), 151.6, 139.5, 137.1, 136.3, 134.5, 129.1, 128.4, 128.3, 128.1, 127.3, 126.1, 73.3 (N*C*), 52.4, 43.1, 36.3, 31.7, 29.8, 21.6, 20.5. Anal. Calcd for $C_{47}H_{54}MoNNaO_6$: C, 66.58; H, 6.42; N, 1.65. Found: C, 66.41; H, 6.34; N, 1.53.

Mo(NAr)(CHCMe$_2$Ph)(O$_2$CCMePh$_2$)$_2$ (3). The procedure was identical to that for preparing **1a** starting from 0.348 g (0.440 mmol) of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) and 0.278 g (0.869 mmol) of NaO$_2$CCMePh$_2$·THF. The product was isolated as 0.287 g (77%)

of yellow microcrystals: ^{1}H NMR (C_6D_6, 300 MHz) δ 13.96 (s, 1, MoC*H*α), 7.49−6.90 (m, 28, Ar), 3.73 (sept, 2, C*H*Me$_2$), 2.04 (s, 6, O_2CC*Me*Ph$_2$), 1.51 (s, 6, C*Me*$_2$Ph), 1.05 (d, 12, CH*Me*$_2$); ^{13}C NMR (75 MHz) δ 308.5 (Mo*C*α, J_{CH} = 121 Hz), 193.9 (*C*O_2), 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 (*C*CO_2), 56.6 (*C*Me$_2$Ph), 31.2, 29.5, 27.0, 23.9. Anal. Calcd for $C_{52}H_{55}NO_4Mo$: C, 73.14; H, 6.49; N, 1.64. Found: C, 73.14; H, 6.37; N, 1.58.

Mo(NAr)(CHCMe$_2$Ph)[O$_2$CSi(SiMe$_3$)$_3$]$_2$ (4). To a −25 °C solution of 0.190 g (0.24 mmol) of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) in 4 mL of THF was added 0.155 g (0.49 mmol) of NaO$_2$CSi(SiMe$_3$)$_3$ 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: ^{1}H NMR (C_6D_6, 300 MHz) δ 13.82 (s, 1, MoC*H*α), 7.36 (d, 2, Ar), 7.25 (t, 2, Ar), 7.09 (t, 1, Ar), 6.99 (br, 3, Ar), 3.98 (sept, 2, C*H*Me$_2$), 1.61 (s, 6, C*Me*$_2$Ph), 1.30 (d, 12, CH*Me*$_2$), 0.39 (s, 54, Si*Me*$_3$); ^{13}C NMR (75 MHz) δ 304.0 (Mo*C*α), 211.4 (*C*O_2), 153.3, 151.5, 149.2, 128.9, 128.7, 126.8, 126.4, 123.6, 56.7 (*C*Me$_2$Ph), 31.9, 29.0, 24.6, 1.7 (Si*Me*$_3$). Anal. Calcd for $C_{42}H_{83}MoO_4Si_8$: C, 51.12; H, 8.48; N, 1.42. Found: C, 50.98; H, 8.69; N, 1.32.

Attempt to Prepare 1e·PMe$_3$. To a suspension of 0.209 g (0.232 mmol) of Mo(N-2,6-Cl$_2$C$_6$H$_3$)(CH-*t*-Bu)(O$_2$CCPh$_3$)$_2$ in toluene was added 50 mL (0.49 mmol) of PMe$_3$ via syringe. Upon addition of PMe$_3$, 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 ^{1}H NMR showed it to be a 1:5 mixture of **1e·PMe$_3$** and what we propose is Mo(NHArCl)(C-*t*-Bu)(Ph$_3$CO$_2$)$_2$(PMe$_3$). Repeated crystallization from toluene/pentane resulted in the same mixture of products: selected ^{1}H NMR data (C_6D_6, 500 MHz) δ 13.47 (d, 1, MoC*H*α, J_{HP} = 5.0 Hz), 10.44 (br s, 1, N*H*Ar^{Cl}); ^{31}P NMR (121 MHz) δ 3.53 (in **1e·PMe$_3$**), 0.21 (in side product).

Spectroscopic Observation of 2·PMe$_3$. To a solution of 13.2 mg of **2** in CD_2Cl_2 was added 2 μL of PMe$_3$ via microsyringe. After 10 min, a precipitate was apparent and the NMR spectrum was recorded: ^{1}H (300 MHz) δ 13.15 (d, 1, MoC*H*α, J_{HP} = 6.0 Hz), 7.54 (d, 2, *o*-CMe$_2$*Ph*), 7.31 (t, 2, *m*-CMe$_2$*Ph*), 7.26 (t, 1, *p*-CMe$_2$*Ph*), 7.05 (br t, 2, *p*-Ar′), 6.90 (br d, 4, *m*-Ar′), 2.23 (m, 12, Ar′-*Me* + 3 C*Me*$_2$Ph + 6 Ad-CH_2), 2.13 (br s, 3, Ad-C*H*), 1.68 (br s, Ad-CH_2), 1.52 (s, 3, C*Me*$_2$Ph), 1.23 (d, 9, P*Me*$_3$); ^{31}P NMR (121 MHz) δ 4.22.

General Procedure for Polymerizations. In a representative example, 3.01 mL of a stock solution of **1d** (6.76 mM in toluene) was diluted with 3.0 mL of toluene. To the stirring catalyst solution was added 1.00 mL of a stock solution of DEDPM (0.406 M in toluene) via syringe in one quick squirt. Within 30 s the reaction solution became deep red. After 6 h, 20 μL of benzaldehyde was added. The mixture was stirred for an additional 3 h and then poured into 100 mL of hexanes, causing precipitation of the polymer as a deep red powder. Pertinent spectroscopic features of the polymer are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.2 (br, 1, C*H*), 5.9 (br, 1, CH), 4.2 (m, CH_2CH$_3$), 3.2 (br, 2, ring-CH_2), 2.9 (br, 2, ring-CH_2), 1.2 (t, CH$_2$CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0 (*C*O_2), 134.3, 133.9, 132.9, 131.7 (4 vinylic-*C*), 61.8 (O*C*H$_2$CH$_3$), 54.6 (C_{quat}), 35.0 (ring-*C*H$_2$), 32.2 (ring-*C*H$_2$), 14.0 (OCH$_2$*C*H$_3$). 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 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.[20] All non-hydrogen atoms were refined anisotropically. Coordinates for the hydrogen atoms on C$_\alpha$ of 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·PMe$_3$**, 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·PMe$_3$** 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.

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Supporting Information Available: Crystallographic information files in cif format for **1d·PMe$_3$** and **5a** are available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for **1d·PMe$_3$** (06052) and **5a** (08026) are also available via the web at www.reciprocalnet.org.

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