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Coupling of Terminal Olefins by Molybdenum(VI) Imido Alkylidene Complexes

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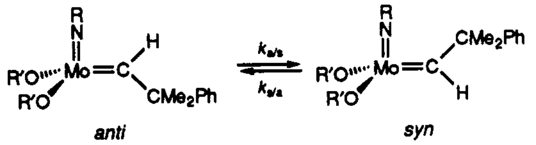
Reactions between alkylidene complexes of the type Mo(NR)(CHR″)(OR′)$_2$ (R = 2,6-i-Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$, 2-i-PrC$_6$H$_4$, 2-t-BuC$_6$H$_4$, 2-CF$_3$C$_6$H$_4$, 1-adamantyl; R″ = CMe$_2$Ph, CMe$_3$; R′ = CMe$_3$, CMe$_2$(CF$_3$), CMe(CF$_3$)$_2$, OC(CF$_3$)$_2$CF$_2$CF$_2$CF$_3$, C(CF$_3$)$_3$) and internal olefins or terminal olefins are explored. Alkylidene complexes that contain relatively electron-withdrawing alkoxide ligands are the most active for metathesis of both internal and terminal olefins. The rate of metathesis of internal olefins by monosubstituted alkylidene complexes is slowed down dramatically in DME compared to the rate in toluene. Methylene complexes are stabilized toward bimolecular decomposition in DME but still react rapidly with internal olefins. Coupling of terminal olefins to give symmetric internal olefins (largely trans) is efficient (typically 0.1 mol % catalyst) and is driven to completion by the loss of ethylene. Trans products are the result of thermodynamic control; methylene species are responsible for rapid secondary metathesis reactions. Methyl 4-pentenoate, methyl 9-decenoate, and 9-(trimethylsiloxy)-1-decene are rapidly and efficiently coupled by Mo(CHCMe$_2$Ph)(N-2,6-i-Pr$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$ (**1a**). Methyl acrylate, allyl cyanide, and (allyloxy)trimethylsilane were not coupled by **1a**. Styrene is efficiently transformed into *trans*-stilbene by Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHMe$_2$Ph)[OCMe$_2$(CF$_3$)]$_2$ in the presence of DME, while the "dimer" and "tetramer" of divinylbenzene have been prepared by analogous methods. Asymmetric internal olefins can be prepared by using a 4–10-fold excess of one olefin.

Introduction

Molybdenum catalysts of the type Mo(CHCMe$_2$Ph)(NR)(OR′)$_2$ can be prepared in wide variety in high yield readily from diammonium dimolybdate.[1–3] Such catalysts are becoming useful in catalytic olefin metathesis reactions because catalyst activity is controllable and because molybdenum is proving to be more tolerant of functionalities than analogous tungsten complexes.[4,5] We have been concerned primarily with polymer synthesis via ring-opening metathesis polymerization (ROMP).[6–14] Other reactions in which molybdenum catalyst of this type have been found to be useful include acyclic diene metathesis polymerizations (ADMET)[15–20] and diene cyclizations.[21–23] The metathesis activity of *tungsten* complexes of this general type had been shown to be proportional to the increasing electron-withdrawing nature of the alkoxide ligands.[2,4,24] The activity of *molybdenum* catalysts appeared to follow the same trend, as one would expect.[2] Recently, the potential importance of syn and anti rotamers (eq 1) and solvent in determining reactivity and stereochemistry or regiochemistry in ROMP by Mo catalysts has been uncovered.[13,25] Therefore, the reasons a metathesis reaction may be fast or slow ultimately may be traced to features that are more subtle than simply a correlation with the electron-withdrawing ability of the alkoxide ligands. Nevertheless, it is worthwhile at this



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$$K_{eq} = k_{a/s}/k_{s/a}$$

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Table 1. Metathesis of *cis*-2-Pentene by Mo(VI) Alkylidene Complexes[a]

catalyst	solvent	time to equilibrium
Me(CHCMe$_2$Ph)(N-2,6-*i*-Pr$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$ (**1a**)	toluene	<2 min[b]
1a	DME	>17 h[c]
Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$ (**1b**)	toluene	<1 min
Mo(CHCMe$_2$Ph)(N-2-*i*-PrC$_6$H$_4$)[OCMe(CF$_3$)$_2$]$_2$ (**1c**)	toluene	<1 min
Mo(CHCMe$_3$)(N-2-*t*-BuC$_6$H$_4$)[OCMe(CF$_3$)$_2$]$_2$ (**1d**)	toluene	<1 min
Mo(CHCMe$_2$Ph)(N-2-CF$_3$C$_6$H$_4$)[OCMe(CF$_3$)$_2$]$_2$ (**1e**)	toluene	<1 min
Mo(CHCMe$_2$Ph)(N-1-adamantyl)[OCMe(CF$_3$)$_2$]$_2$ (**1f**)	toluene	~10 min
Mo(CHCMe$_2$Ph)(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(OCMe$_2$CF$_3$)$_2$ (**2a**)	toluene	>10 h[b]
Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)(OCMe$_2$CF$_3$)$_2$ (**2b**)	toluene	<1 min
Mo(CHCMe$_2$Ph)(N-2,6-*i*-Pr$_2$C$_6$H$_3$)[OC(CF$_3$)$_3$]$_2$ (**3**)	toluene	<2 min[d]
Mo(CHCMe$_2$Ph)(N-2,6-*i*-Pr$_2$C$_6$H$_3$)[OC(CF$_3$)$_2$CF$_2$CF$_2$CF$_3$]$_2$ (**4a**)	toluene	~15 min
Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)[OC(CF$_3$)$_2$CF$_2$CF$_2$CF$_3$]$_2$ (**4b**)	toluene	<10 min
Mo(CHCMe$_2$Ph)(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(OCMe$_3$)$_2$ (**5**)	toluene	days[b]

[a] Catalyst concentration 6.5 mM; [substrate]/[catalyst] = 500. [b] Reference 2. [c] Reference 27. [d] 1000 equiv of *cis*-2-pentene.

point to survey activity of the Mo catalysts from a point of view of practical application. Here we explore the metathesis of selected internal and terminal olefins by complexes of the type Mo(CHCMe$_2$Ph)(NR)(OR$'$)$_2$(R = 2,6-*i*-Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$, 2-*i*-PrC$_6$H$_4$, 2-*t*-BuC$_6$H$_4$, 2-CF$_3$C$_6$H$_4$, 1-adamantyl; R$'$ = CMe$_3$, CMe$_2$(CF$_3$), CMe(CF$_3$)$_2$, C(CF$_3$)$_3$, C(CF$_3$)$_2$CF$_2$CF$_2$CF$_3$).[1-3] The most important finding is that terminal olefins can be coupled efficiently to primarily trans internal olefins (under thermodynamic control) by relatively electrophilic catalysts in the presence of 1,2-dimethoxyethane (DME).

Results

The metathesis of *cis*-2-pentene by various Mo(VI) alkylidene complexes was monitored by gas chromatography. The times required to form an equilibrium mixture of *cis*- and *trans*-2-butene, 2-pentenes, and 3-hexenes (in a closed system; eq 2) are listed in Table 1. As in the case

(2)

of W(VI) alkylidene complexes of this general type,[2,24] the most active [(2,6-diisopropylphenyl)imido]molybdenum(VI) catalysts in toluene contain hexafluoro-*tert*-butoxides. The trifluoro-*tert*-butoxide catalyst is considerably less active and the *tert*-butoxide complex virtually inactive. Catalyst **4a** is not as active as **1a**, possibly because the alkoxide ligands in **4a** are more sterically demanding.

The result of changing the substituents in the phenylimido ligand is in some cases relatively significant. Metathesis by all hexafluoro-*tert*-butoxide phenylimido complexes is rapid, but for trifluro-*tert*-butoxide complexes, changing the imido substituent from 2,6-diisopropylphenyl (**2a**) to 2,6-dimethylphenyl(**2b**) causes the rate to increase dramatically. We have proposed that the reactivity of a (2,6-diisopropylphenyl)imido complex, especially the syn rotamer, is attenuated because the isopropyl groups sterically interact with the alkylidene's substituent in the syn rotamer when the substrate attacks the CNO face of the pseudotetrahedral catalyst.[13,25] A methyl group in an analogous circumstance is considerably less sterically demanding than an isopropyl group.[26] Catalyst **1f** was substantially less active than analogous phenylimido complexes, which could be ascribed either to the increased steric requirements of a relatively spherically symmetric adamantylimido ligand or to the more donating nature of the alkylimido ligand compared to an arylimido ligand.

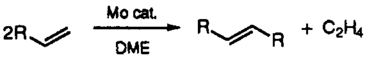
Table 2. Rates of Terminal Olefin Metathesis in DME Using Mo(VI) Alkylidene Complexes[a]

catalyst	olefin[b]	initial rate (min^{-1})[c]	yield (%)	% trans
1a	1-hexene	220	99 (2 h)	
1a	1-decene[d]		80 (3 h)[e]	83
1a	methyl 4-pentenoate	140	84 (1 h)	73
1a	methyl 9-decenoate		85 (8 h)	85
1a	9-(trimethylsiloxy)-1-decene[f]		99 (4 h)	79
1a	styrene		35 (3–24 h)[g] 4 (4 h)[h]	100
1b	1-hexene	220	94 (50 min)	
1c	1-hexene	150	48 (5 min)	
1d	1-hexene	200	95 (50 min)	
1e	1-hexene	160	50 (5 min)	
1f	1-hexene	1	16 (2 h)	
1f	1-decene		52 (3 h)[i]	64
2a	1-hexene	70[j]	84 (30 min)	
2b	1-hexene	320	88 (30 min)	
2b	styrene		36 (150 min)[k] 95 (10 h)	100[l]
3	1-hexene	80	27 (5 min)	
4a	1-hexene	130	75 (30 min)	
4b	1-hexene	90	53 (30 min)	
5	1-hexene		5 (2 h)	73

[a] Catalyst concentration 6.5 mM in DME. [b] [substrate]/[catalyst] = 1000, unless otherwise specified. [c] Appearance of product in equiv min^{-1}, determined by GC. [d] The same experiment in toluene yielded 55% of the coupled product after 3 h (70% trans). [e] In a separate experiment, a second portion of 1-decene (1000 equiv) was added after 90 min (81% after 3 h). [f] [substrate]/[catalyst] = 250. [g] 200 equiv employed.[2] [h] [substrate]/[catalyst] = 5000. [i] 27 mM and 100 equiv of 1-decene for 3 h. [j] Average of two runs. [k] [substrate]/[catalyst] = 3700. [l] 5000 equiv of styrene in toluene gave only 27% *trans*-stilbene after 11 h.

One of the most important findings is that 1,2-dimethoxyethane dramatically attenuates the rate of metathesis of *cis*-2-pentene by **1a**.[27] On the basis of these results, we conclude that DME severely inhibits the rate of reaction between an internal olefin and a monosubstituted alkylidene complex, presumably by coordinating to the relatively electrophilic metal in a bidentate manner. It had already been established that DME stabilizes complexes that contain a relatively small alkylidene ligand such as a benzylidene ligand.[27]

The results of metathesis of several terminal olefins in DME (eq 3; vessel open to ambient dinitrogen atmosphere) are listed in Table 2. Catalyst **1a** remained active in DME



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after 90 min in a reaction involving an initial 1000 equiv

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Table 3. Asymmetric Olefins Prepared by Terminal Olefin Coupling Using 1a in DME[a]

olefin	ratio	composition of products[b]	yield (%)[d]	% trans[c]
1-hexene/methyl 9-decenoate	500/117	92% methyl 9-tetradecenoate 8% dimethyl 9-octadecenedioate	97	80
1-decene/1-pentadecene	1250/250	67% 9-octadecene 30% 9-tricosene 3% 14-octacosene	96	81
1-hexene/9-(trimethylsiloxy)-1-decene	10000/1000	100% 1-(trimethylsiloxy)-9-tetradecene	30[e]	73

[a] Catalyst concentration 6.5 mM in DME The reactions were quenched after 3 h. [b] Relatively nonvolatile products, determined by GC. [c] Trans content of the mixture of olefins determined by ^{13}C NMR. [d] Yield of nonvolatile products. [e] Quenched after 2 h with benzaldehyde.

of 1-decene; a second 1000 equiv was added and an 81% yield of total product realized after 3 h of total reaction time. Primarily trans products are produced, as determined by ^{13}C NMR.[28,29] The importance of DME in some circumstances is demonstrated by the finding that 80% of 1000 equiv of 1-decene was converted to product in 3 h by employing **1a** in DME, whereas in toluene only 55% of the product was obtained using the same catalyst loading. We propose that bimolecular coupling of alkylidene intermediates (with subsequent reduction of the metal), especially bimolecular coupling of methylene complexes, limits catalyst longevity in toluene. Dimethoxyethane has been shown to stabilize complexes containing the methylene ligand;[27] the methylene ligand can be observed by proton NMR in dimethoxyethane and shown to be in rapid equilibrium (on the NMR time scale) with ethylene, whereas in toluene Mo hexafluoro-*tert*-butoxide complexes are reduced by ethylene, most likely via biomolecular coupling of methylene intermediates.[30]

The observed trends in the rates of terminal olefin coupling as imido and alkoxide ligands are varied are similar to observed trends in rates of metathesis of internal olefins. Variations in the imido ligand make little difference in the rate of metathesis for the hexafluoro-*tert*-butoxide complexes (**1a–f**). For the trifluoro-*tert*-butoxide complexes, the less hindered (2,6-dimethylphenyl)imido complex **2b** was far more reactive than **2a**. In fact, although **2b** is less electrophilic than **1b** (or **1a**), it is the most active catalyst for terminal olefin coupling in DME; stronger binding between DME and intermediate alkylidene complexes derived from **1b** could be responsible for diminishing the rate of the reactuion of alkylidene intermediates derived from **1b**. The initial rate of metathesis of 1-hexane and 1-decene by the adamantylimido complex (**1f**) is approximately 2 orders of magnitude slower than the rate for other hexafluoro-*tert*-butoxide complexes, a finding that is consistent with what would be expected to be a greater ability for the nitrogen atom in an adamantylimido ligand to donate electron density to the metal in both a σ and a π fashion compared to the nitrogen atom in an arylimido ligand.

Terminal olefin coupling was carried out in the presence of a traceable internal olefin in DME in order to determine whether the internal olefin is metathesized under coupling conditions. A mixture of 5-decene (75 equiv) and 1-pentadecene (150 equiv) was metathesized with **1a** in DME. After 30 min, 1-hexene (15%), 5-decene (13%), 1-pentadecene (7%), 5-nonadecene (30%), and 14-octacosene (26%) were detected in solution. This result suggests that metathesis of internal as well as terminal olefins under these conditions is rapid. The enhanced rate of metathesis of internal olefins in DME under coupling conditions can be ascribed to the extraordinarily high reactivity of the methylene complex, even in the presence of a coordinating ligand (DME; see Discussion). The formation of predominantly trans olefins therefore is the result of thermodynamic control, and no great significance should be ascribed to differences in the percentage of trans olefin product from one case to another.

Several other terminal olefins are also listed in Table 2. The metathesis of methyl 4-pentenoate by **1a** was slower than metathesis of 1-hexene (84% yield in 1 h). The slower rate is evidence that the ester functionality coordinates to the metal and further slows metathesis activity, but it does not react on the time scale of the reaction to a significant degree with alkylidene intermediates, even $Mo(CH_2)(NAr)[OCMe(CF_3)_2]_2(DME)$ (NAr = N-2,6-*i*-$Pr_2C_6H_3$). Methyl 9-decenoate and 9-(trimethhylsiloxy)-1-decene each produce coupled product in high yields as well. *trans*-Stilbene also can be prepared, but catalyst **2b** turns out to be more suitable in this particular case. Styrene (32.0 g) was coupled to give *trans*-stilbene (90% yield) in 10 h using ~0.1 mol % **2b** in DME. Catalyst **1a** reacted very slowly with styrene in DME, as previously noted,[27] presumably because styrene is less reactive for both steric and electronic reasons. Methyl acrylate, allyl cyanide, and (allyloxy)trimethylsilane were not metathesized by **1a**. It should be noted that no Mo alkylidene complexes of the general type $Mo(CHR'')(NR)(OR')_2$ that contain a heteroatom directly bound to the alkylidene carbon atom have ever been observed. The last negative result is more puzzling but consistent with findings in ADMET polymerization that the functional group must be separated from the olefin by at least two methylene groups.[18]

Unsymmetric olefins also can be prepared if one of the two (the lower boiling or least expensive) is used in excess (Table 3). For example, when a 4:1 ratio of 1-hexene and methyl 9-decenoate are coupled using **1a** in DME and the volatile components are removed in vacuo, methyl 9-tetradecenoate (92%) and dimethyl 9-octadecenedioate (8%) comprise the nonvolatile products (eq 4), the 5-decene having been removed in vacuo. In the cross-metathesis of 1-hexene and 9-(trimethylsiloxy)-1-decene (10:1 ratio) 1-(trimethylsiloxy)-9-tetradecene is the only nonvolatile product observed (30% yield after 2 h). The homocoupled product of the minor olefin must either be disfavored thermodynamically or formed more slowly under the conditions of this particular experiment. Metathesis of a 5:1 mixture of 1-decene and 1-pentadecene using **1a** in DME (eq 5) proceeded in high yield (96%) after 3 h to yield 9-octadecene (67%), 9-tricosene (30%), and 14-octacosene (3%), as determined by gas chromatography of the crude product mixture.

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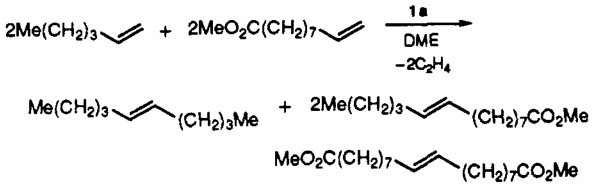

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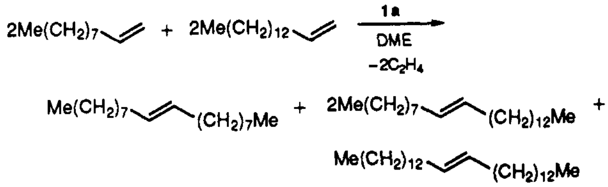

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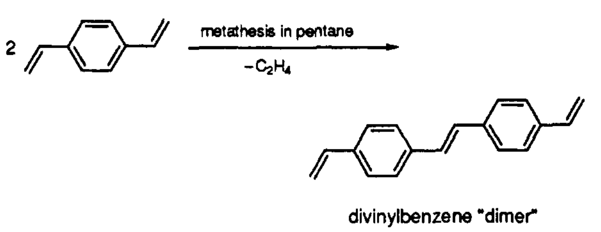
We mentioned in the introduction that ADMET (acyclic diene metathesis) has been a successful method of preparing polymers from α-ω-dienes.[15-20] One unsaturated polymer that is an attractive target to prepare by ADMET is poly(phenylenevinylene) (PPV). A report in the literature that claimed PPV could be prepared via ADMET[31] caused us to examine this reaction in detail. We found that **1a** would successfully couple purified *p*-divinylbenzene in pentane to the "dimer" *trans*-*p*-divinylstilbene (eq 6; λ_{max} = 350 nm), virtually quantitatively. *trans*-*p*-divinylstilbene is relatively insoluble in pentane and precipitates out as it forms, thereby preventing further reaction between it and *p*-divinylbenzene. In dichloromethane, however, **1a** couples *trans*-*p*-divinylstilbene to a sparingly soluble product that was shown to contain the "tetramer" of divinylbenzene (eq 7; λ_{max} = 378 nm) by high-resolution mass spectroscopy. Under the circumstances we must assume that the product consists largely, if not exclusively, of this "tetramer" of divinylbenzene. Step-growth reactions of this type naturally will be limited by the solubility of the oligomeric intermediates. In view of the insolubility of the "tetramer" we believe that it is unlikely that PPV of any significantly greater length can be prepared via ADMET.[31] Synthesis of relatively long oligomers might be possible if solubilizing groups (e.g. alkoxides[32,33]) are present in each monomeric unit, or if oligomers are incorporated into soluble copolymers.[34]



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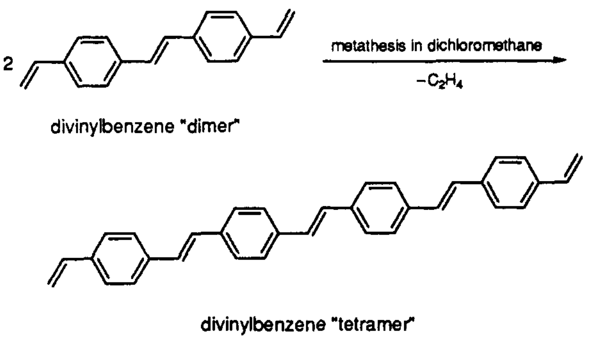

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Discussion

The coupling reaction reported here is related to other couplings of terminal olefins that have been reported using molybdenum alkylidene catalysts, namely ADMET[15-20] and diene cyclizations.[21-23] It is likely that each could be improved in some circumstances if some DME were added in order to stabilize alkylidene intermediates, especially methylene complexes. For example, when **1a** is used as a catalyst in ADMET polymerizations, additional catalyst must be added to compensate for catalyst decomposition at the higher temperatures required to drive the polymerization to higher molecular weight material.[17] A preliminary experiment shows that ADMET can be carried out in DME (see Experimental Section).

The fact that the ethylene formed in the coupling reactions reported here apparently does not reduce hexafluoro-*tert*-butoxide catalysts rapidly at room temperature and pressure is consistent with the proposal that molybdenum is reduced via coupling of methylene complexes, not via rearrangement of the unsubstituted molybdacyclobutane complex.[30] As we have mentioned already, $Mo(CH_2)(NAr)[OCMe(CF_3)_2]_2(DME)$ reacts rapidly enough with ethylene to yield broadened methylene resonances at room temperature, but there is no obvioius decomposition of the methylene complex under these conditions.[27] Coupling is proposed to take place via solvent-free four-coordinate $Mo(CH_2)(NAr)[OCMe(CF_3)_2]_2$, which is in equilibrium with $Mo(CH_2)(NAr)[OCMe(CF_3)_2]_2(DME)$. In DME the effective concentration of $Mo(CH_2)(NAr)[OCMe(CF_3)_2]_2$ must be extremely low and, therefore, the probability of bimolecular decomposition also low. However, the concentration of olefin is many orders of magnitude greater than that of $Mo(CH_2)(NAr)[OCMe(CF_3)_2]_2$, and therefore, rapid reaction of $Mo(CH_2)(NAr)[OCMe(CF_3)_2]_2$ with an olefin is still possible.

We have established here that remote esters and trimethylsiloxy functionalities are tolerated, that styrene, divinylbenzene, and divinylstilbene can be coupled efficiently, and that asymmetric olefins can be synthesized in high yield under the appropriate conditions. It is important to note that catalysts that contain the (2,6-dimethylphenyl)imido ligand are significantly faster than those that contain the (2,6-diisopropylphenyl)imido ligand and that the fastest metathesis catalyst in DME is not always a hexafluoro-*tert*-butoxide complex. It remains to be seen what is the scope of the coupling reaction for more elaborate molecules.[36]

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Pentane was washed with sulfuric acid/nitric acid (95/5 v/v), sodium bicarbonate, and then water, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether, tetrahydrofuran, toluene, and 1,2-dimethoxyethane were distilled from sodium benzophenone ketyl under nitrogen. Reagent grade dichloromethane was distilled from calcium hydride under nitrogen. Toluene used for polymerizations was stored over a Na/K alloy. DME and polymerization grade THF were vacuum-transferred a second time from sodium benzophenone ketyl. Commercially available *p*-divinylbenzene was purified by a method described in the literature.[31]

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It was further purified by low-temperature recrystallization (−40 °C) from pentane. Pentane used for metathesis was passed down a short column of activated alumina before use. All deuterated NMR solvents were passed through a column of activated alumina prior to use. NMR data are listed in parts per million downfield from tetramethysilane for proton and carbon; coupling constants are listed in hertz. Mo(CHCMe$_2$Ph)(N-2,6-*i*-Pr$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$, Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$, Mo(CHCMe$_2$Ph)(N-2-*i*-PrC$_6$H$_4$)[OCMe(CF$_3$)$_2$]$_2$, Mo(CHCMe$_3$)(N-2-*t*-BuC$_6$H$_4$)[OCMe(CF$_3$)$_2$]$_2$, Mo(CHCMe$_2$Ph)(N-2-CF$_3$C$_6$H$_4$)[OCMe(CF$_3$)$_2$]$_2$, Mo(CHCMe$_2$Ph)(N-1-adamantyl)[OCMe(CF$_3$)$_2$]$_2$, Mo(CHCMe$_2$Ph)(N-2,6-*i*-Pr$_2$C$_6$H$_3$)[OCMe$_2$(CF$_3$)]$_2$, Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)[OCMe$_2$(CF$_3$)]$_2$, Mo(CHCMe$_2$Ph)(N-2,6-*i*-Pr$_2$C$_6$H$_3$)[OC(CF$_3$)$_3$]$_2$, Mo(CHCMe$_2$Ph)(N-2,6-*i*-Pr$_2$C$_6$H$_3$)[OC(CF$_3$)$_2$CF$_2$CF$_2$CF$_3$]$_2$, Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)[OC(CF$_3$)$_2$CF$_3$CF$_2$CF$_3$]$_2$, and Mo(CHCMe$_2$Ph((N-2,6-*i*-Pr$_2$C$_6$H$_3$)(OCMe$_3$)$_2$ were prepared by published methods.[1-3,27] All chemicals used were reagent grade and were purified by standard methods.[35]

Metathesis of *cis*-2-Pentene by 1a. **1a** (5 mg, 0.0065 mmol) was dissolved in 1 mL of toluene in a septum-sealed vial, *cis*-2-pentene (228 mg, 3.25 mmol) was added, and the solution was stirred. Aliquots were removed periodically and were quenched over Al$_2$O$_3$. The reaction was monitored by gas chromatography. Studies employing other catalysts were conducted in a similar manner.

Methyl 4-Pentenoate. 1-Pentenoic acid (10 g, 0.10 mol) was dissolved in methanol (30 mL), and concentrated sulfuric acid was added (1.0 mL). The solution was refluxed for 24 h, concentrated in vacuo, and diluted with water (20 mL). The mixture was extracted with diethyl ether (3 × 10 mL), and the ether fraction was neutralized with a saturated aqueous solution of sodium bicarbonate. The ether layer was separated and dried over MgSO$_4$. The ether was removed in vacuo. The ester was distilled from CaH$_2$: yield 1.23 g, 11 mmol, 11%; ^{1}H NMR (CDCl$_3$) δ 5.77 (m, 1, CH olefin), 5.01 (d, 1, CH olefin), 4.95 (d, 1, CH olefin), 3.63 (s, 1, OMe), 2.35 (m, 4, CH$_2$); ^{13}C NMR (CDCl$_3$) δ 172.9 (CO), 136.3 (CH olefin), 115.1 (CH$_2$ olefin), 51.2 (CH$_2$), 33.2 (OMe), 28.7 (CH$_2$).

1-(Trimethylsiloxy)-9-decene. 9-Decen-1-ol (10.16 g, 0.065 mol) was dissolved in 80 mL of pentane and 10 mL of triethylamine, and the solution was cooled to −40 °C. Chlorotrimethylsilane (7.77 g, 0.071 mol) was added dropwise to the stirred solution over a 30-min period. After 12 h the mixture was filtered through Celite. The volatile components were removed in vacuo, and the oil was distilled (64 °C, 0.5 Torr) from CaH$_2$ to yield colorless product (8.5 g, 0.037 mol, 57%): ^{1}H NMR (CDCl$_3$) δ 5.77 (ddt, 1, CH olefin), 4.96 (d, 1, CH$_{trans}$ olefin), 4.89 (d, 1 CH$_{cis}$ olefin), 3.54 (t, 2, C*H*$_2$OSiMe$_e$), 2.01 (m, 2, CH$_2$), 1.51 (m, 2, CH$_2$), 1.33 (m, 2, CH$_2$), 1.27 (m, 8, CH$_2$), 0.08 (s, 9, SiMe$_3$); ^{13}C NMR (CDCl$_3$) δ 139.1 (CH olefin), 114.1 (CH$_2$ olefin), 62.7 (*C*H$_2$OSiMe$_3$), 33.8 (CH$_2$), 32.8 (CH$_2$), 29.5 (CH$_2$), 29.4 (CH$_2$), 29.1 (CH$_2$), 28.9 (CH$_2$), 25.8 (CH$_2$), −0.5 (SiMe$_3$).

Metathesis of 1-Pentadecene in the Presence of 5-Decene. **1a** (5 mg, 0.0065 mmol) was dissolved in 1 mL of DME. A mixture of 5-decene (71 mg, 0.488 mmol) and 1-pentadecene (206 mg, 0.975 mmol) was added, and the solution was stirred for 30 min. A small amount of activated Al$_2$O$_3$ was added to quench the catalyst. The composition of the mixture was determined by gas chromatography.

Metathesis and Cross-Metathesis of Terminal Olefins. In a typical experiment, 5 mg of catalyst was dissolved in 1 mL of DME. The olefin (1000 equiv) was added, and the solution was stirred; the vial was left open to the N$_2$ atmosphere in order that ethylene be lost from solution readily. In order to obtain rates of metathesis, aliquots were removed and quenched over Al$_2$O$_3$. The composition of each aliquot was analyzed by gas chromatography. In cases where nonvolatile olefins could be isolated (1-decene, methyl 9-decenoate, methyl 4-pentenoate, 1-(trimethylsiloxy)-9-decene, and cross-metatheses), the catalyst was quenced by adding Al$_2$O$_3$ to the mixture, filtering the suspension, and removing the volatile components in vacuo.

Metathesis of Styrene Using 2b. **2b** (168 mg, 0.28 mmol) was dissolved in 10 mL of DME, and styrene (32.0 g, 0.0307 mol) was added. The solution was stirred for 10 h, after which time the mixture had turned to a solid crystalline mass. The volatile components were removed in vacuo to afford *trans*-stilbene (25.0 g, 0.139 mol, 90%), which was identical with an authentic sample.

ADMET of 1,5-Hexadiene. **1a** (10 mg, 0.0131 mmol) was dissolved in 500 μL of DME, and 1,5-hexadiene (5.37 g, 65.5 mmol) was added. The solution was stirred for 7.5 h, after which time the solution had become very viscous, although gas evolution could still be observed. Polymerization was terminated by adding 100 μL of pivaldehyde, and the polymer was isolated by precipitation in methanol (3.97 g, 89% yield). By gel permeation chromatography $M_n = 2200$ (versus polystyrene stqandards) and $M_w/M_n = 1.53$. The polymer was shown to contain 80% *trans* double bonds by ^{13}C NMR.

Metathesis of Divinylbenzene by 1a. A few crystals of **1a** (approximately 3 mg) were added to a stirred solution of divinylbenzene (336 mg, 2.58 mmol) in 5 mL of pentane (0.15 mol % of catalyst). After a few minutes a red color consistent with the formation of a benzylidene species was observed and yellow crystals began to precipitate. The reaction mixture was stirred for 16 h, and a drop of benzaldehyde was added to terminate the reaction. The mixture was cooled, and the product was filtered off and washed with 20 mL of cold pentane. The powder was dissolved in 15 mL of ether, the solution was filtered to remove any insoluble material, and the solvent was removed in vacuo to yield 299 mg (82%) of *trans*-divinylstilbene: ^{1}H NMR (CDCl$_3$) δ 7.43 (m, 8, Ar H), 7.07 (s, 2, ArC*H*=*C*HAr), 6.71 (dd, $J = 17.6, 10.9$ Hz, 2, ArC*H*=CH$_2$), 5.76 (dd, $J = 17.6, 0.9$ Hz, 2, ArCH=C*H*), 5.25 (dd, $J = 10.9, 0.9$ Hz, 2, ArCH=C*H*); ^{13}C NMR δ 137.0, 136.9, 136.5, 128.2, 126.6, 113.7; UV $\lambda_{max} = 350$ nm (benzene).

Metathesis of Divinylstilbene by 1a. Divinylstilbene (500 mg, 2.15 mmol) was dissolved in the minimum amount of dichloromethane (about 20 mL), and **1a** (10 mg, 5 mol %) was added. Over the course of 24 h a dark yellow precipitate formed. The solvent was removed in vacuo, and the powder was extracted with hot dichloromethane until the washings showed no divinylstilbene by TLC. The product weighed 350 mg (74% yield). This "tetramer" of divinylbenzene was virtually insoluble in all solvents; therefore, no solution spectral data could be measured, apart from λ_{max} (380 nm) in chlorobenzene. HRMS: calcd for C$_{34}$H$_{28}$ 436.2191, found 436.2187.

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(36) Note added in proof. Related cross-metatheses of terminal olefins with Mo catalysts have been reported recently: Crowe, W. E.; Zhang, Z. J. *J. Am. Chem. Soc.* **1993**, *115*, 10998.