Organometallics **1994,** *13,* 1014-1019

Reactions of a Cationic Molybdenum Complex with Olefins. 2. Oligomerization of 1,1-Disubstituted Olefins

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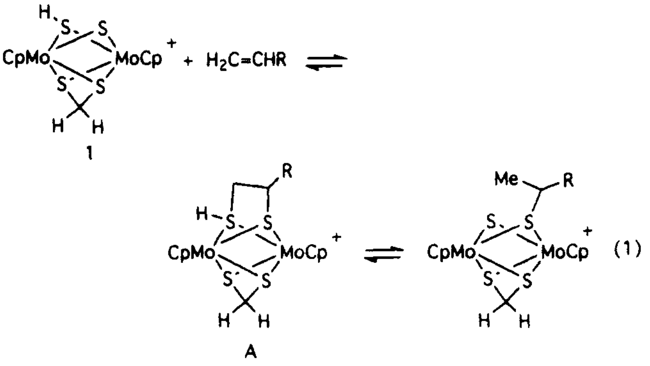
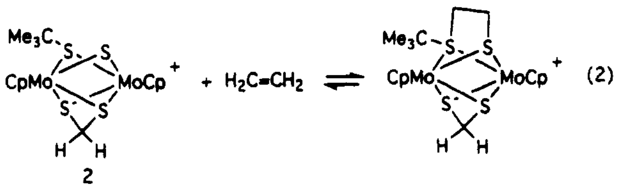
The oligomerization of 2-methylpropene and of other terminal disubstituted olefins in dichloromethane solution was catalyzed by $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]OTf$, where R = H, 1, or CMe_3, 2. Oligomers of 2-methylpropene of the formula $(C_4H_8)_n$, where n = 2–8, were detected, and the major C_8 and C_{12} isomers have been identified. The distribution of oligomers was consistent with a carbocationic coupling mechanism. Molybdenum products isolated from the 2-methylpropene coupling reaction were found by mass spectrometry to have the formula $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}S(C_4H_8)_nH)]^+$, where n = 1–3. The role of the molybdenum catalysts as proton donors and as carbenium ion donors has been investigated, and a mechanism for oligomerization has been proposed which also takes into account the known stoichiometric reactions of 1 and 2 with olefins.

Introduction

We have studied several types of reactivity of bridging sulfur ligands in dinuclear cyclopentadienylmolybdenum complexes. For example, the bridging SH ligand in the cationic complex $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$, 1, has been found to undergo addition reactions with a number of unsaturated molecules.[1,2] Similar reactions may be of fundamental importance in heterogeneous metal sulfide catalyzed processes.[3] We have recently reported a detailed study of the mechanistic features of olefin insertions into the SH bond of 1.[1] Two important observations were that the initial olefin insertion products were formed regioselectively and that the insertion reactions were reversible. A mechanism was proposed in which the more electrophilic sulfur of 1 interacted with the more electron rich carbon of the olefin prior to hydrogen transfer, eq 1.



Intermediate A in eq 1 was not detected spectroscopically. However, analogous structures have been characterized for the reactions of certain alkanethiolate cations with olefins.[4] For example, the reversible interaction of ethylene with the 2-methylpropanethiolate cation, 2, was monitored by NMR spectroscopy; the equilibrium constant for eq 2 was found to be 96 ± 5 M^{-1} at 20 °C. The interaction of propene with 2 was significantly weaker than that of ethene (K_{eq} < 4 M^{-1} at 20 °C), and an adduct with excess 2-methylpropene was only detected by NMR in low concentration at −40 °C. However the NMR spectrum of the methylpropene reaction at this temperature showed the formation of new organic products which were identified as olefin coupled products. In this paper we describe the characterization of this oligomerization reaction which shows features typical of a carbocationic coupling process.



The cationic polymerization of olefins, particularly 2-methylpropene, initiated by protons and other Lewis acids, has been extensively studied.[5] In general, the poor selectivity for product structure and molecular weight in these reactions limits practical applications. Relatively few transition metal complexes have been found to catalyze the oligomerization of branched olefins. Complexes with strong electrophilic properties, such as $[M(NCMe)_4](BF_4)_2$ (M = Pd, Pt),[6] $[Rh(NO)(NCMe)_4]BF_4$,[7] and $CpW(NO)_2BF_4$,[8] have been reported to catalyze the coupling of certain olefins by a cationic mechanism. In some cases, these reactions were proposed to proceed through polarization of a metal-coordinated olefin to generate an incipient organometallic carbocation. The molybdenum cation 2,

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[⊛] Abstract published in *Advance ACS Abstracts*, February 15, 1994.

(1) Birnbaum, J.; Laurie, J. C. V.; Rakowski DuBois, M. *Organometallics* **1990**, *9*, 156.

(2) Bernatis, P.; Laurie, J. C. V.; Rakowski DuBois, M. *Organometallics* **1990**, *9*, 1607.

(3) (a) Gates, B. C.; Katzer, J. R.; Schuit, G. C. *Chemistry of Catalytic Processes*: McGraw-Hill: New York, 1979. (b) Prins, R.; DeBeer, V. H. J.; Somorjai, G. A. *Catal. Rev.-Sci. Eng.* **1989**, *31*, 1.

(4) Birnbaum, J.; Haltiwanger, R. C.; Bernatis, P.; Teachout, C.; Parker, K.; Rakowski DuBois, M. *Organometallics* **1991**, *10*, 1779.

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(6) (a) DeRenzi, A.; Penanzi, A.; Vitagliano, A. *Chem. Commun.* **1976**, 47. (b) Sen, A.; Lai, T. W. *Organometallics* **1982**, *1*, 415.

(7) Connelly, N. G.; Draggett, P. T.; Green, M. *J. Organomet. Chem.* **1977**, *140*, C10.

(8) Legzdins, P.; Richter-Addo, G. B.; Einstein, F. W. B.; Jones, R. H. *Organometallics* **1990**, *9*, 431.

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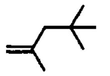
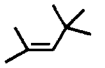
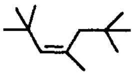
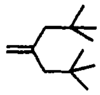
Table 1. Qualitative Rate of Isobutene Oligomerization by Complex 1[a] in CH_2Cl_2

reacn time (days)	% of olefins present						
						other C_{12}	C_{16}[b]
A. Temperature = 50 °C							
4.3	39	30	11	9	10	1	trace
7.3	20	41	11	12	14	3	0.5
12	<5	53	14	13	13	3	0.5
60		10	2	46		4	18
B. Temperature = 25 °C							
0	100						
1	99	trace	trace[c]				
2.7	89	11	trace				
4	84	13	3	trace	trace		
18	38	39	9	3	4		
24	20	~70		4	5		
40	13	~60		7	7		
150	[illegible]	31	5	53		2	6[b]

[a] See Experimental Section for concentrations of reagents. [b] Products identified by GC–MS. [c] Product distributions were estimated from ^1H NMR data.

reported here, is an electrophilic complex which reversibly coordinates olefins, but it is also in equilibrium with the Bronsted acidic complex, 1 (eqs 1 and 2). Our objective in this work was to investigate how these equilibria contribute to the observed olefin coupling reaction.

Results and Discussion

Characterization of Oligomerized Products. When excess 2-methylpropene (80 equiv) was reacted with 1 or 2 (10^{-2} M) at 25 °C in CH_2Cl_2, the olefin was oligomerized primarily to $(C_4H_8)_2$ and $(C_4H_8)_3$ products. The reaction was very slow (see Table 1B) but complete oligomerization was observed after an extended period. When reactions were carried out at 50 °C with >200 equiv of 2-methylpropene, the reactions were also followed to completion in some cases, and oligomers $(C_4H_8)_n$ where $n = 2$–8 were detected by GC/mass spectral characterization.

The major C_8 and C_{12} isomers formed in these reactions have been identified by GC/mass spectral data and by ^1H and ^{13}C NMR spectroscopy and are shown in the headings of Table 1. The observed C_8 isomers result from head to tail coupling of two isobutenes, and the major C_{12} isomers are those expected from the coupling of CMe_3^+ with the major C_8 olefin. Similar products have been identified in protic acid catalyzed oligomerizations of isobutene under different conditions.[9] Table 1 summarizes the formation of the oligomerization products as a function of time on the basis of periodic NMR or gas chromatographic data. A plot of the data suggests that the trimerization product is formed only after significant amounts of both monomer and dimer are present in solution. The oligomerization was also found to proceed in acetonitrile and carbon tetrachloride solvents to give similar product distributions. Since CCl_4 is a good radical scavenging solvent, the results suggest that the oligomerization does not proceed through radical propagating agents.

We have compared the products formed in the reaction of 2-methylpropene with 1 or 2 to those produced with triflic acid. When similar concentrations of 1 and triflic acid (~10^{-2} M) were separately reacted with excess 2-methylpropene at 25 °C in CD_2Cl_2, significantly different product distributions were observed. The triflic acid catalyzed reaction proceeded to form a wide distribution of alkanes, C_nH_{2n+2}, where $n = 8$–20, in contrast to the oligomerized butenes produced by 1. Alkane products have been observed previously in reactions of acids with olefins in CH_2Cl_2 and have been attributed to hydrocarbon cracking reactions.[9b,10]

Control reactions were therefore carried out with 2-methylpropene and lower concentrations of triflic acid in CH_2Cl_2. A concentration of triflic acid was chosen to correspond to an upper limit of proton dissociation from 1, based on previous pK_a measurements in nonaqueous solution.[11] When 2-methylpropene (1 M) was reacted with 2×10^{-5} M triflic acid in CH_2Cl_2 at 25 °C, oligomerization products similar to those produced with 1 were observed. However, there appeared to be significant differences in the efficiency of the termination mechanisms of the two systems. The triflic acid catalyzed reaction was found to proceed for only a limited time period (~1 week, 10% conversion), while the molybdenum complex, 10^{-2} M with 1 M 2-methylpropene in CH_2Cl_2 at 50 °C, catalyzed oligomerization through >95% conversion over a period of ~12 days (see Table 1).

A survey of the catalytic activity of 1 for olefin oligomerization revealed that other terminal disubstituted olefins were also readily coupled. For example, the reactions of 1 with α-methylstyrene and with isoprene at room temperature led to formation of olefin dimers and trimers as major products. However the reaction of the terminal olefin 2-methyl-1-butene with 1 resulted in rapid isomerization of the olefin to 2-methyl-2-butene. This isomerization has been shown previously to proceed by reversible insertion into the S–H bond of 1.[2] Similar rearrangements are expected for other terminal disubstituted olefins with alkyl substituents. The rearranged trisubstituted olefin, 2-methyl-2-butene, was dimerized by 1 only very slowly at 70 °C. No significant oligomerization was observed for monosubstituted olefins, e.g., propene, or for ethene under the conditions studied here.

Characterization of Molybdenum Products. When the oligomerizations were monitored by NMR spectros-

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[9] (a) Schmerling, L.; Ipatieff, V. N. *Advances in Catalysis and Related Subjects*: Academic: New York, 1950; Vol. II, p 21. (b) Higashimura, T.; Miyoshi, Y.; Hasegawa, H. *J. Appl. Polym. Sci.* **1983**, *28*, 241.

[10] Hasegawa, H.; Higashimura, T. *J. Appl. Polym. Sci.* **1982**, *27*, 171.

[11] Birnbaum, J.; Godziela, G.; Maciejewski, M.; Tonker, T. L.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1990**, *9*, 394.

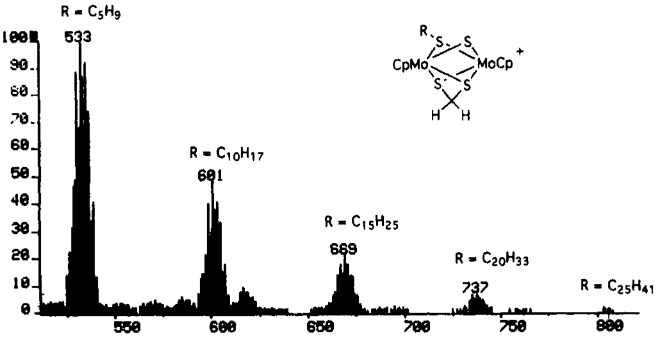


Figure 1. FAB mass spectrum in the high mass region for the mixture of cations isolated from the catalytic oligomerization of isoprene.

copy, cationic alkanethiolate molybdenum complexes were the major organometallic derivatives detected in solution. The NMR spectra of a mixture isolated from the 2-methylpropene coupling reactions appeared to be dominated by resonances of $[(\mathrm{CpMo})_2(\mathrm{S_2CH_2})(\mu\text{-S})(\mu\text{-SR})]^+$, where R = $\mathrm{CMe_3}$ and $\mathrm{CH_2CHMe_2}$, but additional weak resonances for other alkanethiolate cation(s) were also observed. The FAB mass spectrum of such a mixture showed evidence for complexes of the formula $[(\mathrm{CpMo})_2(\mathrm{S_2CH_2})(\mu\text{-S})(\mu\text{-S}(\mathrm{C_4H_8})_n\mathrm{H})]^+$ where $n = 1$–3. The molybdenum products which were isolated from the isoprene and methylstyrene coupling reactions were also characterized by FAB mass spectroscopy and were found to be similar mixtures of alkanethiolate cations. For example, for the molybdenum containing products in the isoprene reaction, the mass spectrum (see Figure 1) showed parent ion envelopes for cationic complexes with alkanethiolate ligands with each of the observed coupled isoprene chain lengths.

A second minor molybdenum product which was observed in up to 20% yield after the isobutene oligomerization was identified as $[(\mathrm{CpMo})(\mathrm{S_2CH})(\mathrm{SCH_2CMe_2S})(\mathrm{MoCp})]\mathrm{SO_3CF_3}$, a product which has been synthesized and characterized previously in our laboratory.[1]

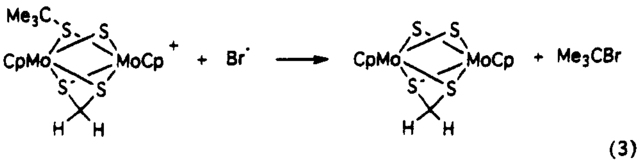
Role of the Molybdenum Complex in the Coupling Reaction. As discussed above, the oligomerization of 2-methylpropene catalyzed by **1** shows an isomer distribution of oligomerized butenes similar to that produced by triflic acid. However, **1** is not likely to function simply as a proton donor in these oligomerizations because, in the presence of a large excess of olefin, the equilibrium shown in eq 1 is shifted far to the right and **2** is the major species in solution. Equilibrium constants at 20 °C in $\mathrm{CD_3CN}$ have been reported for the following reactions.[4,11] These permit us to estimate a constant for proton dissociation from **2**.

$$\mathbf{2} \rightleftharpoons \mathbf{1} + \mathrm{C{=}C}\!< \qquad K = 3.2 \times 10^{-4}$$

$$\mathbf{1} \rightleftharpoons (\mathrm{CpMo{-}S})_2\mathrm{S_2CH_2} + \mathrm{H^+} \qquad K = 5.0 \times 10^{-9}$$

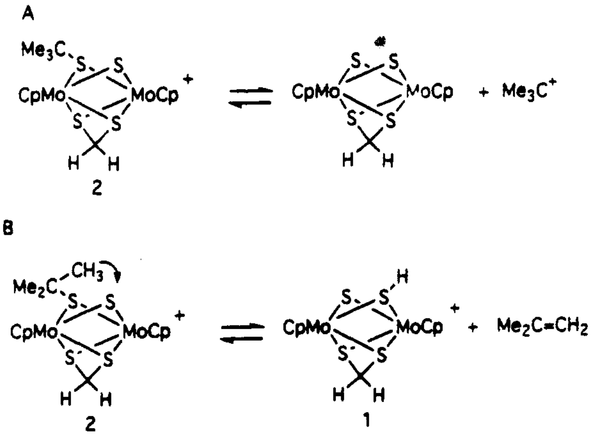
$$\mathbf{2} \rightleftharpoons (\mathrm{CpMo{-}S})_2\mathrm{S_2CH_2} + \mathrm{H^+} + \mathrm{C{=}C} \qquad K = 1.6 \times 10^{-12}$$

Since the equilibrium constant for proton dissociation from **2** is very small, the ability of **2** to initiate oligomerization by an alternate mechanism, i.e., by functioning as a carbenium ion donor, was investigated. The reaction of **2** with bromide salts (e.g., LiBr or $\mathrm{NMe_4Br}$) did lead to the formation of *t*-BuBr, eq 3. The reaction could proceed via the reversible dissociation of the carbenium ion, as shown in mechanism A, Scheme 1. However, this equilibrium has not been detected spectroscopically for the triflate salt. An alternate dissociative mechanism for the formation of *t*-BuBr could involve the previously characterized[1,4] reversible elimination of isobutene from the triflate salt of **2**, B in Scheme 1. In the presence of the bromide ion, the resulting molybdenum complex **1** is deprotonated,[12] and HBr addition to the olefin would give the final products of eq 3.



(3)

Scheme 1



We wished to determine if the addition of excess olefin to **2** might promote the dissociation shown in A and thereby initiate olefin coupling. In order to probe this question, we examined the qualitative effect of ethylene addition on the rate of eq 3. If the reaction proceeds through mechanism A, the dissociative equilibrium would probably be shifted to the right in the presence of ethylene because of the formation of the very stable neutral ethylene adduct.[13] However if carbenium ion dissociation does not occur in this system, excess ethylene should inhibit the rate of the *t*-BuBr formation by adduct formation with the sulfur ligands of **2** (see eq 2). This adduct formation would block the hydrogen transfer from the thiolate to sulfide ligand proposed in the olefin elimination reaction of mechanism B.

An experimental comparison of reaction 3 carried out in the presence and absence of excess ethylene established that the rate of *t*-BuBr formation was enhanced by ethylene (see Experimental Section). The results support the proposal that **2** initiates oligomerization of excess methylpropene by carbenium ion dissociation and its attack on free olefin. The observation that a small amount of $[(\mathrm{CpMo})_2(\mathrm{S_2CH})(\mathrm{SCH_2CMe_2S})]^+$, **3**, is observed by NMR spectroscopy during the oligomerization reaction also suggests that a free carbenium ion is formed, since **3** is known to be produced by carbenium ion abstraction of hydride from the corresponding neutral complex, eq 4.[1]

Although eq 4 represents a termination mechanism, the slow oligomerization catalyzed by **1** was not found to

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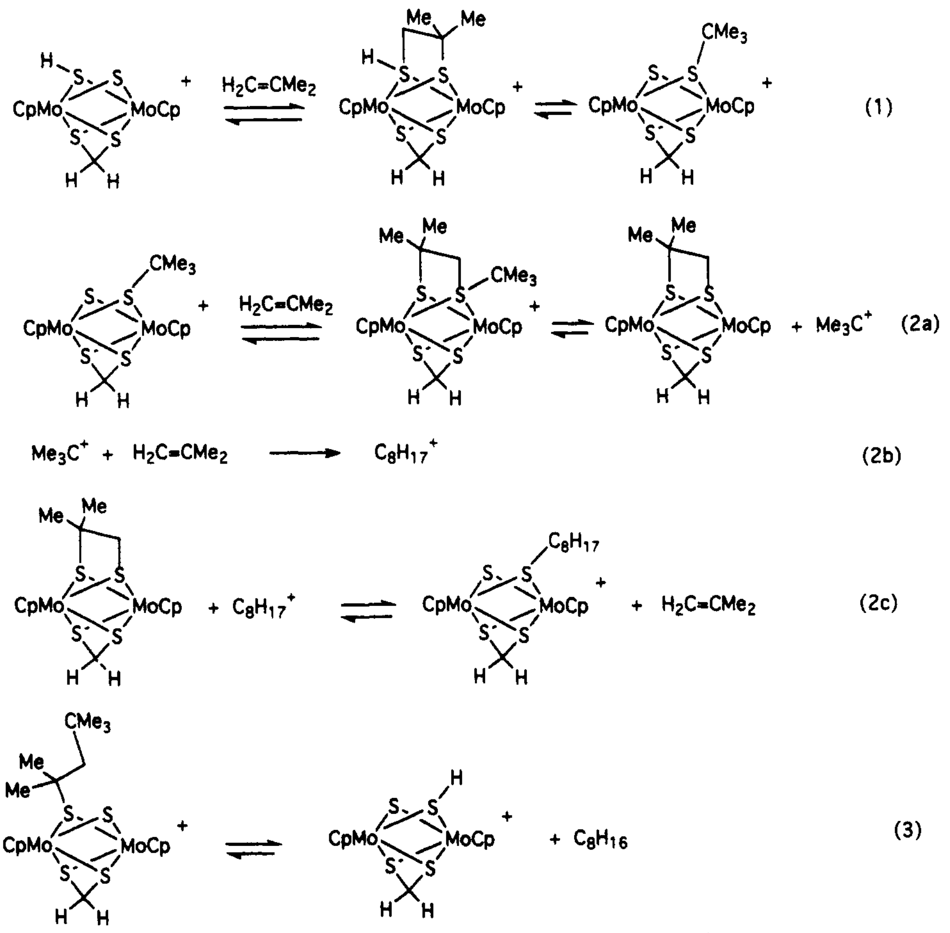
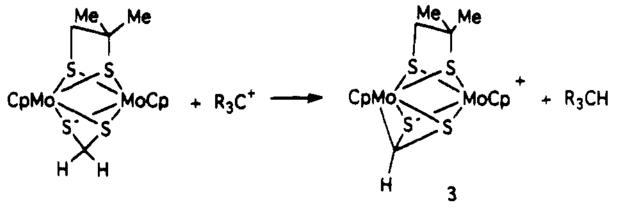
[12] Coons, D. E.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1987**, *6*, 2417.

[13] McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329.

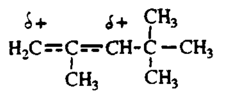
Scheme 2





(4)

undergo significant catalyst decay over extended time periods compared to the triflic acid system. The termination step in the triflic acid catalyzed reaction has not been definitely characterized, but two likely pathways have been discussed.[14] Collapse of the ion pair between carbenium and triflate ions to form a covalent ester has been considered as one possibility. Alternatively, hydride transfer from alkene to the carbenium ion may generate a new carbenium ion which is too stable to sustain chain growth. For example, the olefins formed in the isobutene oligomerization reaction, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, both form the relatively stable allyl cation I upon hydride transfer to the propagating



$$\overset{\delta+}{H_2C}{=}\overset{\delta+}{\underset{CH_3}{C}}{=}CH-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

I

chain, and as a result these olefins function as fairly efficient chain terminating agents.[15] Similar termination reactions should occur in the molybdenum catalyzed system if 1 serves as a source of Me_3C^+, which reacts with free olefin. However, the relatively high concentration of catalyst precursor 1 or 2 which is tolerated, 10^{-2} M, compared to the triflic acid concentration, 10^{-5} M, should allow the molybdenum complex to generate a steady supply of the carbenium ion initiator for much longer reaction periods. Covalent ester formation between the carbenium ion and the triflate ion, present in a relatively high concentration, does not appear to be significant in this molybdenum system.

Summary of the Reactions of the Molybdenum Cation. Although the isobutene oligomerization promoted by the molybdenum complex 1 in dichloromethane displays typical characteristics of carbocationic chain growth, the participation of the sulfide ligands of the dimer in the reaction chemistry is indicated by the formation of molybdenum containing products with alkanethiolate substituents of varying chain lengths. The previously characterized reactivity of 1 and 2 with olefins establishes several steps which are likely to occur in the oligomerization system. A complete series of reactions proposed for this molybdenum catalyzed oligomerization is summarized in Scheme 2.

The reversible olefin interaction with sulfur ligands of 1 followed by insertion into the S–H bond of 1 (step 1 of Scheme 2) is a facile reaction which occurs readily in the 2-methylpropene system. The reaction is similar to the

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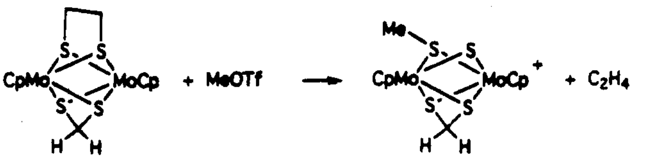
[14] Reference 5, p 216.

[15] Kennedy, J. P.; Squires, R. G. *J. Macromol. Sci., Chem.* **1967**, *A1*, 847.

[16] Pouchert, C. J.; Campbell, J. R. *The Aldrich Library of NMR Spectra*; Aldrich Chemical Co.: Milwaukee, WI, 1974: Vol. 1, pp 23, 25.

π interaction of an olefin with a metal center prior to insertion into a M–H bond. Reactions proposed to be involved in the generation and coupling of free carbenium ions, as discussed above, are included in steps 2a and b of Scheme 2. Step 2c, which accounts for the formation of observed molybdenum products, is the reverse of the reaction type in 2a. This reaction has been characterized for related molybdenum dimers. For example, the equilibrium for such an olefin displacement has been found to lie far to the right when the ethylene adduct is reacted with MeOTf (eq 5).[4] In the final step of the scheme, reaction 3, the previously characterized hydrogen transfer from a β-carbon in an alkanethiolate ligand to an adjacent sulfide ligand provides a means for the release of the free olefin and the regeneration of catalyst 1. There is an analogy between this step and the elimination reaction of a metal-coordinated alkyl ligand. While the reaction steps in Scheme 2 provide a mechanism which is consistent with the known reactivity of 1 and 2, we cannot exclude the possibility that other mechanisms also contribute to product formation in this system.



(5)

Experimental Section

The complexes $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$, 1, and $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCMe_3)]SO_3CF$, 2, were synthesized as described previously.[1,8] 2-Methylpropene and other olefins were purchased from commercial suppliers and used without purification. Dichloromethane and acetonitrile were distilled from calcium hydride and stored over 4-Å molecular sieves. Acetonitrile was further purified by distillation from $CuSO_4$ or P_2O_5.

^1H NMR spectra were measured at 300 MHz on a Varian VXR 300 spectrometer. The same instrument was used to obtain ^{13}C NMR spectra at 75.4 MHz. Chemical shifts were referenced to the residual solvent proton resonances. FAB mass spectra were obtained on a VG Analytical 7070 EQ-HR tandom mass spectrometer using thioglycerol or a 3:1 mixture of dithiothreitol/dithioerythritol as matrix. GC–MS data were obtained on a Hewlett Packard system consisting of a 5790A gas chromatograph, a 5980A mass spectrometer, and a 5933A data system. Samples (1–5 μL) were eluted from a Hewlett Packard fused silica capillary column cross-linked with 5% phenylmethylsilicone having a 0.52-μm film thickness.

Reaction of $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)](CF_3SO_3)$, 1, with Excess Isobutene. Reaction at 50 °C. In a typical procedure, 1 or 2 (11 mg, 0.018 mmol) was dissolved in 5.0 mL of CD_2Cl_2 in a Schlenk flask and the solution was degassed. Isobutene (580 Torr, ca. 4.6 mmol) and N_2 (350 Torr) were transferred to the flask and the flask was sealed at −196 °C. The reaction was stirred at 50 °C for 12 days. The flask was then cooled to −196 °C and the N_2 was removed by vacuum. The flask was warmed to ambient temperature, and head gas pressure was measured and used to estimate that the quantity of unreacted isobutene was 5% (ca. 0.22 mmol). The volatiles were vacuum transferred to an NMR tube and analyzed separately by ^1H and ^{13}C NMR and by GC–MS. Organic products and yields are listed in Table 1A. NMR data for major products, which are given below, were compared with published spectral data.[5a,6b,11,15] In similar experiments with higher pressures of 2-methylpropene (1900 Torr), trace amounts of higher oligomers (C_{20}, C_{24}, C_{28}, and C_{32}) were detected by GC–MS. The nonvolatile residue was washed with pentane and analyzed by mass spectroscopy. MS (FAB), *m/e*: 633, $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_{12}H_{25})]^+$, weak; 577, $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_8H_{17})]^+$; 521, $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_9)]^{.+}$ Additional weak Mo_2S_4 patterns at 875 and 819 m/e were not assigned.

Reaction at Room Temperature. In a similar procedure, 1 (15 mg, 0.024 mmol) was dissolved in 0.8 mL of CD_2Cl_2 in an NMR tube. Isobutene (ca. 80 equiv, 1.9 mmol) was transferred to the NMR tube, and the tube was sealed under vacuum at −196 °C. The reaction was monitored by ^1H NMR over an extended period at ambient temperature, and results are given in Table 1B. After 5 months the reaction solution was analyzed by GC–MS, and products are given in the last entry of the table.

NMR data for 2,4,4-trimethyl-1-pentene ($H_2C{=}C(CH_3)CH_2C(CH_3)_3$): ^1H NMR (300 MHz, CD_2Cl_2) δ 4.83 and 4.62 (m, $=CH_2$), 1.94 (s, $-CH_2-$), 1.78 (s, $=C(CH_3)$), 0.92 (s, $C(CH_3)_3$); ^{13}C NMR (300 MHz, CH_2Cl_2) δ 144.3 and 113.6 (C=C), 51.7, 30.0.

For 2,4,4-trimethyl-2-pentene ($(CH_3)_2C{=}CHC(CH_3)_3$): ^1H NMR (300 MHz, CD_2Cl_2) δ 5.16 (m, =CH), 1.77 (m, $=C(CH_3)_2$), 1.08 (s, $C(CH_3)_3$).

For 2,2,4,6,6-pentamethyl-3-heptene ($(CH_3)_3CC(H){=}C(CH_3)CH_2C(CH_3)_3$): ^1H NMR (300 MHz, CD_2Cl_2) δ 5.10 (m, =CH), 1.88 (m, $=CCH_3$) and 1.80 (m, $=CCH_2-$), 1.11 (s, $C(CH_3)_3$), 0.90 (s, $C(CH_3)_3$); ^{13}C NMR (75.4 MHz, CH_2Cl_2) δ 138.9 and 132.1 (C=C), 55.6, 30.9, 29.9, 20.0.

For 1,1-bis(neopentyl)ethene ($H_2C{=}C(CH_2C(CH_3)_3)_2$): ^1H NMR (300 MHz, CD_2Cl_2) δ 4.79 (m, $=CH_2$), 1.93 (s, $=C(CH_2-)_2$), 0.90 (s, $(CH_3)_6$); ^{13}C NMR (300 MHz, CD_2Cl_2) δ 145.7 and 115.7 (C=C), 51.4, 29.8. Other products present were not identified by ^1H NMR. Later experiments revealed that $C_{16}H_{32}$ isomers yield similar ^1H NMR spectra as does 2,2,4-trimethyl-1-pentene. Therefore the yield of this olefin reported in Table 1B may be high.

Isobutene Oligomerization in CD_3CN. $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)](CF_3SO_3)$, 1 (13 mg, 0.021 mmol), was dissolved in 0.8 mL of CD_3CN in a NMR tube. Isobutene (80 Torr, 0.64 mmol) was transferred to the tube, and the tube was sealed under vacuum at −196 °C. The reaction was heated at 70 °C and monitored by ^1H NMR spectroscopy. Products were formed at a rate similar to that observed for the room temperature reaction of 1 in dichloromethane, Table 1B.

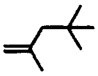
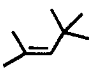
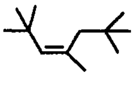
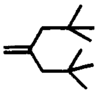
In a similar reaction, isobutene (60 Torr, 0.48 mmol) was added to an acetonitrile solution of 1 (15 mg, 0.021 mmol) and the reaction was maintained at room temperature. After 3 weeks 10% of the isobutene had been converted to 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene.

Isobutene Oligomerization in Carbon Tetrachloride. Complex 1 (17 mg, 0.022 mmol) was slurried in CCl_4, and isobutene (~2.0 mmol) was transferred to the NMR tube. The slurry was frozen at −196 °C, and the tube was sealed under vacuum. The reaction was heated at 50 °C for 26 days. GC–MS indicated that ~2% of the isobutene remained and the following products were present: 2,4,4-trimethyl-1-pentene, 19%; 2,4,4-trimethyl-2-pentene, 5%; three major $C_{12}H_{24}$ isomers, 62%; several isomers of $C_{16}H_{32}$, 9%.

Reaction of Isobutene with HCl. Isobutene (ca. 300 Torr, 2.4 mmol) and HCl (20 Torr, 0.16 mmol) were transferred to a NMR tube containing 0.8 mL of CD_2Cl_2. The tube was sealed under vacuum at −196 °C. Excess isobutene and *tert*-butyl chloride were detected in the ^1H NMR spectrum after 5 min at ambient temperature. No further reaction was observed after 3 days at ambient temperature.

Reaction of Isobutene with Triflic Acid in CD_2Cl_2. Isobutene (ca. 350 Torr, 2.8 mmol) and triflic acid (2 μL, 0.022 mmol) were dissolved in 0.8 mL of CD_2Cl_2 in a NMR tube. The tube was sealed under vacuum at −196 °C. ^1H NMR indicated a reaction had occurred and was complete within 5 min at ambient temperature. The spectrum indicated that mostly alkanes were present. GC–MS detected a mixture of alkanes including C_8H_{18}, C_9H_{20}, ..., $C_{20}H_{42}$ and possibly higher molecular weight alkanes. A small amount of alkenes were also detected. Isobutene was not detected by ^1H NMR or GC–MS.

Table 2. Qualitative Rate of Isobutene Oligomerization by Triflic Acid[a] in CH_2Cl_2 at 25 °C

reacn time (days)	% of olefins present				
					
0	100				
1	97	3	trace[b]		
2.7	95	4	1		
4	92	7	1		
5	92	7	1		
18	87	11	2	trace	trace
27	88	9	2	trace	trace

[a] See Experimental Section for concentrations of reagents. [b] Products identified by GC–MS.

Reaction of Isobutene with Trace Triflic Acid in CD_2Cl_2. Isobutene (125 Torr, 1.0 mmol) was transferred to a NMR tube which contained 2.0×10^{-5} mmol of triflic acid in 1 mL of CD_2Cl_2. The tube was sealed under vacuum at −196 °C. The reaction was monitored at ambient temperature for 60 days by ^1H NMR spectroscopy. The oligomerization of isobutene occurred at a slow rate for ~18 days, and then the reaction stopped. After 60 days the ^1H NMR spectrum indicated that 0.87 mmol (87%) of isobutene was still present in the reaction mixture. GC–MS detected the oligomerized products shown in Table 2.

Reaction of Isobutene with Trace Triflic Acid in CD_3CN. Isobutene (60 Torr, 0.5 mmol) was transferred to a NMR tube, which contained triflic acid (1.0×10^{-4} mmol) in CD_3CN (1 mL). The tube was sealed under vacuum at −196 °C. The reaction was periodically monitored by ^1H NMR at ambient temperature over a period of 5 months. No reaction was observed to occur.

Oligomerization of α-Methylstyrene by $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)](CF_3SO_3)$, 1. Complex 1 (10 mg, 0.016 mmol) and α-methylstyrene (23 μL, 0.18 mmol) were dissolved in 0.8 mL of CD_2Cl_2 in a NMR tube. The tube was sealed under vacuum at −196 °C. After 5 days at ambient temperature, ^1H NMR analysis detected only trace amounts of the original olefin. The reaction was left at ambient temperature for 30 days. The reaction solution was analyzed by GC–MS. The following products were detected: three $C_{18}H_{20}$ isomers of yields 27%, 24%, and 2%; two $C_{27}H_{30}$ isomers of yields ~33% and 11%. Approximately 3% of the monomer was detected. MS (FAB) analysis of the Mo complexes present, *m/e*: 819 $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_{27}H_{31})]^+$, weak; 701 $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_{18}H_{21})]^+$; 583 $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_9H_{11})]^+$.

Oligomerization of Isoprene by $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)](CF_3SO_3)$, 1. Complex 1 (15 mg, 0.024 mmol) and isoprene (200 μL, 2.0 mmol) were dissolved in 0.8 mL of CD_2Cl_2 in a NMR tube. The tube was sealed under vacuum at −196 °C. The reaction was monitored by ^1H NMR at ambient temperature for 23 days. Isoprene insertion into the S–H bond of 1 was observed to be complete within 20 min. After several days, broad multiplets between 0.5 and 2.5 ppm appeared, indicating the formation of isoprene oligomerization products. After 23 days at ambient temperature, ^1H NMR indicated a large amount of isoprene was still present. The reaction was heated at 70 °C for 5 days. Volatiles of the reaction were vacuum transferred to a second NMR tube and analyzed by ^1H NMR and GC–MS. A trace amount of isoprene was detected. GC–MS analysis detected a ca. 1:1 ratio of $C_{10}H_{16}$ and $C_{15}H_{24}$ products. Specific isomers formed were not identified. The residue was washed with CCl_4. The CCl_4 wash was analyzed by GC–MS. GC–MS detected $C_{15}H_{24}$, $C_{20}H_{32}$, and $C_{25}H_{40}$ isomers in the CCl_4 wash, in a ca. 2:2:1 ratio respectively. An accurate ratio of all oligomerization products formed could not be obtained. The MS (FAB) spectra of the residue after the CCl_4 wash is shown in Figure 1: *m/e* 805, parent of $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_{25}H_{41})]^+$, weak; *m/e* 737, parent of $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_{20}H_{33})]^+$; *m/e* 669, parent of $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_{15}H_{25})]^+$; *m/e* 601, parent of $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_{10}H_{17})]^+$; *m/e* 533, parent of $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_5H_9)]^+$.

Reaction of $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)](CF_3SO_3)$, 1, with Excess 2-Methyl-1-butene. Complex 1 (14 mg, 0.023 mmol) was dissolved in 0.8 mL of CD_2Cl_2 in a NMR tube. 2-Methyl-1-butene (40 μL, 0.37 mmol) was added to the NMR tube, and the tube was sealed under vacuum at −196 °C. After 6 h at ambient temperature, ^1H NMR indicated that 93% of the 2-methyl-1-butene had isomerized to 2-methyl-2-butene. After 3.5 months at ambient temperature no olefin oligomerization products were detected. A similar reaction was heated at 70 °C for 2 months. The volatiles were vacuum transferred to a second NMR tube and analyzed by ^1H NMR. Integration indicated ~70% of the volatiles were 2-methyl-2-butene and 2-methyl-1-butene in a 9:1 ratio, respectively. GC–MS analysis of the volatiles detected four major isomers of $C_{10}H_{20}$. Higher oligomerization products were not detected.

Reaction of $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH(CH_3)_2)](CF_3SO_3)$ with Excess Propylene at 70 °C. Attempted Oligomerization of Propylene. The title complex[1] (15 mg, 0.023 mmol) was dissolved in 0.8 mL of CD_2Cl_2 in a NMR tube. Propylene (25 Torr, 0.20 mmol) was transferred to the NMR tube, and the tube was sealed under vacuum at −196 °C. The reaction was heated at 70 °C for 2 months. The reaction progress was monitored by ^1H NMR spectroscopy. After 2 days small resonances between 1 and 2 ppm appeared. However, after their initial appearance, the intensities of these peaks did not increase. The *n*-propanethiolate complex slowly formed during the 2-month period. Yield: 20%. No other reaction was observed to occur.

Reaction of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCMe_3)]OTf$, 2, with Br^-. Complex 2 (0.014 g, 0.022 mmol) and LiBr (~0.030 g, 0.2 mmol) were dissolved in CD_3CN, and the solution was added to two NMR tubes. One tube was purged with N_2 and the other with ethylene. The reaction without ethylene proceeded slowly to form *t*-BuBr and $((CpMo(\mu\text{-}S))_2S_2CH_2$, which was only slightly soluble in acetonitrile. The reaction with ethylene proceeded within seconds to form $[(CpMo)_2(S_2CH_2)(SC_2H_4SCMe_3)]^+$ as shown in eq 2.[4] This product reacted further to form *t*-BuBr and $(CpMo)_2(SC_2H_4S)(S_2CH_2)$ which was not very soluble in CD_3CN. The qualitative rate of formation of *t*-BuBr in each reaction was monitored by comparing peak intensities to those of the solvent as the internal standard, and by comparing the percentage of *t*-Bu resonance present as *t*-BuBr. For the reaction under nitrogen, *t*-BuBr accounted for 8% and 22% of the *t*-Bu resonances after 3 and 5 h, respectively. For the reaction under ethylene, *t*-BuBr accounted for 19% and 42% of the *t*-Bu resonances after 3 and 5 h, respectively.

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