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Activation and Chain-carrying CH_2 Species in Terminal Alkene Metathesis on Molybdena–Titania Catalysts

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The metathesis reaction of terminal alkenes other than isobutene took place on MoO_{3-x}/TiO_2, whereas that of isobutene proceeded in the presence of ethylene and following treatment of the catalyst with $SnMe_4$ at room temperature. These results infer that chain-carrying CH_2 species are generated to only a small extent by the adsorption of isobutene on MoO_{3-x}/TiO_2, although they are formed by the adsorption of alk-1-enes and $SnMe_4$. The metathesis-inactive material, fully oxidized MoO_3/TiO_2, was changed to a metathesis-active catalyst by treating it with $SnMe_4$. This suggests that MoO_3/TiO_2 has no ability to yield CH_2 species with terminal alkenes but that these species can be supplied with $SnMe_4$. An analysis by X-ray photolectron spectroscopy infers that $SnMe_4$ adsorbed on MoO_3/TiO_2 releases methyl groups concomitant with the oxidation of Sn.

At the present time, a mechanism proceeding *via* metal–alkylidene and metallacyclobutane intermediates is accepted as an approved route for catalytic alkene metathesis reactions.[1] In fact, some non-Fischer-type metal–alkylidene complexes[2] have been found to promote metathesis-like reactions, and metallacyclobutane derivatives of Ti[3] and W[4] undergo metathesis-like reactions with alkenes. It has also been shown by means of n.m.r. spectroscopy that the neopentylidene ligand in a tungsten complex is replaced by ethylidene and propylidene ligands on reaction with pent-2-ene.[5] Homogeneous catalysts for alkene metathesis sometimes require a cocatalyst, such as the addition of $EtAlCl_2$ to WCl_6,[6] and the role of Lewis acids or hard ligands in the cocatalysts is interpreted in terms of electronic effects due to the central metal.[5,7] Unlike the electronic effect produced by electron-deficient molecules, the activation of WCl_6 by $ZnMe_2$ may be caused by the formation of $W{=}CH_2$ species in the reaction with $ZnMe_2$.[8] Similar phenomena have been found using Cp_2TaMe_3[2b] and $CpTiCl_2$[9] treated with $AlCl_3$. On the other hand, alkene metathesis on heterogeneous catalysts proceeds in general by contact with the alkenes. This fact implies that the key intermediates for alkene metathesis, metal alkylidenes, are produced automatically in the initial stages of the reaction by contact with the alkenes. If this is the case, whether or not a solid surface is active for alkene metathesis should be determined by the ability for the alkylidene formation process to take place. In this paper we will demonstrate that alkylidene formation is a significant step in heterogeneous alkene metathesis.

Experimental

Catalyst Preparation

Molybdena–titania catalysts were prepared by immersing β-titanic acid, $TiO_2 \cdot H_2O$, into an aqueous solution of ammonium paramolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The solid was then dried at 120 °C in air for 12 h, and its MoO_3 content was found to be 6.7 wt%. Details of the preparation of β-titanic acid have been described previously.[10]

Freshly prepared catalyst was oxidized with O_2 (*ca.* 200 Torr, 1 Torr = 101325/760 Pa) at 500 °C for 1 h, which resulted in the fully oxidized MoO_3TiO_2 catalyst. Partially reduced MoO_{3-x}/TiO_2 ($0.1 < x < 0.7$) was prepared by reoxidizing a MoO_x/TiO_2 catalyst (reduced with H_2; 100–200 Torr, 500 °C, 1 h) with a 1:1 mixture of N_2O and H_2 at *ca.* 300 Torr and 200 °C for 1 h.[10] Prior to the catalytic reaction or treatment with $SnMe_4$, the catalyst was evacuated at 500 °C for 1 h.

Reactions and Product Analysis

Pretreatment of the catalyst and the reaction were performed in a closed glass circulation system with a volume of *ca.* 260 cm^3. 0.5 g of catalyst was treated with diluted $SnMe_4$ (5 Torr of $SnMe_4$ in *ca.* 60 Torr of He) for 30 min at room temperature, and this was followed by evacuation at the same temperature for 30 min.[11] Metathesis was carried out at room temperature with an alkene pressure between 4 and 65 Torr. Analysis of ethylene, propene, but-1-ene, isobutene, but-2-ene, hex-3-ene and 2,3-dimethylbut-2-ene was performed using a gas-chromatograph with a 13 m length column comprising Sebaconitrile (25%) on Uniport C (60–80 mesh), while for methane, ethane and ethylene the column comprised 2 m of Gaskuropack 54 (a copolymer of polystyrene and divinylbenzene, commercially available from Gasukuro Kogyo Co.). Deuterium atom distributions in the alkene products were calculated by mass-spectrometric analysis with an ionization voltage of 10–15 eV. [$^2H_4$]Ethylene, [$^2H_6$]propene (Merck Sharp & Dohme) and [$^{13}C_2$]ethylene (Amersham International, 92% ^{13}C) were used without further purification. [$^2H_8$]But-1-ene was prepared by deuteration of commercially available [$^2H_4$]butadiene on ZnO at room temperature. [$^2H_8$]Isobutene was obtained by reacting isobutene with deuterium gas at room temperature on Mg $(OH)_2$ evacuated at 450 °C. The prepared samples of [$^2H_8$]but-1-ene and [$^2H_8$]isobutene were purified using gas-chromatographic separation.

X.P.S. Analysis

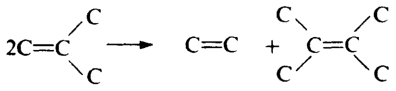
X-Ray photoelectron spectra of the catalyst were measured with a VG-ESCA 3 spectrometer. MoO_3/TiO_2 powder was compressed into a disc and was mounted on a Ni holder with an internal standard Au wire. The catalyst was treated in the preparation chamber using the same procedure as performed in the circulation system. However, the adsorption of tetramethyl tin on the MoO_3/TiO_2 disc was performed at liquid-nitrogen temperature (*ca.* -190 °C). Binding energy (E_b) values were referenced to the O 1*s* peak at 530 eV, and $2p_{3/2}$ for Ti^{4+} was found to be at 458.7 eV, in good agreement with the value reported for Ti^{4+} on TiO_2.[12]

Results and Discussion

Alkene Metathesis on MoO_{3-x}/TiO_2 and MoO_{3-x}/TiO_2–$SnMe_4$

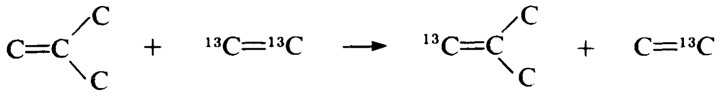
Table 1 summarises turnover frequencies for the metatheses of ethylene, propene, but-1-ene and isobutene on MoO_{3-x}/TiO_2 and MoO_{3-x}/TiO_2–$SnMe_4$ at room temperature. The turnover frequencies are evaluated by assuming that all the Mo cations on TiO_2 participate in metathesis. Therefore the true turnover frequencies should be larger than those in table 1. It is of interest that ethylene, propene and but-1-ene undergo metathesis, whereas for isobutene, metathesis was entirely prohibited and the polymerization of isobutene occurred on MoO_{3-x}/TiO_2. This polymerization may be cationic, *via* the tertiary butyl cation, or it may be an addition polymerization of α-alkenes *via* a Ziegler–Natta mechanism on reduced TiO_x. Despite the fact that the metathesis of isobutene does not proceed on MoO_{3-x}/TiO_2, when a 1:1:1 mixture of isobutene,

Table 1. Turnover frequencies of metathesis reactions of ethylene, propene, but-1-ene and isobutene on MoO_{3-x}/TiO_2 and MoO_{3-x}/TiO_2–$SnMe_4$ at room temperature

metathesis reaction	MoO_{3-x}/TiO_2	MoO_{3-x}/TiO_2–$SnMe_4$
$CH_2{=}CH_2 + CD_2{=}CD_2 \longrightarrow 2\ CH_2{=}CD_2$	3.2×10^{-5}	1.9×10^{-3}
$2C{=}C{-}C \longrightarrow C{=}C + C{-}C{=}C{-}C$	2.0×10^{-7a}	5.4×10^{-4a}
$2C{=}C{-}C{-}C \longrightarrow C{=}C + C{-}C{-}C{=}C{-}C{-}C$	7.9×10^{-6}	2.0×10^{-5}
	0	3.3×10^{-3}

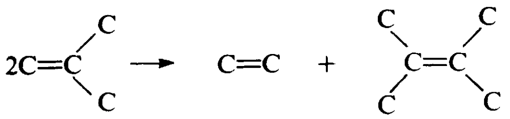
[a] Ref. (11). Turnover frequencies (ethylene molecules per Molybdenum ration per second) were obtained by assuming that all Mo cations participate in metathesis.

[$^{12}C_2$]ethylene and [$^{13}C_2$]ethylene was added on MoO_{3-x}/TiO_2 at room temperature, [$^{13}C_1$]ethylene and [$^{13}C_1$]isobutene were formed by the following metathesis reaction (see fig. 1):



(1*a*)

$$C{=}C + {}^{13}C{=}{}^{13}C \longrightarrow 2C{=}{}^{13}C \qquad (1b)$$



(1*c*)

[$^{13}C_1$]ethylene is produced by the reactions (1*a*) and (1*b*), and reaction (1*a*) yields equal amounts of [$^{13}C_1$]isobutene and [$^{13}C_1$] ethylene. Accordingly, reaction (1*b*) is *ca.* 10 times faster than reaction (1*a*). 2,3-Dimethyl but-2-ene was formed distinctly [reaction (1*c*)] in the co-metathesis of isobutene and ethylene on MoO_{3-x}/TiO_2; however, its rate was extremely slow. From these results it is concluded that the metathesis of isobutene proceeds on MoO_{3-x}/TiO_2 in the presence of ethylene. Such a phenomenon can be interpreted as follows. Any metal alkylidene species required for alkene metathesis are not produced on MoO_{3-x}/TiO_2 by the adsorption of isobutene; however, the adsorption of ethylene gives a metal alkylidene species on the surface. As a result, the metathesis of isobutene can proceed in the presence of ethylene *via* the alkylidene species furnished from ethylene in the initiation steps. The fact that polymerization of isobutene is suppressed in the presence of ethylene while simultaneously metal alkylidene is supplied from ethylene under such conditions suggests that the metal alkylidene formation might proceed through a metal alkyl species formed by a reaction between ethylene and hydrogen species which yields the tertiary carbonium cation on the MoO_{3-x}/TiO_2 catalyst.

When MoO_{3-x}/TiO_2 was treated with $SnMe_4$ at room temperature, it changed to a super-active alkene metathesis catalyst. The turnover frequency for the metathesis of propene was enhanced more than three orders of magnitude, and those of ethylene and but-1-ene were increased by factors of *ca.* 10^2 and 3, respectively. Note that the

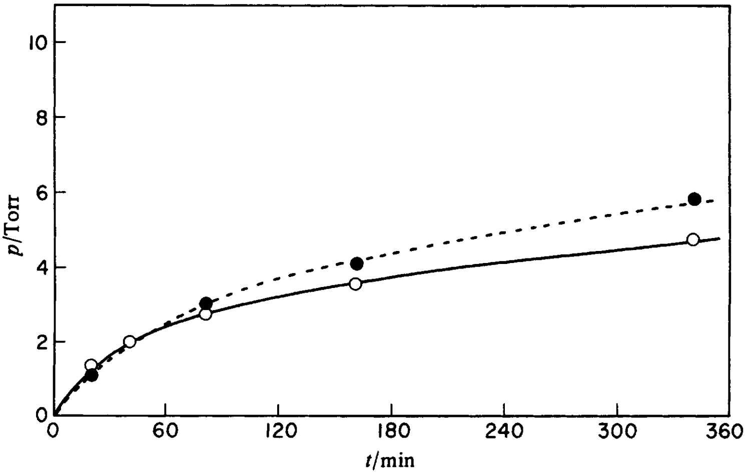


Fig. 1. Metathesis of a 1:1:1 mixture of isobutene, ethylene and $[^{13}C_2]$ethylene on MoO_{3-x}/TiO_2 at room temperature: ○, $[^{13}C_1]$ethylene [reaction (1*a*)]; ●, $[^{13}C_1]$isobutene, × 10 [reactions (1*b*) and (1*c*)]: total pressure, 48 Torr; catalyst 0.5 g.

metathesis of isobutene proceeded on MoO_{3-x}/TiO_2–$SnMe_4$. This result clearly indicates that chain-carrying metal alkylidene species are formed on the MoO_{3-x}/TiO_2 surface by the adsorption of $SnMe_4$.

When a 1:1 mixture of $[^2H_0]$- and $[^2H_4]$-ethylene, $[^2H_0]$- and $[^2H_6]$-propene or $[^2H_0]$- and $[^2H_8]$-but-1-ene was added on MoO_{3-x}/TiO_2 at room temperature, neither the hydrogen-scrambling nor the double-bond shift reactions occurred during metathesis. In contrast, when a 1:1 mixture of $[^2H_0]$- and $[^2H_8]$isobutene was reacted on MoO_{3-x}/TiO_2 at room temperature, hydrogen scrambling proceeded rapidly, concurrent with polymerization. This result may be due to a rapid equilibration between isobutene and the butyl carbonium cation, in which three equivalent methyl groups can participate in hydrogen exchange. When a 1:1 mixture of $[^2H_0]$- and $[^2H_8]$-isobutene was reacted on MoO_{3-x} TiO_2–$SnMe_4$ at room temperature, metathesis occurred with little hydrogen mixing; *i.e.* the productive metathesis of isobutene [reaction (2*a*)] yielded ethylene composed of $[^2H_0]$, $[^2H_2]$ and $[^2H_4]$ isomers and 2,3-dimethylbut-2-ene composed of $[^2H_0]$ $[^2H_6]$ and $[^2H_{12}]$ isomers, and the degenerate metathesis [reaction (2*b*)] gave $[^2H_2]$- and $[^2H_6]$isobutene:

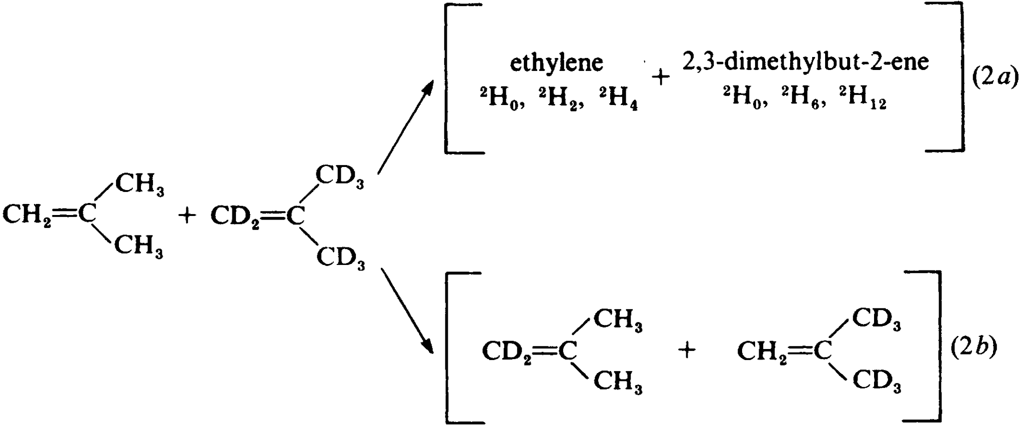


Table 2. Initial formation rates of methane, and ratios of ethane to methane formed in the early stages of the reaction of $SnMe_4$ (5 Torr) on molybdena–titanias (0.5 g of each) at room temperature

catalyst	CH_4 formation rate /(molecules Mo)$^{-1}$ s^{-1}	initial C_2H_6/CH_4 ratio
MoO_3/TiO_2	6.3×10^{-6}	4.0
MoO_{3-x}/TiO_2	4.0×10^{-6}	0.5
MoO_x/TiO_2	2.5×10^{-5}	0.0_3

From this result it is deduced that the activation of MoO_{3-x}/TiO_2 with $SnMe_4$ is responsible for the introduction of chain-carrying CH_2 species on the surface and that the adsorption of $SnMe_4$ inhibits the formation of t-butyl carbonium ions on acidic sites. Note that the treatment of inactive MoO_3/TiO_2 with $SnMe_4$ results in the formation of an active catalyst for the metathesis of isobutene, as well as of ethylene, propene and but-1-ene at room temperature. In addition, productive and degenerate metathesis occurred selectively on the catalyst in a 1:1 mixture of [$^2H_0$]- and [$^2H_8$]-isobutene.

Reaction of $SnMe_4$ on Molybdene Titania

As discussed above, the role of $SnMe_4$ in activating molybdena–titania is undoubtedly to graft the CH_2 chain-carrying species required for alkene metathesis. When $SnMe_4$ was contacted with a molybdena–titania surface at room temperature, small amounts of methane, ethane and ethylene were evolved. Table 2 shows the rate of methane formation and the ratio of C_2H_6 to CH_4 obtained in the initial stage of the reaction with $SnMe_4$ on MoO_3/TiO_2, MoO_{3-x}/TiO_2 and MoO_x/TiO_2. Not such a big difference is seen in the rate of methane formation on these catalysts, but the initial C_2H_6/CH_4 ratios strongly depend on the extent reduction of molybdenum oxide, *i.e.* ethane formation selectively proceeds on MoO_3/TiO_2. The turnover frequency of propene metathesis was 9.3×10^{-5} on MoO_3/TiO_2–$SnMe_4$. Consequently, CH_2 species may be produced on the MoO_3/TiO_2 surface by the reaction of $2CH_3 \rightarrow CH_4 + CH_2$.

A reductive coupling of CH_3 giving ethane, $2CH_3 \rightarrow C_2H_6$, may occur also on the MoO_3/TiO_2 surface. So far, five different modes of alkyl metal cleavage have been proposed:[10] (i) β-elimination, (ii) reductive coupling, (iii) α-elimination, (iv) hydrogen and alkyl transfer and (v) electrophilic attack.[13] Cases (ii), (iii) and (iv) are relevant to the reaction of $SnMe_4$ on molybdenum oxides on TiO_2. If the reductive coupling occurs on MoO_3/TiO_2 in the reaction with $SnMe_4$, the valence states of Sn and Mo should be of considerable interest. The X-ray photoelectron spectra of the Sn 3*d* region are shown in fig. 2. When MoO_3/TiO_2 was exposed to $SnMe_4$ with 60 [1 L (1 langmuir) = 1×10^{-6} Torr s] at liquid-nitrogen temperature, the peaks indicated as species I were observed at *ca.* 483 and 492 eV; these correspond to a $3d_{5/2}$ and $3d_{3/2}$ doublet [fig. 2(*a*)] and were accompanied by weak peaks at *ca.* 486 and 495 eV indicated as species II. The peaks were little influenced by continuing X-irradiation for 30 min [fig. 2(*b*)]. However, if the MoO_3/TiO_2–$SnMe_4$ sample was left *in vacuo* overnight to reach room temperature, species II remained with the same intensity as in fig. 2(*a*) [see fig. 2(*c*)]. Species I corresponds to Sn^0;[14] however, the weak species II may be assigned to Sn^{2+} or Sn^{4+} because of their close binding energies.[14,15]

These results imply that monolayer adsorption of $SnMe_4$ results in the oxidation of the Sn species, giving ethane and leaving the $SnMe_4$ overlayer in the $Sn^{\delta+}$ state. The oxidation of Sn may compensate the reduction of Mo^{6+} in MoO_3/TiO_2. The X.p.s. band for Mo 3*d* did not appreciably change on adsorption of $SnMe_4$, perhaps because of the

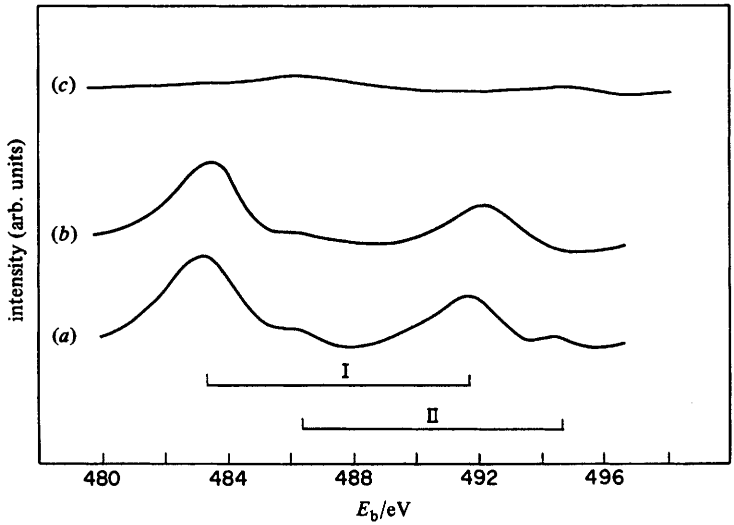


Fig. 2. X-Ray photoelectron spectra of the Sn 3*d* region following addition of $SnMe_4$ to MoO_3/TiO_2: (*a*) 60 L of $SnMe_4$ at *ca.* −190 °C; (*b*) under X-irradiation for 30 min; (*c*) at room temperature following (*b*).

Table 3. ^2H distribution of methane, ethane and ethylene formed after 30 min of the reaction of $SnMe_4$ (10 Torr) on an MoO_3/TiO_2 catalyst (1.0 g) at room temperature[a]

product	amount formed /mol	amount formed per total Mo	^2H distribution		
			$^2H_0$	$^2H_1$	$^2H_2$
methane	1.16×10^{-6}	2.5×10^{-3}	81.5	18.5	0
ethane	2.78×10^{-6}	6.0×10^{-3}	100.0	0	0
ethylene	0.20×10^{-6}	0.4×10^{-3}	96.2	3.8	0

[a] The H atoms on the surface were replaced by ^2H atoms. Amount of Mo in 1 g catalyst 4.66×10^{-4} mol.

amount of reduced Mo species. In the case of Re_2O_7/γ-Al_2O_3, reduction of the Re species by SnR_4 (where R = methyl, ethyl or butyl) is detected by e.s.r. spectroscopy.[16] Note that the reduction of the MoO_3/TiO_2 surface by $SnMe_4$ is not indispensable for activation: partially reduced MoO_{3-x}/TiO_2 is not so active for metathesis but is changed into a superactive catalyst by treatment with $SnMe_4$ as shown in table 1.

To clarify the role of $SnMe_4$, surface hydrogen on MoO_3/TiO_2 was exchanged with deuterium to 97 %, and was subjected to reaction with $SnMe_4$. The amount of methane, ethane and ethylene and their ratios to the total amount of Mo cation are listed in table 3. The amount of methane is *ca.* 0.25 % of that of the total amount of Mo cations. Methane involves 18.7 % CH_3D, but there is no deuterium present in ethane. 85 % of the [$^2H_0$]methane in table 3 should be formed by an α-hydrogen abstraction between two CH_3 groups supplied from $SnMe_4$, and [$^2H_1$]methane is formed by the reaction of the CH_3 group with deuterium atoms on on the surface:

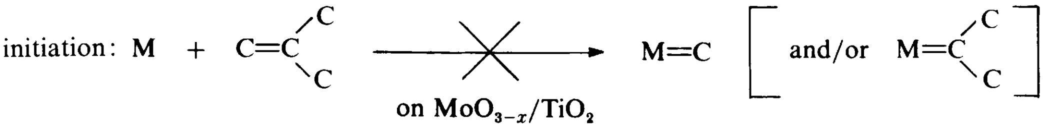
$$2CH_3 \rightarrow C_2H_6 \quad \text{(reductive coupling)}$$
$$2CH_3 \rightarrow CH_4 + CH_2 \quad (\alpha\text{-hydrogen abstraction})$$
$$CH_3 + OD \rightarrow CH_3D + [O] \quad \text{(hydrogen and methyl transfer).}$$

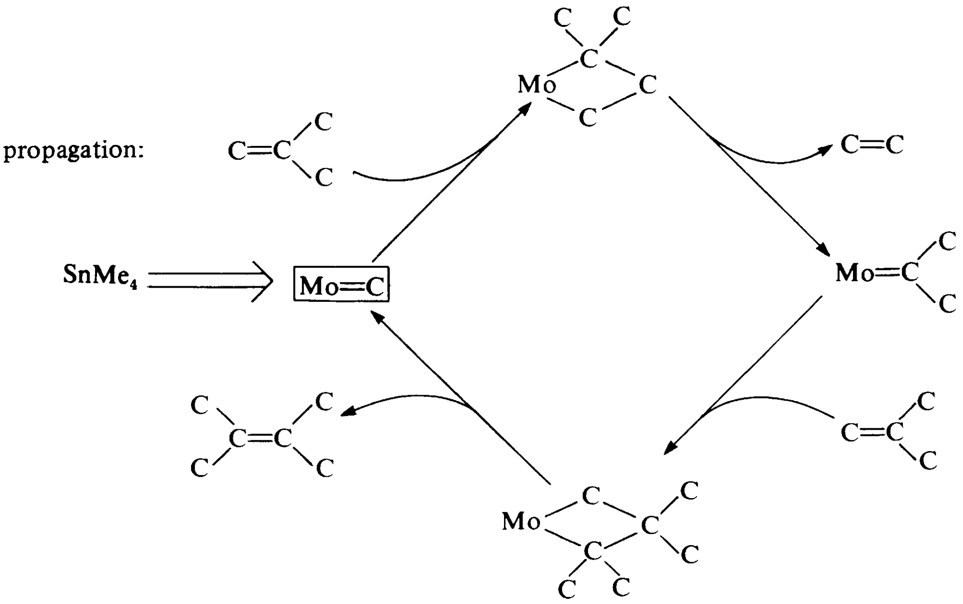
The abstraction of hydrogen from the CH_3 group results in a grafting of CH_2 species onto the surface. A similar phenomenon was reported in the homogeneous metathesis system, WCl_6–$ZnMe_2$, in which methane formation is noted in the activation of WCl_6 by $ZnMe_2$.[8] The formation of ethylene shown in table 3 may reflect the formation of CH_2 species during the activation process, because ethylene is formed either by coupling of two CH_2 species or by the insertion of CH_2 into M—CH_3 (M=Mo and/or Sn). The fact that the amount of [$^2H_1$]ethylene (3.8 %) is far lower than that of [$^2H_1$]methane (18.5 %) in fig. 3 seems to support the following processes:

$$CH_2 + CH_2 \rightarrow C_2H_4 \qquad \text{(}CH_2\text{ coupling)}$$

$$M{-}CH_3 + CH_2 \rightarrow M{-}CH_2 \rightarrow CH_3 \rightarrow M{-}H + C_2H_4 \qquad \text{(}CH_2\text{ insertion; (}\beta\text{-hydrogen abstraction).}$$

In conclusion, the formation of highly active metathesis catalysts by treatment with $SnMe_4$ may be explained by the introduction of chain-carrying CH_2 species on their surfaces. Here a ligand effect of $SnMe_4$ is not excluded, because the activity in homogenous catalysis is known to be enhanced by the ligand effect, but the remarkable enhancement of metathesis activity observed here is interpreted by the grafting of chain-carrying CH_2 species onto the catalysts. This conclusion is quite feasible in the case of isobutene metathesis observed on MoO_{3-x}/TiO_2: Alk-1-enes can furnish alkylidene species by being adsorbed on MoO_{3-x}/TiO_2, but isobutene cannot furnish such a key species on the surface. (This may eventually aid the alkylidene formation process on solid metathesis catalysts, so that metathesis of isobutene is not catalysed by MoO_{3-x}/TiO_2). However, if chain-carrying CH_2 species are supplied from alk-1-ene or from $SnMe_4$, the propagation process *via* CH_2 species proceeds. According to this mechanism, hydrogen mixing in alkenes is a side reaction, and the metathesis of a 1:1 mixture of [$^2H_0$]- and [$^2H_8$]-isobutene also proceeds with no hydrogen mixing on MoO_{3-x}/TiO_2–$SnMe_4$:





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