STUDIES ON OLEFIN METATHESIS WITH BINARY CATALYST SYSTEMS OF TUNGSTEN HEXACHLORIDE AND COCATALYSTS

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STUDIES ON OLEFIN METATHESIS WITH BINARY CATALYST SYSTEMS OF TUNGSTEN HEXACHLORIDE AND COCATALYSTS

A DISSERTATION
FOR
THE DEGREE OF DOCTOR OF ENGINEERING

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PREFACE

This dissertation has been carried out during 1974-1976 as a doctrate thesis under the direction of

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at the Institute of Applied Chemistry, Faculty of Engineering, Nagoya University.

This thesis presents the STUDIES ON OLEFIN METATHESIS WITH BINARY CATALYST SYSTEMS OF TUNGSTEN HEXACHLORIDE AND COCATALYSTS. The major purpose of this study is to develop the new reaction systems effective for olefin metathesis and to clarify the mechanism of this reaction.

The author wishes to express his sincere gratitude to Professor Kazuo Fukuzumi for his kind and fruitful suggestions and encouragement throughout the course of this work.

He thanks also Professor Dr. Toru Takagi of Hokkaido University and Dr. Tsuyoshi Nishiguchi for their valuable discussions.

He extends his thankfulness to Mr. Nobuo Ikeda, and the rest of members in the Laboratory of Professor Fukuzumi for their occasional discussions and hearty cooperations with him.

Finally, an acknowledgement must be made to my parents for their patience and understanding which permitted the completion of this work.

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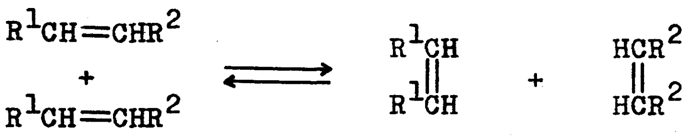
CHAPTER I
INTRODUCTION

1. Olefin Metathesis Reaction

The olefin metathesis reaction is one of the most remarkable catalytic reactions discovered in recent years.[1] In this reaction, olefin alkylidene moieties are redistributed according to Eq. 1. Catalysts used generally involve the combination of a transition metal salt or coordination complex with a compound of a non-transition metal. Both heterogeneous and homogeneous catalyst systems are known. The reaction is reversible, so that equilibrium can be reached from either side of reaction (1), and the distribution of products is then statistical. For example, metathesis of 2-heptene gives, at equilibrium, a 2-butene/2-heptene/5-decene mixture of 1/2/1. The metathesis reaction is essentially thermoneutral, involving just the making and breaking of carbon-carbon double bonds. This fact results from about the same enthalpies of formation of both reactant and product olefins. The thermal activation of this entropy-controlled reaction is symmetry forbidden according to the Woodward-Hoffmann rules.[2]



$$\begin{array}{c} R^1CH{=}CHR^2 \\ + \\ R^1CH{=}CHR^2 \end{array} \rightleftharpoons \begin{array}{c} R^1CH \\ \| \\ R^1CH \end{array} + \begin{array}{c} HCR^2 \\ \| \\ HCR^2 \end{array} \qquad (1)$$

2. Catalyst Systems

In 1964, Banks and Bailey reported the conversion of propylene to ethylene and n-butene over a heterogeneous catalyst consisting of molybdenum hexacarbonyl on alumina.[1] This was the first report of olefin metathesis. Subsequently, a great number of heterogeneous catalyst systems have been reported to be active for olefin metathesis.* Most of these are

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*There are several reviews on the field of heterogeneous olefin metathesis.[3-5]

normally composed of a ‘promoter’, molybdenum or tungsten oxides or carbonyls for instance, and a refractory ‘support’ having a high surface area, alumina or silica for instance. These catalysts prepared are generally activated at elevated temperature in a stream of dry or inert gas. Typical activation is carried out at 500 to 600°C for two to ten hours. The olefins are usually passed over the catalyst for several hours at high temperatures and pressures. For example, near equilibrium conversions, about 44%, were obtained in the metathesis of propylene over WO_3-SiO_2 at 425°C, 450psig, and 60 weight hourly space velocity.[6] Catalysts consisting of rhenium oxide on alumina are notable for their metathesis activity at relatively low temperature.[7]

In 1967, Calderon[8] reported the first use of a homogeneous catalyst system. The preferred catalyst was obtained by the interaction of WCl_6, ethanol and $EtAlCl_2$. Since Calderon’s system was announced, numerous other homogeneous systems have been reported*. Most of these systems involve a soluble mixture of a transition metal component and a cocatalyst. Reactions with these catalysts are normally run in benzene or chlorobenzene at room temperature.

Some of the more important homogeneous catalyst systems are summerized in Table 1. These catalyst systems can be categorized into five classes from A to E. This study deals with the olefin metathesis catalyzed by the WCl_6-cocatalyst systems in Class A.

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*There are several reviews on the field of homogeneous olefin metathesis.[9-12] The question of homogeneity of the WCl_6-alkylmetal system is not resolved.[13-15]

Table 1. Homogeneous Metathesis Catalysts

Class	Transition metal component	Cocatalyst	References
A. Transition metal halide or oxyhalide-based binary system			
	WCl_6	$EtAlCl_2 + EtOH$	8,16
	WCl_6	Et_3Al	17,18
	WCl_6	$Et_3Al_2Cl_3$	19
	WCl_6	nBuLi	20
	WCl_6	nBuMgI	21
	WCl_6	nPrMgBr	22
	WCl_6	nBu_4Sn, Me_4Sn	23
	WCl_6	$LiAlH_4, NaBH_4$	24,25
	$WOCl_4$	$EtAlCl_2$	26
	$WOCl_4$	nBu_4Sn	27
	$ReCl_5$	nBu_4Sn	28
	WBr_5	$EtAlCl_2$	29
	WCl_4	$AlCl_3$	9,30
	WCl_6, WBr_5	$AlCl_3, AlBr_3$	9,31
B. Transition metal carbonyl compound-based binary system			
	$W(CO)_5PPh_3$	$AlCl_3$	26
	$W(CO)_3(PPh_3)_2Cl_2$	$EtAlCl_2, AlCl_3$	32,33
	$W(CO)_5L$ ($L=CO, PPh_3, P(nBu)_3, P(OPh)_3$)	$EtAlCl_2 + O_2$	34-36
	$W(CO)_4(PPh_3)_2$	$EtAlCl_2 + O_2$	34
	$W(CO)_5CH_3CN$	$EtAlCl_2, AlCl_3$	37

Table 1. Homogeneous Metathesis Catalysts (Continued)

Class	Transition metal component	Cocatalyst	References
	$nBu_4NM(CO)_5COR$ (M=Mo,W; R=Me,Ph)	$MeAlCl_2$	38
	$nBu_4N^+(M(CO)_5X)^-$ (M=Cr,Mo,W; X=Cl, Br,OCOR)	$RAlCl_2$,$Me_3Al_2Cl_3$ (R=Me,Et)	38
	$An^+((CO)_5M\text{-}M'(CO)_5)^{n-}$ (A=alkali metal,NR_4; M=Mo, W; M'=Mo,W,Mn,Re; n=1,2)	$MeAlCl_2$ + R_4NCl (R=alkyl)	39
	$Re(CO)_5X$ (X=Cl,Br)	$RAlCl_2$ (R=Me,Et)	40
	$Mo(CO)(PPh_3)_2$	$AlCl_3$	41
C. Transition metal nitrosyl compound-based binary system			
	$M(NO)_2Cl_2L_2$ (M=Mo,W; L=Py,PPh_3,Ph_3PO,$AsPh_3$)	$EtAlCl_2$,$R_3Al_2Cl_3$ (R=Me,Et)	42-45
D. Other binary system			
	WCl_4Py_2	$EtAlCl_2$ (+CO)	32
	$W(C_2H_4(PPh_3)_2)Cl_3$	$EtAlCl_2$ (+CO)	32
	$MoCl_4L_2$ (L=PPh_3,Py,nPrCN)	$Me_3Al_2Cl_3$ + NO	43
	$MoCl_3(PhCO_2)_2$	$Me_3Al_2Cl_3$ + NO	43
	$MoCl_5$,$MoOCl_3$	$Me_3Al_2Cl_3$ + NO	43
	$MoN_2(PPh_3)_2$(toluene)	$AlCl_3$,$AlBr_3$	41
	$PhWCl_3$	$AlCl_3$	46-49

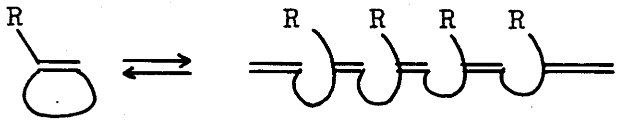
Table 1. Homogeneous Metathesis Catalysts (Continued)

Class	Transition metal component	Cocatalyst	References
	$W(CH_2Ph)_4$	$AlCl_3$,$EtAlCl_2$	50
E. Transition metal system without apparent cocatalyst			
	$W(CO)_3$(toluene)	None	51
	$PhWCl_3$	None	46
	$W(CO)_6 + CCl_4 + h\nu$	None	52-54
	$R_2C{=}W(CO)_5$ (R=Ph,tolyl)	None	55-59

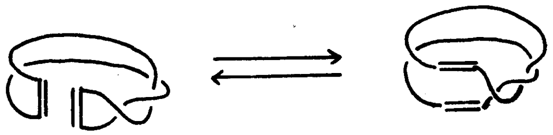
3. Reactant Olefins

Metathesis of acyclic mono-olefins, both linear and branched, has been reported. Acyclic unsaturated hydrocarbons containing more than one olefinic bond also undergo the olefin metathesis reaction. They can react either intermolecularly or intramolecularly. The metathesis of functional olefins is thus far little exploited. Examples reported are the metathesis of unsaturated fatty acid esters[60-65] such as methyl oleate and methyl linolate, that of acrylonitrile and propylene,[66] that of 5-bromo-1-pentene and 2-pentene,[67] that of p-chlorostyrene and 2-pentene,[67] and that of 3-pentenenitrile.[68] ω-Arylolefins[38,69] and ω-cyclohexenylolefins[38] are perfectly satisfactory substrates for the metathesis. Unsaturated polymer is degradated to low-molecular-weight species by olefin metathesis with low molecular olefins such as 4-octene.[70-75] Such a reaction has been used to characterize polymer structures.

Cyclic olefins except cyclohexene undergo ring-opening polymerization* by the metathesis to yield polyalkenamer. Cyclic trisubstituted olefins such as 1-methylcyclobutene can be polymerized to perfectly alternating polymers[57] (Eq. 2). One elegant application of metathesis involves the preparation of interlocking ring systems such as catenanes from cyclic olefins such as cyclododecene as shown in Eq. 3.[79-81]

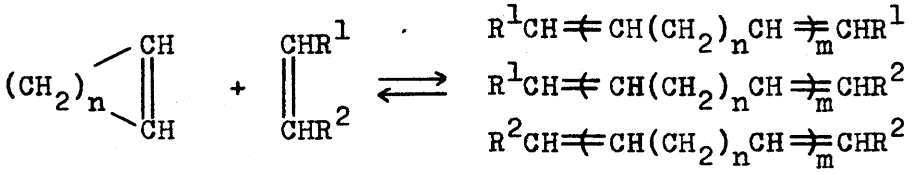


(2)



(3)

The cross metathesis of cyclic mono-olefin with acyclic mono-olefin provides three homologous series (symmetric/unsymmetric/symmetric) of polyenes (Eq. 4).[27,82,83]



(4)

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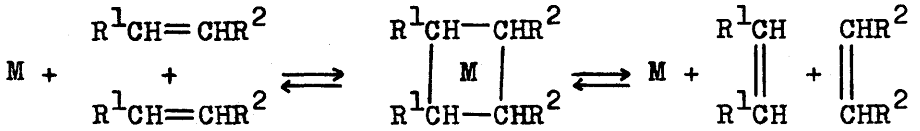
*There are several reviews on the area of ring-opening polymerization of cyclic olefins.[76-78]

Acetylenes are metathesized over a heterogeneous catalyst.[84] Metathesis of 1-alkyne has also been observed when the proper reaction conditions are chosen, but cyclotrimerization has occurred as a quantitatively more important reaction.[85] The metathesis of aromatic disubstituted acetylenes has been catalyzed by a homogeneous catalyst.[86] Cyclododecyne has been converted to oligomers in the presence of the metathesis catalyst.[87]

The industrial potential of the olefin metathesis is considerable.*

4. Mechanistic Studies

Early isotope-labeling experiments established that olefin metathesis proceeded by transalkylidenation rather than by transalkylation.[16,89] Transalkylidenation is consistent with a "four-center" process. Bradshow[90] concluded that their results with heterogeneous catalyst systems supported a "quasicyclobutane" intermediate (Eq. 5).



$$M + \begin{array}{c} R^1CH{=}CHR^2 \\ + \\ R^1CH{=}CHR^2 \end{array} \rightleftharpoons \begin{array}{c} R^1CH-CHR^2 \\ |\;\; M \;\;| \\ R^1CH-CHR^2 \end{array} \rightleftharpoons M + \begin{array}{c} R^1CH \\ \| \\ R^1CH \end{array} + \begin{array}{c} CHR^2 \\ \| \\ CHR^2 \end{array} \qquad (5)$$

Kinetic studies have been done in the metathesis of propylene over a $CoO\text{-}MoO_3\text{-}Al_2O_3$ catalyst, where the rates are consistent with a two-sites mechanism.[91]

Mango[92] described that a transition metal complex, having atomic d orbitals of the proper symmetries and an available electron pair, can switch a symmetry-forbidden (2+2) cycloaddition to a symmetry-allowed transformation. Thus, the electron pair in the olefin π_{AS} orbital is delocalized into the metal d_{zx} orbital while simultaneously electron density from the metal d_{zy} orbital is donated to the incipient olefin σ_{SA}-bonding combination (Fig. 1).

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*There is a review on the application of the olefin metathesis.[88]

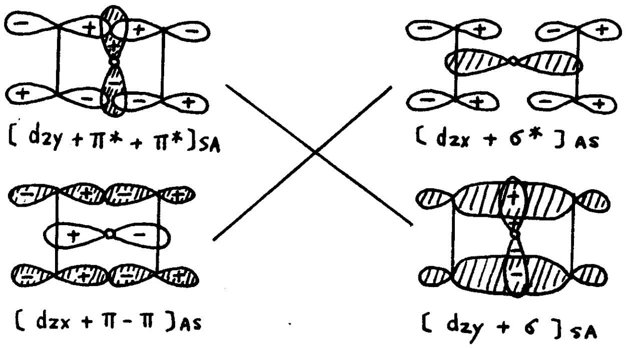
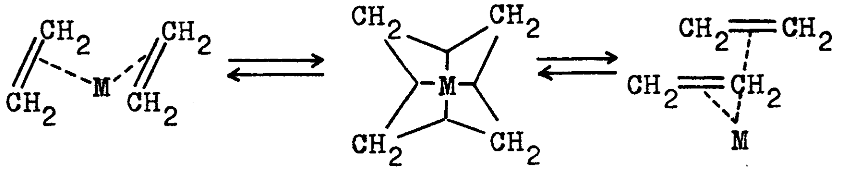


Fig.1. Redistribution of electron density between metal and olefins

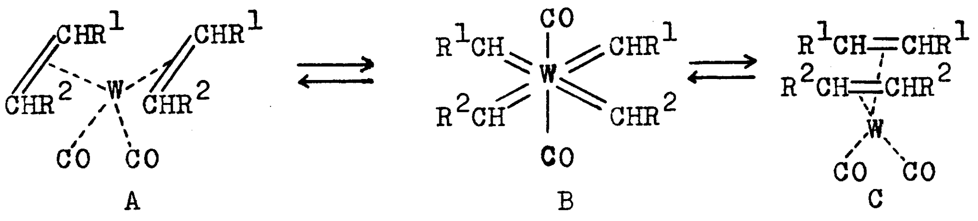
Mango[93] additionally explained that the cyclobutane is not formed as a distinct, free intermediate, but exists as a short-lived species fixed to the metal center responsible for its formation.

Pettit[94] found that metathesis of ethylene failed to yield significant amounts of cyclobutane and exposure of cyclobutane to the catalyst failed to produce a significant amount of ethylene, and proposed "tetramethylene" as an alternative to the quasicyclobutane intermediate (Eq. 6). In this intermediate, the four olefinic carbons and the metal are joined by four three-center bonds formed by



(6)

overlap of C_{sp^3} and metal d orbitals. This interpretation was supported by the metathesis of 4-nonene with the (toluene) W $(CO)_3$catalyst in heptane at 98° C.[51] The data are consistent with a species $(\text{olefin})_2$ $W(CO)_2$ being involved (Eq. 7). The conversion of A or C into B involves a change in the

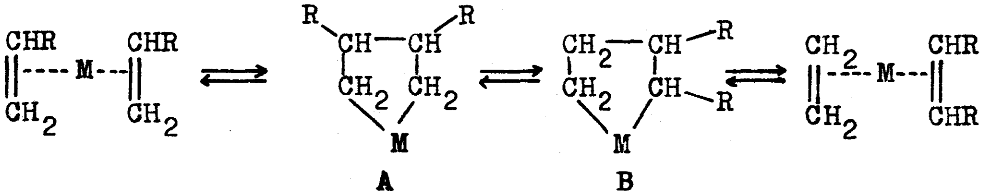


(7)

number of electrons in the valence shell of tungsten from 14 to 18 and the intermediate B thus obeys the inert-gas rule. However, this system may not be typical, which requires high temperature and the extremely lower olefin/W ratios (3:1) as compared to the conventional metathesis systems.

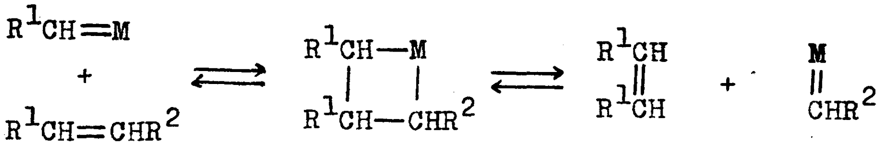
Rooney [95] observed that a CoO/MoO_3 supported catalyst, which is active in propylene metathesis, readily decomposed diazomethane into ethylene and N_2. Hence, they assumed that both reactions proceeded through the same transition state, metal-carbene. Subsequently, Rooney[96] demonstrated that a $Mo(CO)_6/Al_2O_3$ catalyst was capable of converting ethylene into propylene directly. In order to outline a mechanism for this unique $3C_2 \rightarrow 2C_3$ process, they suggested a pathway involved a splitting of one ethylene into methylenes, and addition of each of the latter to another ethylene, followed by rearrangement of the resulting trimethylene into propylene. They allowed for the possibility that carbene complexes might also be involved in metathesis.

Grubbs[97] proposed still another intermediate, "a five-membered metallocycle." As shown in Eq. 8, the olefins are first complexed to the metal and then rearrange to form a metallocycle A. A rearrangement of the alkyl groups in A leads to another metallocycle B which gives a bisolefin complex containing the metathesized olefins.



(8)

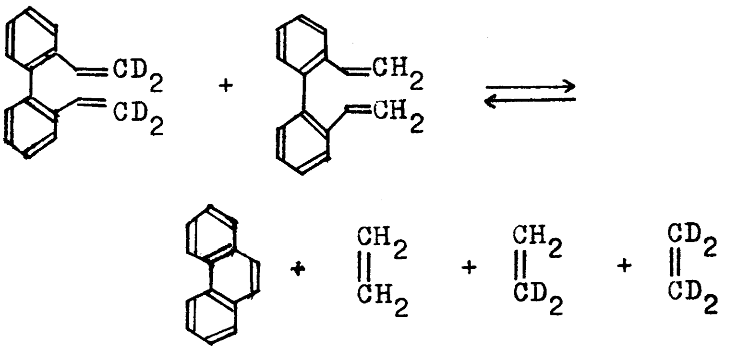
Recent publications disclosed results that appear to be incompatible with a pairwise scrambling depicted in Eq.5, 6 and 8 that required an initial bisolefin-metal entity bearing two olefinic ligands in a *cis* configuration about the metal. They point to a non-pairwise chain mechanism that favors a single olefin molecule complexed to a carbene-bearing metal undergoing interchange *via* a metallocyclobutane intermediate(Eq. 9).



$$\begin{matrix} R^1CH{=}M \\ + \\ R^1CH{=}CHR^2 \end{matrix} \rightleftarrows \begin{matrix} R^1CH{-}M \\ | \quad\; | \\ R^1CH{-}CHR^2 \end{matrix} \rightleftarrows \begin{matrix} R^1CH \\ \| \\ R^1CH \end{matrix} + \begin{matrix} M \\ \| \\ CHR^2 \end{matrix}$$

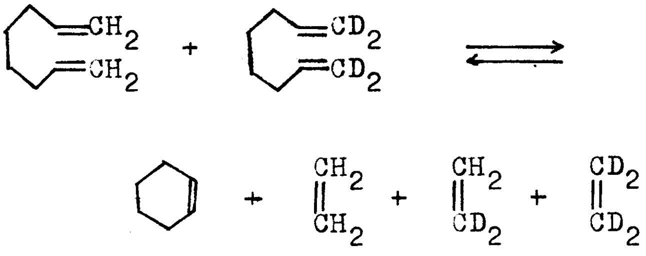
(9)

Katz[98,99] has described that the chain reaction accounts more satisfactorily than the pairwise mechanism for the various facts which have been observed by Katz and other workers[100] in olefin metathesis. However Katz conceded that these explanations and demonstrations did not prove the non-pairwise chain mechanism since almost all the facts have also been explained using the pairwise mechanism. To confirm that the mechanism of the olefin metathesis involves the carbene chain mechanism, Katz[99] tried the metathesis of divinylbiphenyl-d_4 and undeuterated divinylbiphenyl with the $M(Ph_3P)_2(NO)_2Cl_2(M=W, Mo)-Me_3Al_2Cl_3$ system (Eq. 10).



(10)

He considered two different mechanisms and the expected ratios of ethylene-d_4,-d_2 and -d_0 for each mechanism. The results conflicted with the pairwise mechanism, no matter whether the transalkylidenation or the olefin exchange step is rate determining. The results agreed with expectation based on the chain reaction mechanism as shown in Eq. 9. Grubbs[47,101] also has confirmed that the results were most consistent with the chain mechanism in the olefin metathesis using mixtures of 1,7-octadiene and 1,7-octadiene-1,1,8,8-d_4 as the



(11)

olefin (Eq. 11).

Views regarding the nature of the transition state of olefin metathesis are in a state of flux,* but there now appears to be a growing consensus that a chain process involving a metal-carbene species is operating.

As is apparent from the preceding outline, olefin metathesis reaction is unique and significantly useful process. However this reaction has suffered some disadvantage. This reaction is extremely sensitive to the catalyst recipes, trace impurities and actual experimental conditions. Additionally catalytic side reactions often compete with metathesis and considerably decrease the selectivity of this reaction. When benzene is used as a solvent, olefin metathesis is accompanied by the Friedel-Crafts reaction between benzene and olefins. In order to improve these faults, we searched new catalyst systems and new solvents. We have found that several catalyst systems are effective for the metathesis of 2-heptene and also that some of these catalysts possess the excellent characteristics (Chapter II). The catalyst systems which we discovered contain WCl_6-Et_2Zn, WCl_6-nBuMgI, WCl_6-Ph_3Bi, WCl_6-Ph_4Sn, WCl_6-Ph_4Pb, WCl_6-C_5H_5Na, WCl_6-PhC≡CNa, WCl_6-PhNa, WCl_6-RC≡CNa (R = alkyl), modified WCl_6-nBu_4Sn and also some of the $WOCl_4$-based systems. From these studies with new and conventional catalysts, we were able to glean considerable knowledge about the catalyst formation mechanism and the nature of the active species (Chapter III). On the other hand, many kinds of halogenated hydrocarbon were found to be the more excellent medium than benzene and chlorobenzene (Chapter IV). The results of Chapters II and IV were applied to the metathesis of 1-alkene (Chapter V) and to the metathesis of methyl oleate (Chapter VI). The results and discussion of our investigations are presented in the sections which follow.

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* There is a review[102] which presents an up-to-date account of recent developments toward understanding the mechanism of olefin metathesis.

CHAPTER II

THE CHARACTERISTICS OF NEW AND CONVENTIONAL CATALYST SYSTEMS

1. The Tungsten Hexachloride — Alkylmetal Systems

1-1. Research for the Optimum Reaction Conditions

The metathesis yield and the selectivity are affected by the cocatalyst/WCl_6 ratio and the olefin/WCl_6 ratio. These ratios are decisive factors of optimum reaction conditions. The comparison of the behaviors of the WCl_6-alkylmetal systems (alkylmetals are nBu_4Sn, Et_2Zn, Et_3Al and nBuLi) was carried out in 2-heptene metathesis in benzene at room temperature. The effect of the cocatalyst/WCl_6 ratio is shown in Table 2. The WCl_6-alkylmetal systems converted 2-heptene to 2-butene and 5-decene. The simultaneous occurrence of the Friedel-Crafts reaction between benzene and 2-heptene was observed. The side reaction products were mainly heptylbenzenes. In the WCl_6-nBu_4Sn and the WCl_6-Et_3Al systems, the good metathesis yield was obtained in the wide range of the cocatalyst/WCl_6 ratio, 2-4 and 0.5-3, respectively. In contrast, the sharp dependence of metathesis on the cocatalyst/WCl_6 ratio was observed in the WCl_6-Et_2Zn and the WCl_6-nBuLi systems, and the good results were obtained only at the ratios, 1 and 2, respectively. This means that the latter systems require the strict conditions for the formation of the active catalyst species. Probably alkylmetals act as reducing agents, and at the optimum cocatalyst/WCl_6 ratios form active catalyst sites "$W^{IV}Cl_4$" which permit the coodination of reactive groups such as an olefin and a carbene (Chapter III). On the other hand these catalyst systems catalyzed the Friedel-Crafts reaction more intensively with a decrease in the cocatalyst/WCl_6 ratio, though the WCl_6-nBuLi system barely did this reaction. The fact that the increase in the amount of the cocatalysts decreased the yield of heptylbenzenes, suggests that the side reaction is mainly catalyzed by a W^{VI} species. Tungsten hexachloride itself is an active catalyst for the Friedel-Crafts reaction. A part of tungsten compounds will still remain in the active form as a Friedel-Crafts reaction catalyst when the cocatalysts are not sufficient. The use of highly acidic cocatalysts appears to pro-

Table 2. Effect of Cocatalyst/WCl_6 Ratio [a)]

Cocatalyst		Cocatalyst/WCl_6 ratio				
		0.5	1	2	3	4
nBu_4Sn	Metathesis [b)]	1	8	24	32	26
	F.C. [c)]	20	18	6	5	2
Et_2Zn	Metathesis	3	36	3	0	0
	F.C.	16	4	0	0	0
Et_3Al	Metathesis	34	37	39	40	17
	F.C.	9	5	3	0	0
nBuLi	Metathesis	1	2	33	3	1
	F.C.	1	1	0	0	0

a) WCl_6 0.028 mol/l, 2-Heptene/W 50, Solvent Benzene, room temp., 3 hr.

b) 100 X (2-Butene + 5-Decene)/2-Heptene used, mol%.

c) Friedel-Crafts products, heptylbenzenes.

mote this side reaction. The deactivation of the catalyst for both metathesis and the Friedel-Crafts reaction at high cocatalyst/WCl_6 ratio may be the result of further alkylation of WCl_4, leading to over reduction of tungsten (Chapter III).

The effect of the olefin/WCl_6 ratio is shown in Table 3. The yield of the Friedel-Crafts products decreased with an increase in the amount of olefin, though the WCl_6-nBuLi system did not catalyze this side reaction. The result of Table 2 suggests that in the WCl_6-nBu_4Sn, the WCl_6-Et_2Zn and the WCl_6-Et_3Al systems, the highly cationic tungsten species responsible for the Friedel-Crafts reaction remain at the optimum cocatalyst/WCl_6 ratio whereas in the WCl_6-nBuLi system they do not. Since the interactions among 2-heptene, benzene and highly cationic tungsten species are necessary for the occurrence of the Friedel-Crafts reaction, the

Table 3. Effect of Olefin/WCl_6 Ratio [a)]

Cocatalyst	Cocat./WCl_6		Olefin/WCl_6 ratio 25	50	100	200	300
nBu_4Sn	3	Metathesis[b)]	36	44	36	10	4
		F.C.[c)]	6	2	1	0	0
Et_2Zn	1	Metathesis	18	33	43	19	3
		F.C.	12	3	1	0	0
Et_3Al	1	Metathesis	11	36	41	17	8
		F.C.	13	4	0	0	0
nBuLi	2	Metathesis	32	23	6	1	1
		F.C.	0	0	0	0	0

a) WCl_6 2.8 X 10^{-5}mol, Solvent Benzene, room temp., 3 hr.
b) 100 X (2-Butene + 5-Decene)/2-Heptene used, mol%.
c) Friedel-Crafts products, heptylbenzenes.

trends of Table 3 may result from the decrease of the chance of the interaction between highly cationic species and benzene due to the decrease of benzene concentration. An excess of olefin to the catalyst depressed metathesis also. Probably this results from the deactivation of the catalyst. In the WCl_6-nBuLi system, the optimum olefin/WCl_6 ratio was less than 50, and the yield decreased greatly at 100. While in other catalyst systems the good yield was obtained in the wider range of the olefin/WCl_6 ratio as compared to the one in the WCl_6-nBuLi system. The WCl_6-nBuLi system is less active than the other catalyst systems. The results of Tables 2 and 3 show that the nature of the cocatalyst metal affected the catalyst formation and/or the activity of the actual catalyst.

1-2. The Use of Various Organic Tin Compounds as Cocatalysts

As shown in Table 4, R_4Sn (R=nBu, Ph) were effective as cocatalysts with WCl_6, whereas nBu_3SnCl, nBu_2SnCl_2, nBu_2SnO and $nBu_2Sn(OAc)_2$ were not. The combinations of the latter compounds with WCl_6 exclusively catalyzed the Friedel-Crafts reaction. These results suggest that the latter compounds hardly have the ability to alkylate WCl_6.

Table 4. Conversion of 2-Heptene to 5-Decene with WCl_6 and Organotin Compounds[a)]

Cocatalyst	Sn/W ratio	Metathesis % [b)]	Friedel-Crafts products %
Bu_4Sn	2	33	5
Ph_4Sn	2	30	6
Bu_3SnCl[c)]	8	0.7	9
Bu_2SnCl_2	3	0	56
Bu_2SnO	3	0	55
$Bu_2Sn(OAc)_2$	3	0	0.3

a) WCl_6 0.024 mol/l, 2-Heptene/W 100, room temp., 5 hr.

b) 100 X 5-Decene/(2-Heptene + 5-Decene), mol%.

c) The metathesis yield was negligible at Sn/W $<$ 6.

The WCl_6-nBu_4Sn system deserves mention. This catalyst system is highly active in the wide ranges of the Sn/W and the 2-heptene/W ratios, and less poisoned than the other WCl_6-alkylmetal systems. Also, tetra-n-butyltin is easier to handle due to its stability and less toxic than tetramethyltin.[23,60-63]

1-3. Modification of the Tungsten Hexachloride — Tetra-n-butyltin System by Organic Additives

As shown in Table 5, the modification of the WCl_6-nBu_4Sn system with a proper amount of additives led exclusively to the metathesis without the Friedel-Crafts reaction. On the other hand, 2-nonyne and acetonitrile inhibited both the metathesis and the Friedel-

Table 5. Effect of Adding Organic Compounds[a)]

Additive	Additive / WCl_6	Metathesis[b)]	F.C.[c)]	Selectivity
Dicyclopentadiene	0	8	14	11
	1	13	15	26
	2	23	3	53
	3	27	1	58
	4	35	1	95
Phenylacetylene	0	2	42	2
	1	21	10	24
	2	41	2	79
	3	36	1	80
	4	39	0	64
Ethyl ether	0	6	64	6
	1	48	1	98
	2	45	0	100
	3	22	0	69
	4	5	0	12
Ethanol	0	5	40	6
	1	20	3	50
	2	5	0	13
	3	0	0	0
n-Propyl acetate	0	2	45	2
	1	45	0	91
	2	6	0	0
	3	0	0	—
iso-Propyl acetate	0	13	27	15
	1	46	0	82
	2	8	0	85
	3	0	0	—
Methyl oleate	0	2	45	2
	1	38	0	66
	2	0	0	—
Methyl stearate	0	2	45	2
	1	27	0	62
	2	9	0	27
	3	0	0	—

a) WCl_6 0.038 mol/l, 2-Heptene/W 20, nBu_4Sn/W 1, Solvent Benzene, room temp., 3 hr.

b) 100 X (2-Butene + 5-Decene)/2-Heptene used, mol%.

c) Friedel-Crafts products, heptylbenzenes.

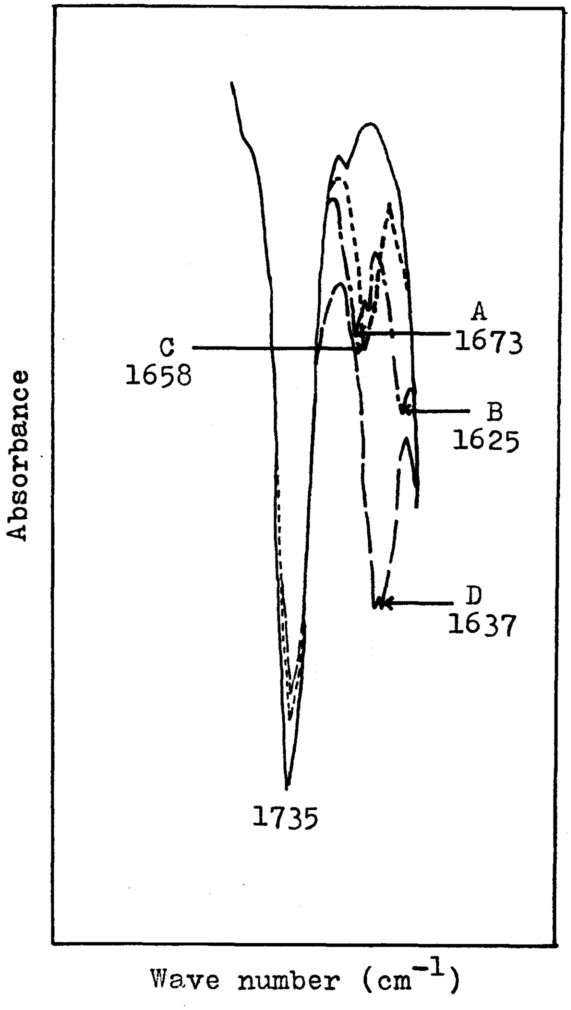


Fig.2. Infrared spectra of n-propyl acetate: WCl_6-nBu_4Sn(WCl_6 0.026 mol/l, $CH_3COOnPr/W$ 8, Sn/W 5):peaks A,B. WCl_6(WCl_6 0.026 mol/l, $CH_3COOnPr/W$ 8):peak C. $SnCl_4$($SnCl_4$ 0.073 mol/l, $CH_3COOnPr/Sn$ 4):peak D. Solvent Trichloroethylene.

Crafts reaction at the additive/WCl_6 ratio of 1,2,3 and 4. Mesitylene did not provide any effect at the same ratios. An excess amount of additive to the catalyst inhibited the metathesis also. The effects of esters were independent of their chain length. These additives, except mesitylene, probably form acid-base complexes with metal species. Ir spectra study suggests that esters coordinate on the highly acidic metal species with carbonyl group (Fig. 2). That is, when catalyst components were added to the trichloroethylene solution of n-propyl acetate, the strength of the peak due to the carbonyl group of n-propyl acetate at 1735cm^{-1} decreased and the new absorption peaks appeared at low wave numbers. The addition of n-Bu_4Sn, nBu_3SnCl, or nBu_2SnCl_2 gave no new peak and the peak at 1735cm^{-1} was unchanged, but the addition of $SnCl_4$ decreased the peak at 1735cm^{-1} and gave a new peak. With respect to methyl oleate, the similar changes were observed. The results of Table 5 may be explained by the inference that only the metathesis catalyst survives after these additives poison the highly cationic species, such as W^{VI} responsible for the Friedel-Crafts reaction, more intensively than the active species, such as W^{IV} responsible for metathesis. The intensive poisoning effect of 2-nonyne and acetonitrile may be due to their strong coordinating power to tungsten. The fact that ethyl ether hardly decreased the metathesis yield even at the additive/WCl_6 ratio of 3 may be explained by its weak coordinating power which may cause the competitive coordination with olefins. The facts that dicyclopentadiene and phenylacetylene provided good results at the additive/WCl_6 ratios of 2-4 may be explained by the same inference, but also there seems to be the other factor (This chapter, 3-3).

1-4. Reaction Progress vs. Time

At an optimum cocatalyst/WCl_6 ratio and an optimum olefin/WCl_6 ratio, the extent of 2-heptene metathesis produced by the WCl_6-alkylmetal systems was studied as a function of time (Fig. 3). The metathesis with the WCl_6-Et_3Al system proceeded extremely faster than those with other catalyst systems. This is due to the specific action of aluminum (Chapter III). The initial rates decreased in the following order:

$$WCl_6\text{-}Et_3Al > WCl_6\text{-}nBu_4Sn > WCl_6\text{-}nBuLi.$$

The differences of the initial rates may reflect the relative rates of the catalyst formation

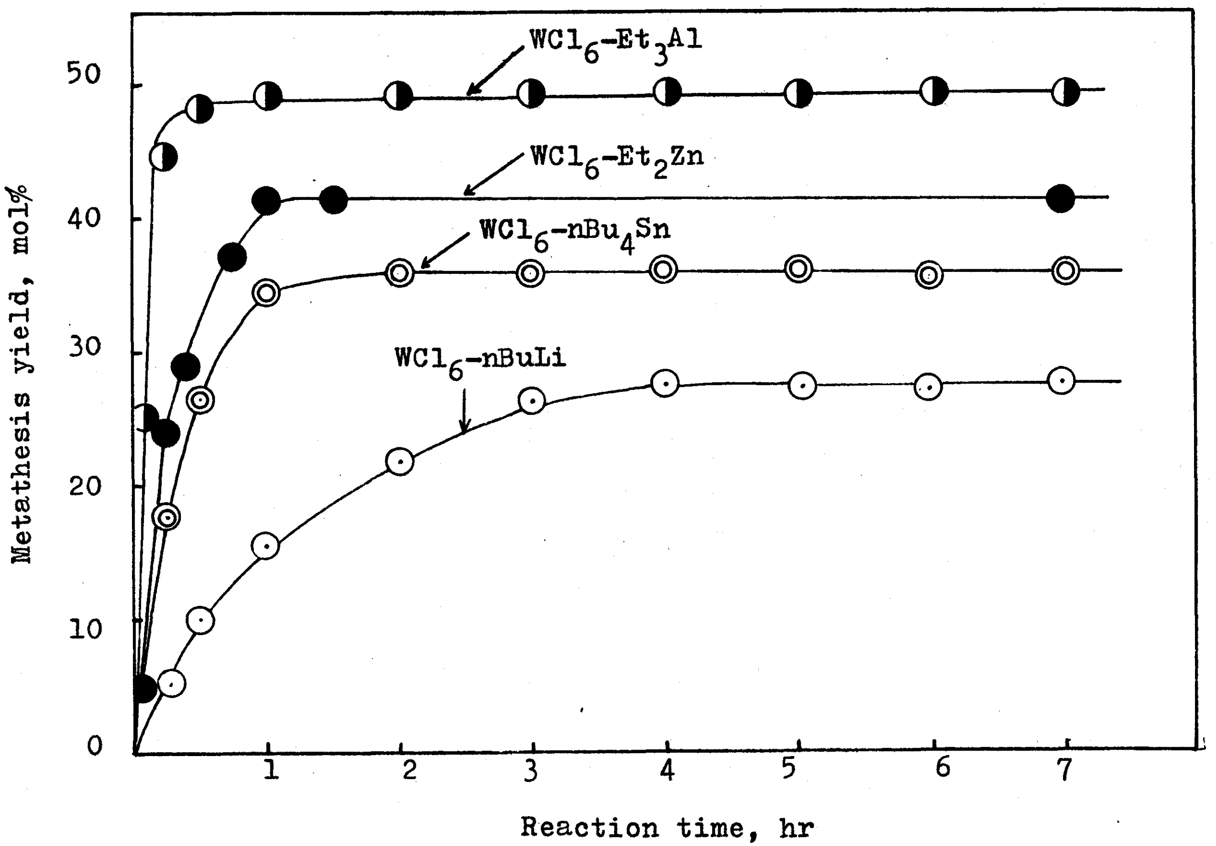


Fig.3. Plot of yield vs. time: WCl_6-Et_2Zn system (WCl_6 0.034 mol/l, 2-Heptene/W 20, Zn/W 1); other systems (WCl_6 0.024 mol/l, 2-Heptene/W 50, Li/W 2, Sn/W 1, Al/W 1); Solvent 1,2,4-trichlorobenzene, room temp.. Yield is mol% to 2-butene + 5-decene.

and/or the relative activity of the catalysts produced. In the metathesis of 2-heptene (75% *cis*) with WCl_6-nBu_4Sn, *cis*-isomer contents of olefins approached their thermodynamic equilibrium values[16] (Table 6). The *cis-trans* isomerization proceeded considerably even after the metathesis yield nearly attained the final level in 3 hours. In the course of the reaction, 2-butene always showed higher *cis* content than 5-decene. It is attributable to the steric effect of methyl groups of 2-butene to tungsten species.

Table 6. Variation of Cis-Isomer Contents of Olefins with Time in 2-Heptene Metathesis with WCl_6-nBu_4Sn [a)]

Time	Metathesis[b)] %	F.C.[c)] %	Cis-Isomer Contents, % 2-Butene	2-Heptene	5-Decene
0(min)	0	0		75	
5	14	3	54	51	44
30	19	3	52	43	37
1(hr)	23	3	49	39	35
2	25	3	46	36	33
3	26	3	45	34	33
5	26	3	44	32	29
24	27	3	43	29	27

a) WCl_6 0.024 mol/l, 2-Heptene/W 100, Sn/W 1, room temp..
b) 100 X 5-Decene/(2-Heptene + 5-Decene), mol%.
c) Friedel-Crafts products, heptylbenzenes.

2. The Tungsten Hexachloride — Unsolvated Grignard Reagent Systems

2-1. Unsolvated Grignard Reagent

Grignard reagents prepared in hydrocarbon medium are called "Unsolvated Grignard reagents", since they are much less solvated in comparison with the ordinary ethereal Grignard reagents.[103] In our laboratory, it was found that a mixture of WCl_6 and unsolvated

Grignard reagent is an excellent homogeneous catalyst for olefin metathesis.[21] Independently, Raven[22] discovered that WCl_6-ethereal Grignard reagent is an effective catalyst for olefin metathesis. Under our reaction condition, the metathesis was inhibited by the addition of small amount of ether. The unsolvated Grignard reagents of carbon number 4-6 were found to be preferable for the preparation of an effective catalyst for olefin metathesis. The lower Grignard reagents showed too poor solubility to prepare the catalyst solution of the sufficient concentration, and the higher Grignard reagents gave less active catalysts probably due to the inhibitory effect of long alkyl chain. It seemed to be suitable to use the iodide for tis higher reactivity rather than the bromide and the chloride in order to prepare the unsolvated Grignard reagent smoothly. Hence, n-butylmagnesium iodide was used as a cocatalyst.

2-2. Research for the Optimum Reaction Conditions

The most favourable catalyst was obtained near Mg/W = 2 in the 2-heptene metathesis with WCl_6-nBuMgI (Fig. 4). The fact agreed with those reported by Raven[22] and our laboratory.[21] In nmr study, the peak of methylene protons attached to lithium at -0.6 ppm in δ value in nBuLi disappeared completely as soon as WCl_6 was added in the various proportions. This suggests that irreversible alkylation of WCl_6 with nBuLi occurs rapidly. The sharp dependence of the yield on the Li or Mg/W ratio may be due to the further rapid alkylation of active WCl_4 species with excess of these basic cocatalysts. It is noteworthy that the good metathesis yield was obtained in the moderately wide range of the cocatalyst/WCl_6 ratio in the metathesis with WCl_6-nBuMgI in comparison with WCl_6-nBuLi. It may be partially attributed to the less reactivity of nBuMgI to active WCl_4 species due to the less basicity of magnesium and due to the influence of iodine combined to magnesium. The yield of the Friedel-Crafts products was extremely small — such as 1—% when the Mg/W ratio was 2.

In this system, the wider optimum ranges of the olefin/WCl_6 ratio, 30-130, were obtained as compared to the one, less than 50, in the WCl_6-nBuLi system (Fig. 5). This catalyst system seems more active than the WCl_6-nBuLi system. The Friedel-Crafts products were less than 1% at the olefin/WCl_6 ratios examined.

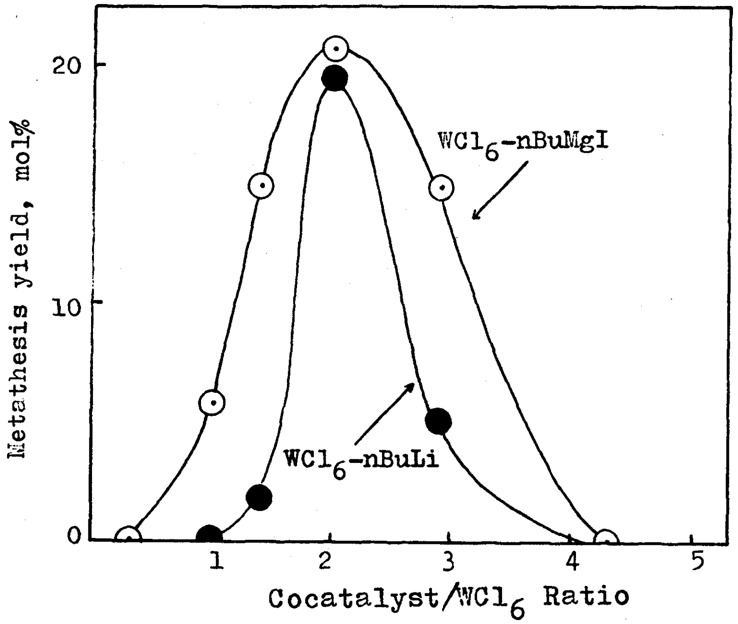


Fig.4. Effect of cocatalyst/WCl_6 ratio: WCl_6 0.018 mol/l, 2-Heptene/W nBuMgI:100 nBuLi:50, Solvent Benzene, room temp., 5 hr. Yield(mol%) = 100 X 5-Decene/(2-Heptene + 5-Decene).

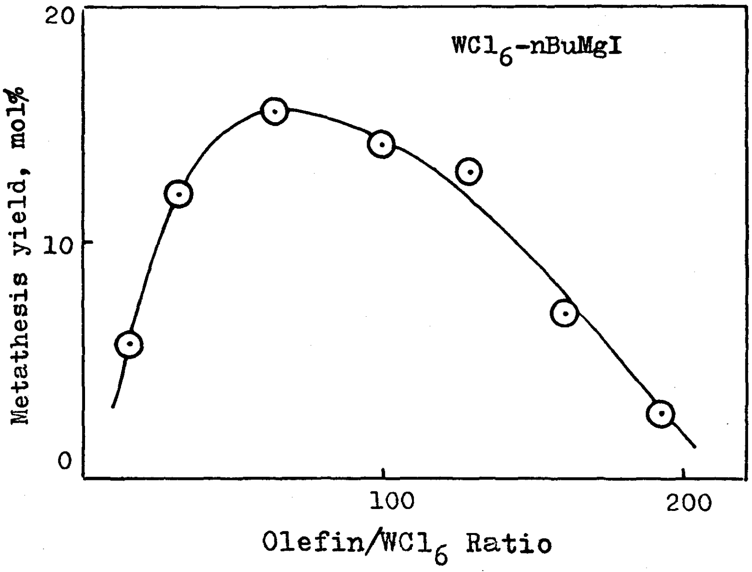


Fig.5. Effect of olefin/WCl_6 ratio: WCl_6 0.013 mol/l, nBuMgI/W 2, Solvent Benzene, room temp., 3 hr. Yield(mol%) = 100 X 5-Decene/(2-Heptene + 5-Decene).

2-3. Reaction Progress vs. Time

The reaction proceeded rapidly during the first 5 min and then slowly, and reveled off in 2 hours (Table7). The initial rate of this system lies between that of the WCl_6-Et_3Al system and that of the WCl_6-nBu_4Sn system:

WCl_6-Et_3Al > WCl_6-nBuMgI > WCl_6-nBu_4Sn.

Table 7. Reaction Progress vs. Time in the Metathesis of 2-Heptene with WCl_6-nBuMgI[a)]

Time	Metathesis[b)]	Cis-Isomer contents, %	
	%	2-Heptene	5-Decene
0(min)	0	75	--
5	16	54	46
30	20	42	40
1(hr)	24	41	39
2	27	40	38
3	28	37	34
5	28	35	33
24	29	29	30

a) WCl_6 0.019 mol/l, 2-Heptene/W 100, Mg/W 2, room temp..
b) 100 X 5-Decene/(2-Heptene + 5-Decene), mol%.

Cis-isomer contents of olefins approached their thermodynamic equilibrium values. *Trans*-isomerization proceeded considerably after the metathesis yield nearly attained the final level.

2-4. Stereochemistry in Early Reaction Stages

In the early stages of the metathesis catalyzed by WCl_6-nBuMgI, the initial isomer distributions in the products were dependent upon the isomeric nature of the starting 2-pentene (Table 8). That is, 2-pentenes preferentially yielded products of the same stereochemistry as reactant — i.e., *cis*-2-pentene gave *cis*-2-butene and *cis*-3-hexene, whereas *trans*-

Table 8. Initial Isomer Distributions in the Metathesis of Cis- and of Trans-2-Pentene with WCl_6-nBuMgI[a)]

Starting olefin	Metathesis %	Cis-Isomer Contents, %		
		2-Butene	2-Pentene	3-Hexene
cis-2-Pentene	0	--	95	--
	2.5	60	92	42
	2.8	60	91	41
trans-2-Pentene	0	--	0.1	--
	1.9	33	1.4	19
	2.7	30	1.6	18

a) WCl_6 0.02 mol/l, 2-Heptene/W 100, Mg/W 2, room temp..

-2-pentene provided *trans*-2-butene and *trans*-3-hexene. However the results also show that substantial amounts of both *cis* and *trans* isomers of 2-butene and 3-hexene are formed at the outset in both cases. This demonstrates the weak stereoselectivity of the metathesis reaction. Calderon has reported the similar results in the metathesis of pure *cis*- or *trans*-2-pentene with the WCl_6-$EtAlCl_2$-EtOH system.[16] It is vague why metathesis shows the weak stereoselectivity in the early stages of the reaction, in spite of interpretations by Hughes,[44,104] Grubbs[97] and Katz[98] according to their mechanistic proposals.

3. The Tungsten Hexachloride — Organosodium Systems

3-1. The Use of Cyclopentadienylsodium and Phenylethynylsodium as Cocatalysts

Because of the highly acidic character of the hydrogens of cyclopentadiene and phenylacetylene, these cocatalysts are easily synthesized. Moreover, they are less hazardous and more stable than aluminum, zinc and lithium cocatalysts and less toxic than R_4Sn.

They showed the solubility necessary for the preparation of the catalyst solution of the sufficient concentration, though the solubility was apparently low.

Figure 6 shows that good metathesis yield was obtained at a Na/W ratio near 2 in the WCl_6-C_5H_5Na and the WCl_6-$PhC{\equiv}CNa$ systems. In the WCl_6-$PhC{\equiv}CNa$ system, the formation of diphenyldiacetylene was confirmed by glc analysis. These facts suggest that the active catalyst species, WCl_4, forms as follows:

$$\begin{aligned} &WCl_6 + 2\ PhC{\equiv}CNa \xrightarrow{-NaCl} \\ &\qquad (PhC{\equiv}C)_2WCl_4 \longrightarrow WCl_4 + PhC{\equiv}C{-}C{\equiv}CPh \end{aligned} \tag{12}$$

In the nmr study, when WCl_6 was added to the C_5H_5Na benzene solution, the proton signal of $C_5H_5^-$ (5.67 ppm in δ value, a singlet) disappeared and a new peak assignable to the vinyl protons of cyclopentadiene (about 6.52 ppm in δ value, a multiplet) appeared. Also, in the WCl_6-C_5H_5Na system, it is speculated that the catalyst formation proceeds by a mechanism similar to that of the WCl_6-$PhC{\equiv}CNa$ system.

The optimum ranges of the cocatalyst/WCl_6 ratio decreased as follows:

C_5H_5Na, 1.5-3.0 > $PhC{\equiv}CNa$, 1.5-2.5 > nBuLi, 2

The wider optimum range of the Na/W ratio in the WCl_6-C_5H_5Na system as compared to that of the Li/W ratio in the WCl_6-nBuLi system suggests that $C_5H_5^-$ from C_5H_5Na does not destroy the active WCl_4 species to any considerable extent, because of the weaker nucleophilicity of the carbanion. As the optimum range of the Na/W ratio in the WCl_6-$PhC{\equiv}CNa$ system lies in between that in WCl_6-C_5H_5Na and that in WCl_6-nBuLi, the nucleophilicity of $PhC{\equiv}C^-$ may be stronger than that of $C_5H_5^-$ and weaker than that of nBu^-. These cocatalysts are different from any other cocatalyst reported in that, in C_5H_5Na, the negative charge of the cyclopentadienide anion is delocalized on all the five carbon atoms, while in $PhC{\equiv}CNa$ the anion is composed of the carbon atoms of the sp hybridization.
The weak nucleophilicity may be attributable to this unique character.

The higher activity of the WCl_6-C_5H_5Na and WCl_6-$PhC{\equiv}CNa$ systems than the WCl_6-nBuLi system in the region of the cocatalyst/WCl_6 < 2 may be explained by either one or

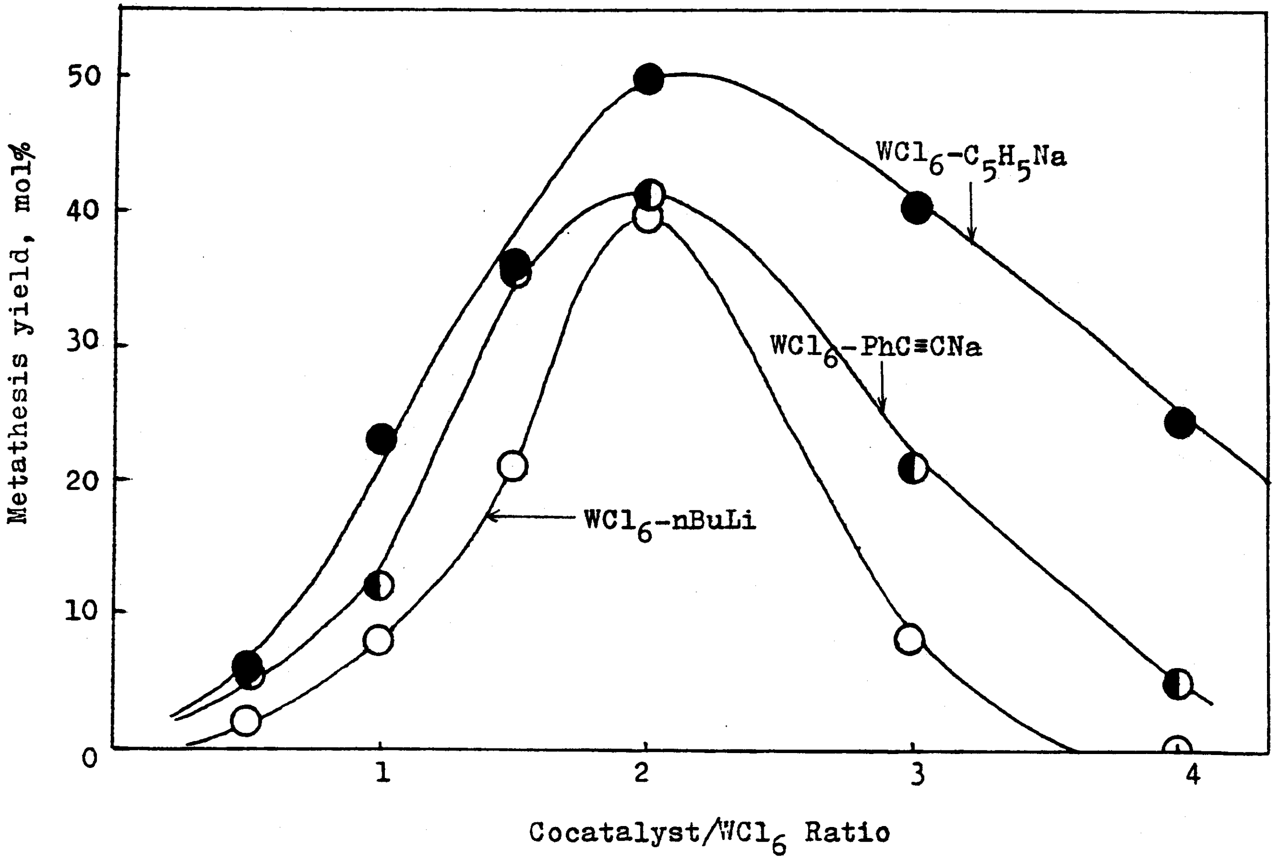


Fig.6. Plot of metathesis yield vs. cocatalyst/WCl_6 ratio: WCl_6 0.024 mol/l, 2-Heptene/W 50, Solvent Benzene, room temp., 15 hr. Metathesis yield is mol% to 2-butene + 5-decene.

both of the following reasons: (a) the slower deactivation of the WCl_6-C_5H_5Na and WCl_6-PhC≡CNa systems than the WCl_6-nBuLi system, as will be described later, and (b) n-BuLi reacts completely and irreversibly with water, but C_5H_5Na and PhC≡CNa do so only reversibly and incompletely. Moreover, the hydroxide anion resulting from the reactions may be a more powerful inhibitor than water itself. Water is presumed to be the main inhibitor, since the deactivation of the metathesis catalyst was observed upon the addition of water and trace amount of water is inferred to exist in the solvent and the olefin, and on the wall of the reaction tube, though it was excluded as much as possible. Similarly, the higher activity of these catalyst systems than that of the WCl_6-nBuLi system in the cocatalyst/ $WCl_6 \geqq 2$ region may be attributed to the slower deactivation of these catalyst systems and the weaker nucleophilicity of the carbanions of the cocatalysts.

The formation of the Friedel-Crafts products was extremely small — such as 1 — %, if the Na/W ratio was about 2 in both systems.

3-2. Reaction Progress vs. Time

The catalyst from WCl_6-C_5H_5Na required preformation periods to reach its maximum activity toward metathesis (Fig. 7). In Curve A, WCl_6 and C_5H_5Na had been allowed to stand for half an hour at room temperature before the olefin was added. The two reactions of A and B were identical in all other respects. The S shape of Curve B may be attributed to the incompleteness of the formation of active species at the initial stage of the reaction without standing, whereas the catalysts from WCl_6 and alkylmetals do not require the preformation periods. These facts suggest that in the WCl_6-C_5H_5Na system the catalyst formation proceeded more slowly than in the WCl_6-alkylmetal systems. Figure 7 also shows that the reaction progress with WCl_6-C_5H_5Na is similar to that with WCl_6-nBuLi.

3-3. Stability of Catalyst

In the olefin metathesis, the metathesis yield should attain the equilibrium yield, 50%. The failure to reach the equilibrium value results from catalytic deactivation. As is shown in Fig. 7, when nBuLi or nBu_4Sn was used as a cocatalyst, the yield leveled off within 3 hr. On the other hand, in the WCl_6-C_5H_5Na system, the increase in the yield continued and the equilibrium yield

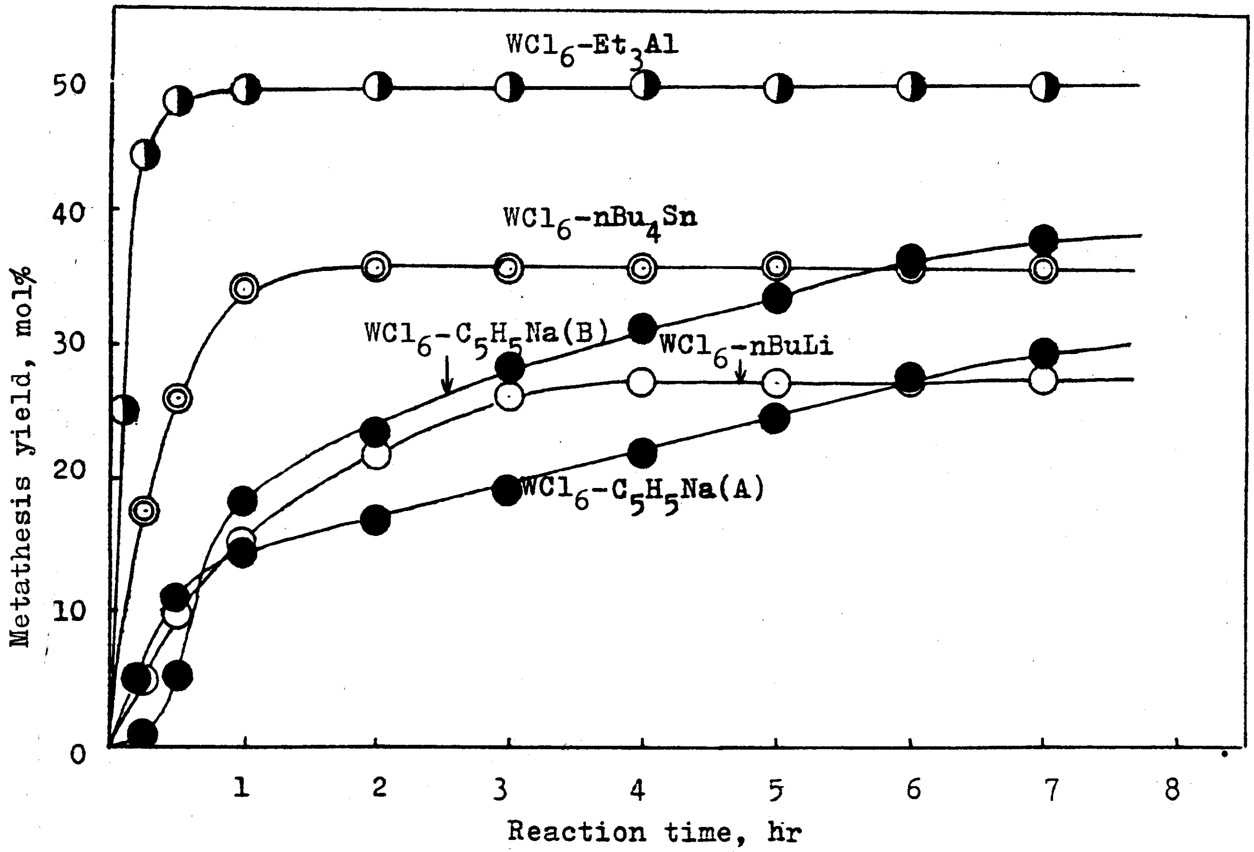


Fig.7. Plot of yield vs. time: WCl_6 0.024 mol/l, 2-Heptene/W 50, Na/W 2, Li/W 2, Sn/W 1, Al/W 1, Solvent 1,2,4-Trichlorobenzene, room temp.. $C_5H_5Na(A)$:Preformed system, $C_5H_5Na(B)$:In situ system. Yield is mol% to 2-butene + 5-decene.

was reached. This result and Table 9 show that the deactivation of the WCl_6-C_5H_5Na system proceeded more slowly than those of the WCl_6-nBuLi and the WCl_6-nBu_4Sn systems.

Table 9. Stability of Catalyst[a)]

Cocatalyst (M)	M/W ratio		Products, mol% [b)]		
			C_4	C_7	C_{10}
C_5H_5Na	2	In situ	25	50	25
		Preformed	16	68	16
Bu_4Sn	1	In situ	25	50	25
		Preformed	3	94	3

a) WCl_6 0.024 mol/l, 2-Heptene/W 25, Solvent 1,2,4-Trichlorobenzene, room temp., 15 hr. In the in situ system, 2-heptene, WCl_6 and the listed cocatalyst were added successively. In the preformed system, 2-heptene was added 1 hr later after WCl_6 and the listed cocatalyst were mixed.

b) Mol% of each product to the total amounts of 2-butene, 2-heptene and 5-decene.

The WCl_6-C_5H_5Na and the WCl_6-PhC≡CNa systems were less poisoned by ether than the WCl_6-nBuLi and the WCl_6-nBu_4Sn systems (Table 10). The fact suggests that the former systems are less deactivated by the water present in the reaction systems. The deactivation of the catalysts by ether may be explained by the following inferences: (a) the coordination of the inhibitor at its heteroatom to tungsten, which interrupts the coordination of incoming olefins; (b) the decomposition of the bimetallic catalyst system by the coordination of the basic inhibitor to the cocatalyst metal,[33] though no evidence for the formation of the tungsten — lithium or sodium binary complex has been reported in the olefin meta-

Table 10. Effect of Ether Addition to System [a)]

Cocatalyst (M)	M/W ratio	Et_2O/W ratio	Products, mol% [b)] C_4	C_7	C_{10}	F.C. [c)]
C_5H_5Na	2	0	25	49	25	1
		1	21	56	22	1
		2	15	68	16	1
		4	8	83	8	1
PhC≡CNa	2	0	24	50	25	1
		1	20	58	21	1
		2	14	70	15	1
		4	7	86	7	0
BuLi	2	0	21	55	22	2
		1	9	80	10	1
		2	2	95	2	1
		4	0	100	0	0
Bu_4Sn	1	0	23	47	23	7
		1	22	53	22	3
		2	11	76	12	1
		4	4	92	4	0

a) WCl_6 0.024 mol/l, 2-Heptene/W 50, Solvent Benzene, room temp., 15 hr.

b) Mol% of each product to the total amounts of 2-butene, 2-heptene, 5-decene and Friedel-Crafts products.

c) Friedel-Crafts products, heptylbenzenes.

thesis, and (c) the decomposition of the cocatalysts by a reaction with ether, such as a Wittig rearrangement.

The WCl_6-nBu_4Sn and WCl_6-nBuLi systems showed the optimum yield when 2-3 equivalent moles of dicyclopentadiene, cyclopentadiene, or phenylacetylene to WCl_6 were added. This suggests that the stability of the catalyst from the WCl_6-C_5H_5Na or PhC≡CNa system is also attributable to the organogroups from the cocatalysts, which may interrupt the coordination of the inhibitor, water, to tungsten by means of the coordination at the cyclopentadienyl ring or the triple bond.

3-4. Other Organosodium Cocatalysts

Phenylsodium and 1-hexynylsodium were also effective as cocatalysts of metathesis. However, triphenylmethylsodium and diphenylmethylsodium were not effective. These facts can be explained by the difficulties of the displacement of Cl in WCl_6 with the carbanions from triphenylmethylsodium and diphenylmethylsodium due to their weak nucleophilicity, itself attributable to the steric hindrance and the electronic effect.

4. The Tungsten Hexachloride — Arylmetal Systems

4-1. Research for the Optimum Reaction Conditions

A good metathesis yield was obtained in the extremely narrow Bi/W ratio range of 0.7-1 in the WCl_6-Ph_3Bi system, whereas in the WCl_6-Ph_4Pb and the WCl_6-Ph_4Sn systems good metathesis yields have been observed for the wider range of cocatalyst/WCl_6 ratios, 0.7-2 and 1-3, respectively (Table 11). The selectivity was better at the optimum cocatalyst/WCl_6 ratio in each system. As a solvent 1,2,4-trichlorobenzene was used, in order to depress the Friedel-Crafts reaction, since the WCl_6-Ph_4Sn system somewhat more catalyzed this side reaction than the WCl_6-nBu_4Sn system in benzene. These arylmetals as cocatalysts are easier to handle due to their stability than aluminum, zinc, magnesium and alkali cocatalysts. The yield and the selectivity both decreased as the cocatalyst/WCl_6 ratio deviated from the optimum value. Probably a lowering of the selectivity is the result of the occurrence of the

Table 11. Effect of Cocatalyst/WCl_6 Ratio [a)]

Cocat. (M)	M/W ratio	Metathesis yield[b)]	Selectivity [c)]
Ph_3Bi	0.3	0	0
	0.5	11	21
	0.7	31	50
	1	21	94
	2	3	34
	3	1	1
Ph_4Pb	0.3	5	13
	0.5	12	24
	0.7	32	100
	1	46	100
	2	40	81
	3	10	78
Ph_4Sn	0.3	3	12
	0.5	10	25
	0.7	14	28
	1	19	36
	2	40	90
	3	20	27

a) WCl_6 0.041 mol/l, 2-Heptene/W 20, Solvent 1,2,4-Trichlorobenzene, room temp., 24 hr.

b) (2-Butene + 5-Decene) X 100/2-Heptene used,mol%.

c) (2-Butene + 5-Decene) X 100/2-Heptene consumed,mol%.

Table 12. Effect of Olefin/WCl_6 Ratio[a)]

Cocat. (M)	M/W ratio	Olefin/W ratio	Yield[b)]	Selectivity
Ph_3Bi	1	10	35	100
		20	31	94
		50	36	100
		100	8	100
		200	1	100
Ph_4Pb	2	10	10	100
		20	14	100
		50	36	100
		100	50	100
		200	50	100
Ph_4Sn	2	10	26	55
		20	40	74
		50	47	100
		100	44	100
		200	1	100

a) WCl_6 6.9 X 10^{-5}mol, Solvent 1,2,4-Trichlorobenzene, room temp., 24 hr.

b) 100 X (2-Butene + 5-Decene)/2-Heptene used, mol%.

side reaction such as polymerization.

The optimum range of the olefin/WCl_6 ratio considerably varied with the catalyst system used (Table 12). Good selectivity was obtained in the ratio range of 10-200 in any system. It may be due to the use of 1,2,4-trichlorobenzene as a medium.

4-2. Reaction Progress vs. Time

The rate of the 2-heptene metathesis catalyzed by the WCl_6-Ph_3Bi system was slower than those catalyzed by the WCl_6-Ph_4Pb and the WCl_6-Ph_4Sn systems (Fig. 8).

At the end of the reactions, *cis* content of olefins approached at the thermodynamic equilibrium in any systems (Table 13).

Table 13. **Cis Content of Olefins from Metathesis Reactions**[a)]

Cocat. (M)	M/W ratio	% Cis content 2-Heptene	 5-Decene	Yield[b)]
Ph_3Bi	0.7	38	37	28
Ph_4Pb	1	23	24	50
Ph_4Sn	2	22	22	50

a) WCl_6 0.036 mol/l, 2-Heptene/W 23, Solvent 1,2,4-Trichlorobenzene, room temp., 24 hr.

b) 100 X (2-Butene + 5-Decene)/2-Heptene used, mol%.

TUNGSTEN HEXACHLORIDE AND COCATALYSTS

KAZUAKI ICHIKAWA

5. The Tungsten Oxytetrachloride — Cocatalyst Systems

When tungsten oxytetrachloride was used in the place of tungsten hexachloride, the combinations with the cocatalysts also produced the active catalysts for 2-heptene metathesis (Fig. 9). The solubility of $WOCl_4$ in benzene, chlorobenzene, 1,2,4-trichlorobenzene, and trichloroethylene was too poor to prepare the catalyst solution of the sufficient concentration. The micro-dispersion of $WOCl_4$ in chlorobenzene was used, since it was most soluble in chlorobenzene of above solvents. The data show the similar trends to those in the WCl_6-cocatalyst systems. That is, the $WOCl_4$-nBu_4Sn, the $WOCl_4$-Ph_4Sn and the $WOCl_4$-Et_3Al systems gave wide optimum ranges of the cocatalyst/$WOCl_4$ ratio, whereas the $WOCl_4$-nBuLi, the $WOCl_4$-Et_2Zn and the $WOCl_4$-Ph_3Bi systems showed the sharp dependence of the yield on the cocatalyst/$WOCl_4$ ratio. Most recently, Muetterties[105] reported that the optimal cocatalyst/W ratios are one-half those reported for the WCl_6 recipes in the $WOCl_4$-nBuLi and the $WOCl_4$-Me_2Zn systems, namely 1 and 0.5 respectively. The results of Fig. 9 roughly agree with those of Muetterties.[105] In any catalyst systems, the selectivity of 85-70% was obtained at the optimum cocatalyst/$WOCl_4$ ratios. The $WOCl_4$-Ph_4Pb system barely catalyzed 2-heptene metathesis, though the WCl_6-Ph_4Pb system was highly active. These catalyst systems are under investigation.

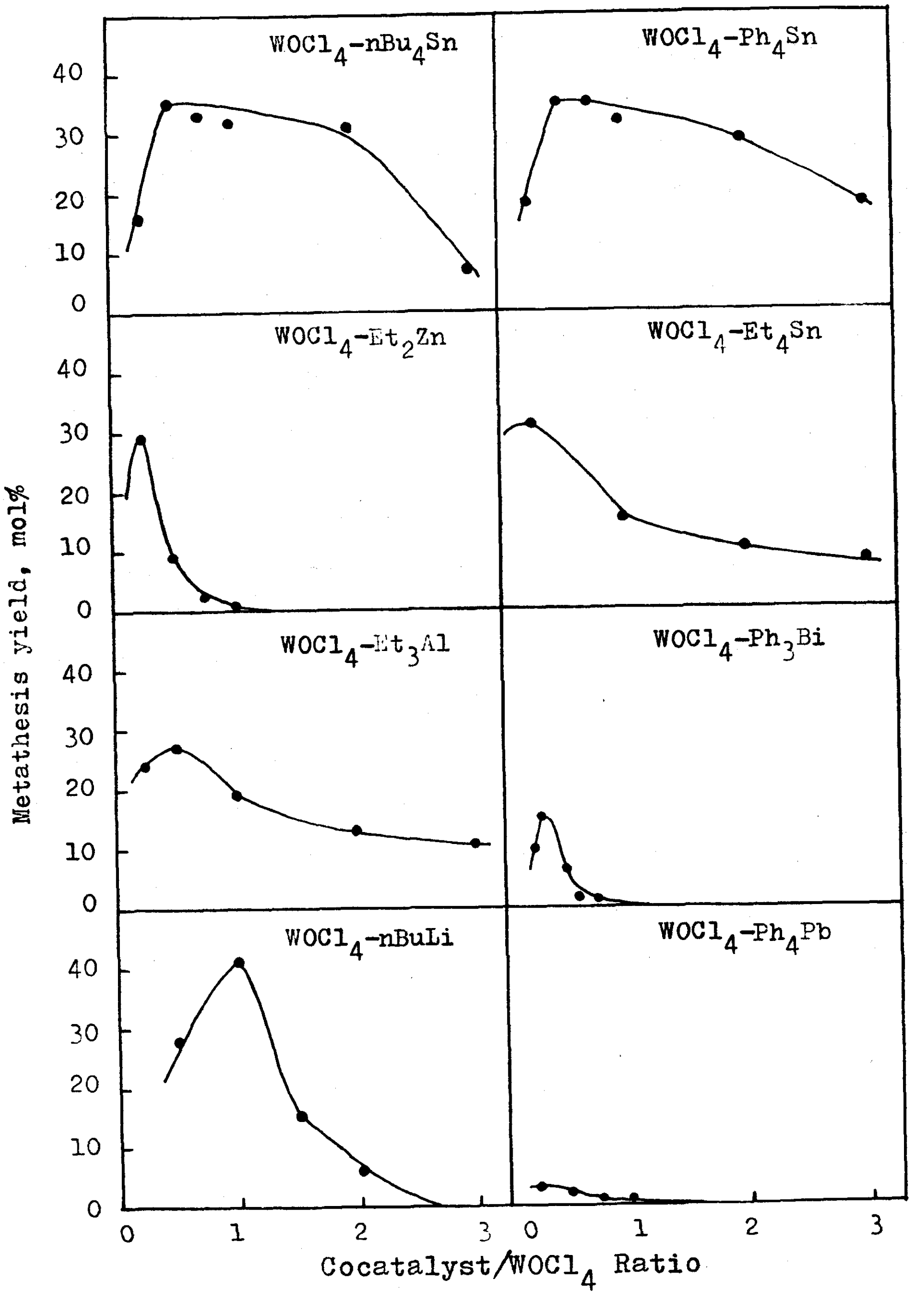


Fig.9. Metathesis of 2-heptene with $WOCl_4$-cocatalysts: $WOCl_4$ 0.04 mol/l, 2-Heptene/W 20, Solvent Chlorobenzene, room temp., 24 hr.

6. Summary of the Optimum Reaction Conditions

Table 14 summarizes the optimum ranges of the cocatalyst/WCl_6 and the olefin/WCl_6 ratios in the 2-heptene metathesis catalyzed by the WCl_6-cocatalyst systems. The optimum ranges in the WCl_6-alkylmetal systems show the interesting trends: both ranges widen with the increase in the electronegativity of the cocatalyst metal, except the narrow optimum cocatalyst/WCl_6 ratio range in the WCl_6-Et_2Zn system. In the WCl_6-arylmetal systems, the optimum ranges vary with the cocatalyst used, in spite of the analogous electronegativity of cocatalyst metal.

Table 14. Summary of Optimum Ranges a)

Catalyst		Cocatalyst/WCl_6 ratio	Olefin/WCl_6 ratio	E.N. b)
WCl_6	nBuLi	2 (O/W 50)	25 - 50 (Li/W 2)	1.0
	nBuMgI	2 (O/W 100)	30 - 130 (Mg/W 2)	1.2
	Et_3Al	0.5 - 3 (O/W 50)	50 - 200 (Al/W 1)	1.5
		0.6 - 1.5(O/W 100)	25 - 50 (Al/W 2)	
	Et_2Zn	1 (O/W 50)	50 - 200 (Zn/W 1)	1.6
	nBu_4Sn	2 - 4 (O/W 50)	50 - 200 (Sn/W 1)	1.8
		1 - 3 (O/W 100)	25 - 100 (Sn/W 3)	
	Ph_3Bi	0.7 - 1 (O/W 20)	10 - 50 (Bi/W 1)	1.9
	Ph_4Sn	1 - 3 (O/W 20)	20 - 100 (Sn/W 2)	1.8
	Ph_4Pb	0.7 - 2 (O/W 20)	50 - 200 (Pb/W 2)	1.8
	PhC≡CNa	1.5 - 2.5(O/W 50)		0.9
	C_5H_5Na	1.5 - 3 (O/W 50)		

a) Olefin=2-Heptene, Solvent=Benzene:WCl_6-alkylmetals, PhC≡CNa or C_5H_5Na;1,2,4-Trichlorobenzene:WCl_6-arylmetals.

b) Electronegativity of the cocatalyst metal.

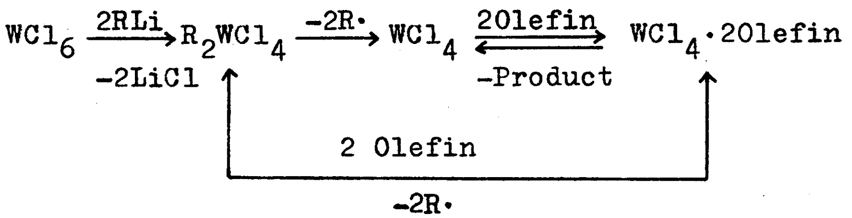
CHAPTER III

THE MECHANISM OF CATALYST FORMATION

1. The Catalyst Formation in the Tungsten Hexachloride — Alkylmetal Systems

1-1. Products from Catalyst Components

Menapace[20] has proposed the following mechanism (Scheme 1) that WCl_4 is an active catalyst species for the reaction with WCl_6-nBuLi, based on the observation that the catalytic activity is maximal for the Li/W ratio of 2. This mechanism is also supported by our observations: the catalytic activity is maximal (a) at Zn/W = 1 in the WCl_6-Et_2Zn system, (b) at Mg/W = 2 in the WCl_6-nBuMgI system, (c) at Na/W = 2 in the WCl_6-C_5H_5Na and the WCl_6-PhC≡CNa systems, and (d) the formation of diphenylacetylene in the WCl_6-PhC≡CNa system. However, using the catalyst system WCl_6-R_4Sn (R = nBu, Ph), WCl_6-Et_3Al or WCl_6-Ph_4Pb, the catalytic activity is not maximal when the number of alkyl or phenyl groups in the added cocatalyst per mole of WCl_6 is two.



$$\begin{tikzcd} WCl_6 \arrow[r, "2RLi", "-2LiCl"'] & R_2WCl_4 \arrow[r, "-2R\cdot"] & WCl_4 \arrow[r, shift left, "2Olefin"] & WCl_4\cdot 2Olefin \arrow[l, shift left, "-Product"] \arrow[lll, bend left, "2\ Olefin", "-2R\cdot"'] \end{tikzcd}$$

Scheme 1

In the metathesis of 2-heptene catalyzed by WCl_6-nBu_4Sn and WCl_6-nBuLi, the products RH, RCl and RR (R=nBu) were found in addition to the expected olefins in amounts which greately varied with the catalyst system (Table 15). Probably, the products RH, RCl and RR species are formed *via* the decomposition of alkyl-tungsten intermediates, $RWCl_5$ or R_2WCl_4 by a nonradical mechanism.[106–110] In the WCl_6-nBu_4Sn system, butane and butyl chloride were formed without octane species, whereas in the WCl_6-nBuLi system, butane was the main product. Mechanistically, two processes could be envisaged, which

Table 15. Dependence of Products from Catalyst Components on the Cocatalyst/WCl_6 Ratio

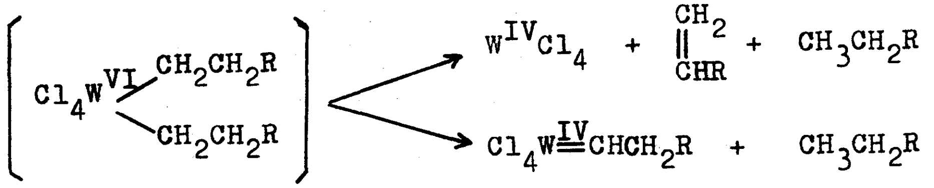
Cocat.	Cocat./WCl_6 ratio	Metathesis yield a)	Reaction products of catalyst components b)			n c)
			RH	RCl	RR (10^5mol)	
nBu_4Sn	0.5	17	0.6	2.3	0	0.8
	1	28	2.0	4.0	0	1.6
	2	30	2.9	5.1	0	2.2
	3	26	4.0	5.6	0	2.6
	4	17	4.5	6.4	0	3.0
nBuLi	0.5	4	0.8	1.8	0.2	0.7
	1	6	1.8	2.3	0.3	1.2
	2	21	6.7	0.3	0.6	2.0
	3	7	9.4	0.4	1.5	3.0
	4	2	13.2	0.6	2.0	4.2

a) WCl_6 0.021 mol/l, 2-Heptene/W nBu_4Sn:100 nBuLi:50, Solvent Benzene, room temp., 5 hr. Yield(mol%)= 100 X 5-Decene/(2-Heptene + 5-Decene).

b) WCl_6 0.05 mol/l (7.5 X 10^{-5}mol), Solvent Benzene, room temp., 5 hr.

c) n = (Twice the total of moles of products detected)/(moles of added WCl_6).

would account for the formation of butane (Eq. 13). One possibility would involve the β-hydrogen abstraction from an alkyl ligand by another alkyl in R_2WCl_4, which produces equal amounts of 1-alkene and alkane (Eq. 13a). Another mechanistic picture would involve the α-hydrogen abstraction from an alkyl ligand by another alkyl in R_2WCl_4, which forms tungsten-carbene complex and alkane (Eq. 13b). If the non-pairwise carbene-to-metallocycle mechanism[98] is to be accepted, Eq. 13b is a potential route to the formation of the initial carbene-metal entity. Recently, Muetterties[111] observed that in the reaction of Me_2Zn with WCl_6 carried



$$\left[Cl_4W^{VI}(CH_2CH_2R)_2\right] \rightarrow W^{IV}Cl_4 + CH_2{=}CHR + CH_3CH_2R \qquad (13a)$$

$$\left[Cl_4W^{VI}(CH_2CH_2R)_2\right] \rightarrow Cl_4W^{IV}{=}CHCH_2R + CH_3CH_2R \qquad (13b)$$

out in a deuterated solvent, methane free of deuterium was produced. It has been proposed that α-hydrogen elimination from the tungsten-methyl group occurs leading to the formation of the initial carbene-tungsten complex. Undoubtedly, the WCl_6-Me_2Zn system is prone to transform into carbene-metal entities, since methyl has no β-hydrogen. If alkyl ligand contains β-hydrogen, butane may be formed *via* the route according to Eq. 13a. Actually, WCl_6-arylmetal or WCl_6-PhC≡CNa that cannot transform into a carbene-metal entity is sufficiently active for olefin metathesis.

The number of the ligands displaced from one mole of tungsten (VI) complex, n, shown in Table 15, is defined, assuming that equal amounts of 1-butene and butane are produced, *viz*:

n = (Twice the total of moles of products detected)/(moles of added WCl_6)

The formation of 1-butene was not recognized. The species may be consumed for the successive reactions such as polymerization by olefin metathesis catalysts as has been observed for other 1-alkenes,[112] and the double bond migration followed by the cross metathesis of isomers.

The metathesis yield depends upon the value of n(Table15) and the good yield was obtained only for values of n, *Ca*. 2. The results suggest that WCl_4 formed from $RWCl_5$ and /or R_2WCl_4 provides an active catalyst site.

1-2. Comparison of the Characteristics of Cocatalysts

In Fig. 10, n and the metathesis yield are plotted against the cocatalyst/WCl_6 ratio. In the catalyst system of WCl_6-nBu_4Sn, n gradually increases to values greater than 2 as the Sn/W ratio increases in the range, Sn/W $\geqq$ 1, and good metathesis yield was obtained for the wider range Sn/W ratio of 1-3. On the other hand, in the system WCl_6-nBuLi, n increases linearly as the Li/W ratio increases, and good yield is obtained in the extremely narrow Li/W ratio range, *Ca* 2. These facts suggest that the optimum cocatalyst/WCl_6 ratio is obtained for n=2. The difference in behavior between nBu_4Sn and nBuLi in catalyst formation may be explained on the basis of the weaker nucleophilicity of n-butyl groups derived from nBu_4Sn as compared to those derived from nBuLi, and by the inference that nBu_4Sn can barely replace more than two chlorines from WCl_6 whereas nBuLi can easily displace more than two chlorines. Moreover, in the WCl_6-nBu_4Sn catalyst system, WCl_4 species formed are unlikely to be deactivated by attack of an excess of nBu_4Sn in the wide

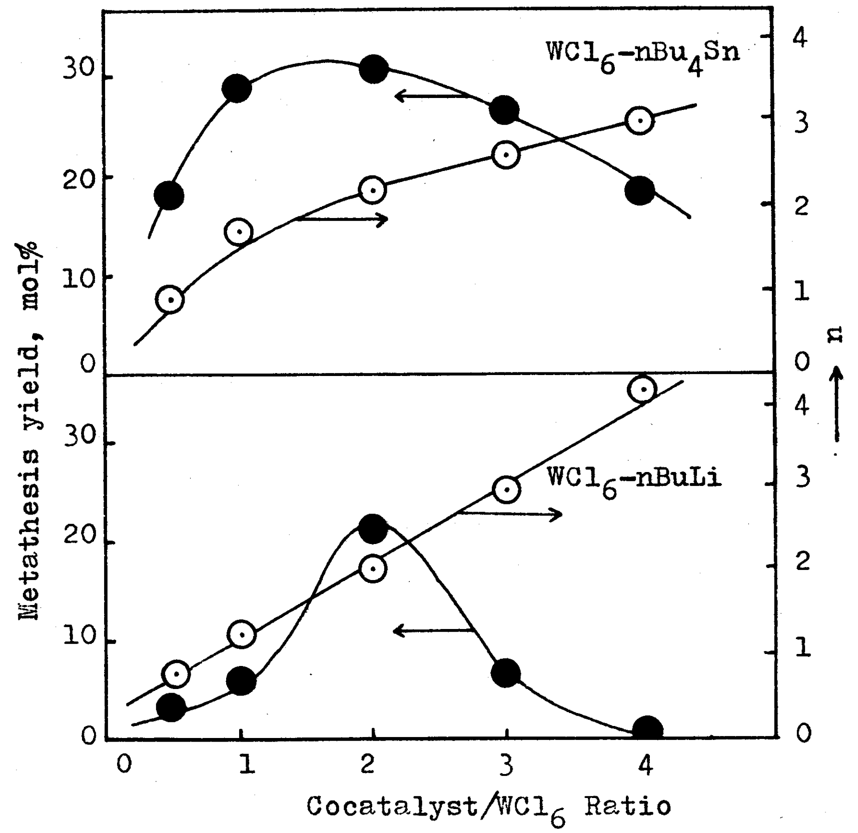


Fig.10. Plot of metathesis yield and n vs. cocatalyst/WCl_6 ratio.

Sn/W ratio range, while in the catalyst system, WCl_6-nBuLi, WCl_4 species formed are easily attacked and deactivated by an excess of nBuLi.

Table 15 also shows that in the WCl_6-nBu_4Sn system, the ratio of the amount of nBuCl to the product total increases as the Sn/W ratio decreases and that the ratio of butane to the total amounts of products increases as the Sn/W ratio increases. These facts suggest that mono-substituted tungsten intermediates, which give WCl_4 species and RCl, were mainly formed when the Sn/W ratio is low, and that di-substituted tungsten intermediates, which give WCl_4 species, RH and 1-alkene or RR, gradually increased by further displacement of chlorine by n-butyl groups on mono-substituted tungsten intermediates with an increase in the Sn/W ratio. Moreover, Table 15 shows that in the WCl_6-nBuLi system, the ratio of nBuCl to the total quantity of products is extremely small when the nBuLi/WCl_6 ratio is 2. This fact indicates that in the WCl_6-nBuLi system displacement of chlorine from mono-substituted tungsten intermediates occurs quickly to give nBu_2WCl_4 before the elimination of n-butyl chloride from $nBuWCl_5$ because of the strong nucleophilicity of nBuLi.

1-3. Glc Analysis of Tetra-n-butyltin and Tri-n-butyltin Chloride from the Reaction of Tungsten Hexachloride with Tetra-n-butyltin

In the reaction of WCl_6 with nBu_4Sn and a variety of cocatalyst/WCl_6 ratios, tin-containing products were identified and their concentrations measured by glc analysis.[113] The results are shown in Table 16. Tetra-n-butyltin and tri-n-butyltin chloride were detected, but di-n-butyltin dichloride was not found in any reaction. The result shows that a mole of nBu_4Sn provides only one butyl group per mole of WCl_6 and that the butyl group of nBu_3SnCl is unable to displace chlorine from tungsten. In fact the WCl_6-nBu_3SnCl system was almost ineffective as a catalyst for metathesis (Chapter II, Table 4). The number of n-butyl groups transferred (Table 16) represents the number of n-butyl groups which nBu_4Sn provides for the substitution of chlorine in WCl_6 and that of n-butyl groups in the products, as butane, 1-butene, and n-butyl chloride. This datum indicates that the n-butyl groups of nBu_4Sn provided for the substitution in WCl_6 were all converted into these products because each butyl group leaving from nBu_4Sn is found in one in the products. One tetra-n-butyltin molecule provides only one n-butyl group for substitution in WCl_6 in the range

Sn/W≦1, but in the range Sn/W>1 one tetra-n-butyltin provides less than one n-butyl group on average. Also, on average, only 0.5 mole of n-butyl groups were transferred from nBu_4Sn when the Sn/W ratio is 4. This fact indicates that the further displacement of chlorine by n-butyl on tungsten is more difficult because of the weak nucleophilicity of n-butyl groups derived from nBu_4Sn.

Table 16. Tetra-n-butyltin and Tri-n-butyltin Chloride in the Reaction of WCl_6 and nBu_4Sn [a)]

Sn/W ratio	Tin compounds in the reaction mixture (10^5mol)		Number of transferred n-butyl groups per WCl_6	
	nBu_4Sn	nBu_3SnCl	From nBu_4Sn [b)]	In Products [c)]
0.5	0.1	3.4	0.5	0.5
1	0.9	6.2	0.9	1.1
2	4.8	9.5	1.3	1.5
3	8.9	12.2	1.7	1.8
4	14.2	14.1	2.0	2.1

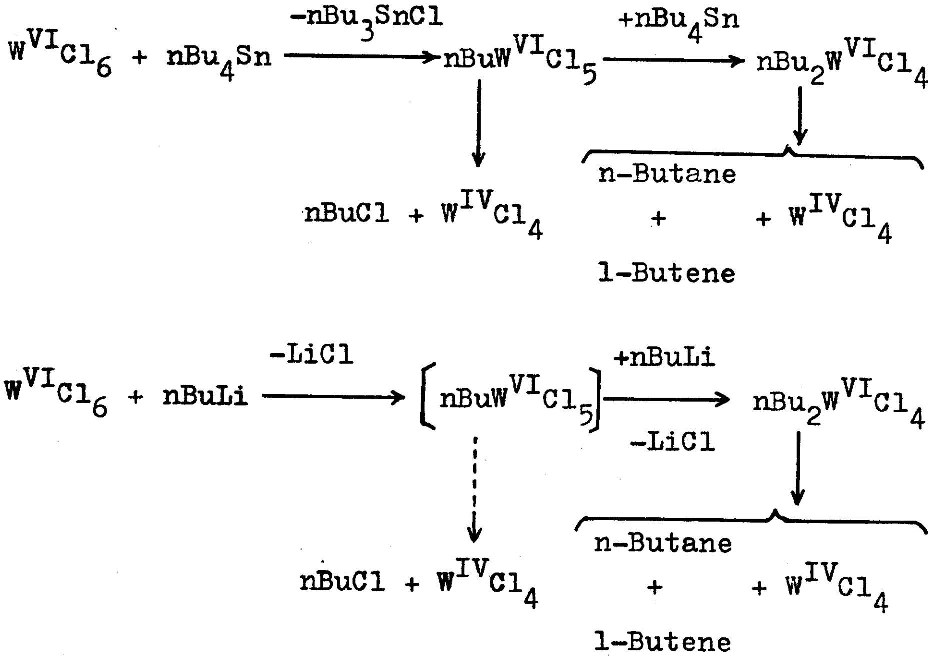
a) WCl_6 0.047 mol/l (7.1×10^{-5}mol), Solvent Benzene, room temp., 5 hr.

b) (moles of nBu_3SnCl)/(moles of WCl_6).

c) (moles of n-butane X 2 + moles of n-BuCl)/(moles of WCl_6).

The mechanism of catalyst formation from WCl_6 and nBu_4Sn or nBuLi in olefin metathesis is illustrated in Scheme 2, on the basis of the facts described above.

We infer that a WCl_4 species is formed by reductive elimination of RH, 1-alkene, RCl and RR from $RWCl_5$ and/or R_2WCl_4. The scheme proposed by Menapace[20] constitutes part of this reaction scheme.



Scheme 2

2. The Catalyst Formation in the Tungsten Hexachloride — Arylmetal Systems

2-1. Products from Catalyst Components

In the WCl_6-arylmetal systems, PhH, PhCl and PhPh species were produced, and good metathesis yield was also obtained for n=*Ca.*2 in each systems (Table 17), where n is the number of ligands displaced from W^{VI} complexes in the reaction of WCl_6 with an arylmetal, *viz*:

n = (moles of PhCl + moles of PhPh) × 2/moles of added WCl_6.

The catalytic activity decreased when n deviated from two and more than a *Ca.*2 equimolar quantity of benzene relative to tungsten was detected. Probably, benzene was formed from the decomposition of aryltungsten intermediates by moisture. The compounds Ph_3Bi and Ph_4Sn themselves did not give any benzene when left in 1,2,4-trichlorobenzene solution for 24 hr, although Ph_4Pb gave a small amount of benzene. These facts suggest that WCl_4 and $PhWCl_3$ species are formed as active catalyst sites. Recently, it has been reported that $PhWCl_3$ is active without any cocatalyst in the metathesis of linear chain olefins.[46] The compound $PhWCl_3$ may be formed by successive displacement of chloride of WCl_4 by benzenide derived from the cocatalyst, and may be deactivated by the attack of an excess of cocatalyst. Moreover Table 17 shows that in the WCl_6-Ph_3Bi system, diphenyl was produced in preference to chlorobenzene over the whole series of Bi/W ratios. Whereas in the WCl_6-Ph_4Pb and the WCl_6-Ph_4Sn systems chlorobenzene was produced in preference to diphenyl at low cocatalyst/WCl_6 ratios, *e.g.* 0.3-1, and decreased as the amount of diphenyl increased in the ratio range $\geqq$ 0.7. Diphenyl was produced in preference to chlorobenzene at high ratios, *e.g.* 2-3. These facts suggest that in the WCl_6-Ph_4Pb and the WCl_6-Ph_4Sn systems, the displacement of chlorine by phenyl occurs in a stepwise fashion to give Ph_2WCl_4 *via* $PhWCl_5$, whereas in the WCl_6-Ph_3Bi system the displacement of chlorine from $PhWCl_5$ occurs quickly to give Ph_2WCl_4 before the elimination of PhCl species from $PhWCl_5$. It has been reported that the reaction of $TiCl_4$ with Ph_3Al leads to the formation of diphenyl without chlorobenzene by a non-radical mechanism.[114,115]

2-2. Dependence of the Metathesis Yield and Amount of PhCl and PhPh species on Reaction Time

In the WCl_6-Ph_4Pb system, the metathesis yield increased as the amounts of PhCl

Table 17. Dependence of Products from Catalyst Components on the Cocatalyst/WCl_6 Ratio

Cocat. (M)	M/W ratio	Metathesis products[a)] Yield	Metathesis products[a)] Selectivity	Reaction products of catalyst components PhH (10^5 mol)	PhCl (10^5 mol)	PhPh (10^5 mol)	n[b)]
Ph_3Bi	0.3	0	0	1.5	0.4	1.9	0.7
	0.5	11	21	2.2	0.6	2.8	1.1
	0.7	31	50	2.6	0.8	3.4	1.4
	1	21	94	8.4	0.7	4.0	1.5
	2	3	34	23.9	0.4	4.8	1.7
	3	1	1	22.4	0.4	5.1	1.8
Ph_4Pb	0.3	5	13	2.6	1.7	0.9	0.8
	0.5	12	24	3.4	3.1	1.0	1.3
	0.7	32	100	6.8	3.3	1.3	1.5
	1	46	100	8.0	2.7	2.3	1.6
	2	40	81	21.2	2.3	5.1	2.4
	3	10	78	25.3	2.5	5.8	2.7
Ph_4Sn	0.3	3	12	3.6	0.4	0.1	0.2
	0.5	10	25	4.5	2.3	0.3	0.8
	0.7	14	28	6.4	3.4	0.6	1.3
	1	19	36	6.0	3.2	1.6	1.5
	2	40	90	10.1	2.7	3.5	2.0
	3	20	27	11.6	2.3	4.0	2.0

a) WCl_6 0.041 mol/l (6.9×10^{-5}mol), 2-Heptene/W 20, Solvent 1,2,4-Trichlorobenzene, room temp., 24 hr.

b) n=(moles of PhCl + moles of PhPh)/moles of added WCl_6.

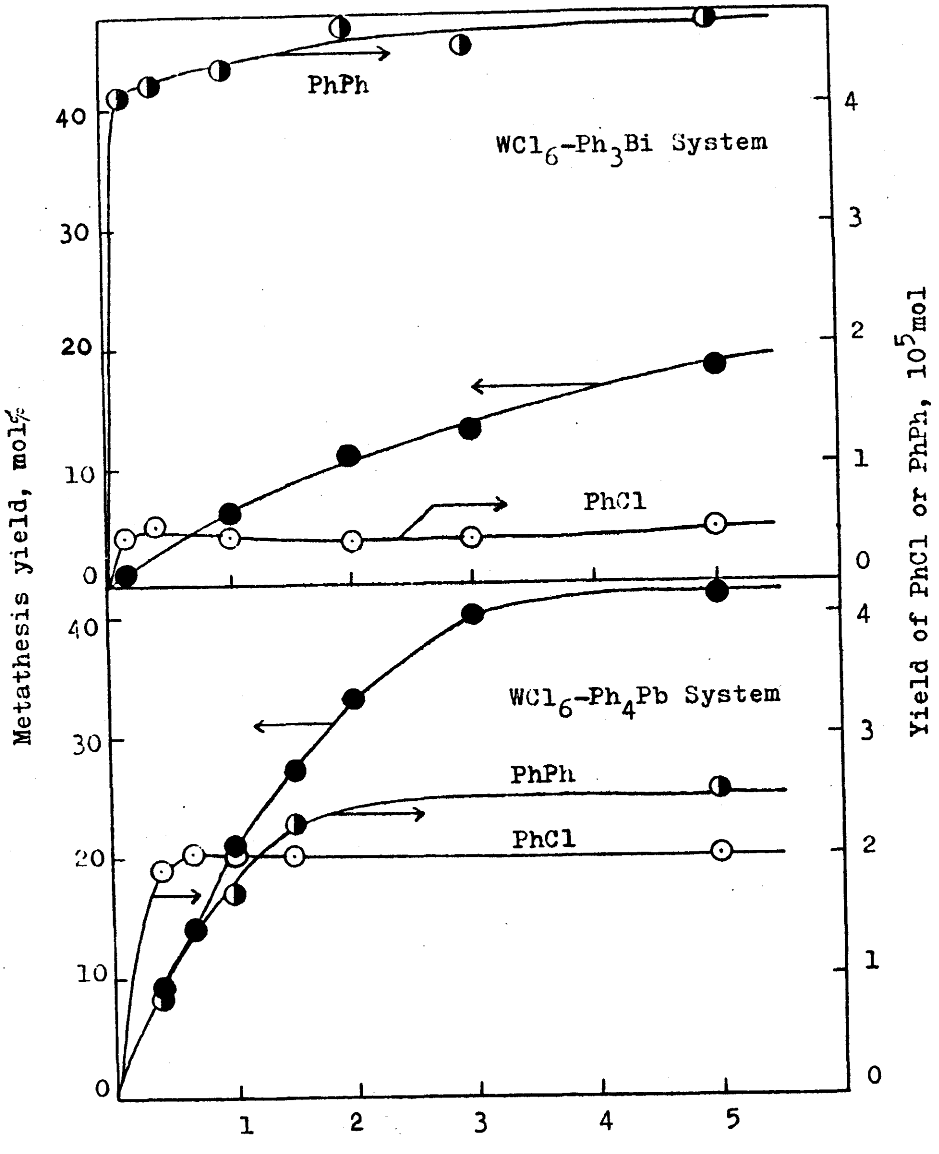
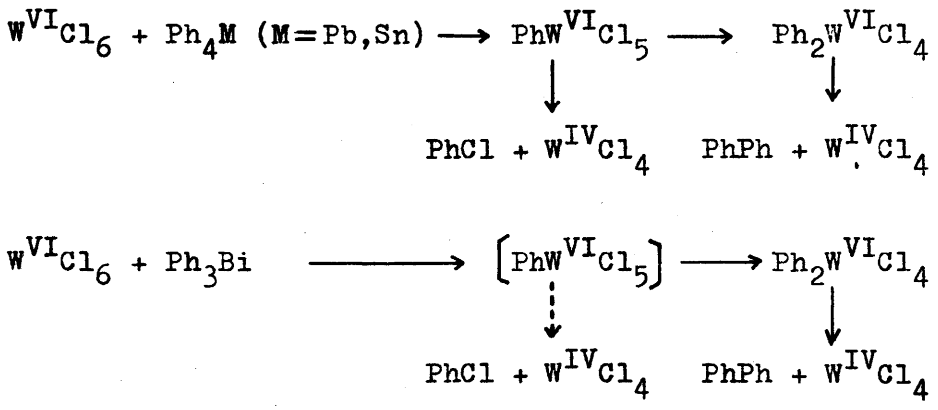


Fig.11. Plot of the amounts of reaction products from catalyst components and the yield of metathesis products vs. time: WCl_6 0.036 mol/l(6.2 X 10^{-5}mol), 2-Heptene/W 23, Bi/W 0.7, Pb/W 1, Solvent 1,2,4-Trichlorobenzene, room temp..

and PhPh species increased, as shown in Fig. 11. Chlorobenzene has formed before diphenyl, and the formation of the latter continued even after the formation of chlorobenzene had stopped. The similar results were obtained in the WCl_6-Ph_4Sn system. These facts suggest that chlorobenzene and diphenyl are produced during the steps in which the WCl_4 species is formed, and that even after the disappearance of the intermediate to give chlorobenzene, the intermediate responsible for diphenyl is still formed. The early formation of chlorobenzene to diphenyl also suggests that the displacement of chlorine by phenyl in the catalyst systems containing WCl_6 and Ph_4Pb or Ph_4Sn occurs stepwise to give Ph_2WCl_4 *via* $PhWCl_5$. On the other hand, in the WCl_6-Ph_3Bi system the metathesis yield increased slowly in spite of the rapid formation of diphenyl and chlorobenzene. The fact suggests that the rapid displacement of chlorine of WCl_6 by phenyl of Ph_3Bi occurs to give Ph_2WCl_4 directly and that the activity of the actual catalyst from WCl_6-Ph_3Bi is lower than those from WCl_6-Ph_4Pb and WCl_6-Ph_4Sn.

The mechanism of catalyst formation from WCl_6 and arylmetals in olefin metathesis is illustrated in Scheme 3.



Scheme 3

The observed behavior of triphenylbismuthine in the catalyst formation may be due to the easiness of Bi-C bond cleavage. In fact, the average scission energy of Bi-C is lower than that of Sn-C.

Finally, the width of the cocatalyst/WCl_6 ratio (Table 14) may be affected by both (a) the nucleophilicity of carbanions from cocatalysts. (MR) due to the nature of M and R, and (b) the level of the activity of the active species formed.

2-3. Effect of Group Va atom containing Compounds

The limitation of the cocatalyst was investigated with respect to compounds containing group Va elements. While triphenylarsine and triphenylstibine were not effective as cocatalysts for 2-heptene metathesis at As/W or Sb/W ratios of 0.5,1,2,3 and 4, triphenylbismuthine was effective essentially. In addition, the mixture of WCl_6 and Ph_3As or Ph_3Sb did not give chlorobenzene and diphenyl, although a small amount of benzene was detected, while the mixture of WCl_6 and Ph_3Bi gave benzene, chlorobenzene and diphenyl. The facts indicate that the metalloid compounds such as Ph_3As and Ph_3Sb can barely donate benzenide to WCl_6. On the other hand, the addition of Va atom compounds such as Ph_3N, Ph_3P, Ph_3As and Ph_3Sb inhibited both the WCl_6-Ph_4Sn catalyzed 2-heptene metathesis and the production of PhH, PhCl, and PhPh species from a mixture of WCl_6 and Ph_4Sn. The fact shows that the Va atom compounds prevented the catalyst formation from WCl_6 and Ph_4Sn. Metalloid compounds such as triphenylarsine and triphenylstibine seem to function as bases, similarly to triphenylamine and triphenylphosphine. It may be concluded that the central atom of the cocatalyst is capable of donating carbanion to tungsten hexachloride and functions as a Lewis acid.

Probably transition metal derivatives except IIb atom compounds are not contained in the cocatalyst, which decompose by the reductive elimination of alkyl or aryl ligands before they donate carbanions to tungsten and/or catalyze the other reactions. The IIb atom derivatives probably can donate carbanion to tungsten without causing other reactions, since IIb elements are regarded as nontransition elements. In fact, diethylzinc was an effective cocatalyst in the 2-heptene metathesis with WCl_6.

3. General Discussion

The foregoing results suggest that the cocatalysts reduce WCl_6 so as to open up all-important coordination vacancies for an olefin and a carbene.* The need to provide coordination vacancies in order to produce a catalytically active species has also been recognized in other catalyst systems. For example, Whan[116] reported that an X-ray photoelectron spectrum of a $Mo(CO)_6$/alumina catalyst system revealed the loss of carbon monoxide ligands when the catalyst was activated. Probably it is *cis* coordination vacancies that is required for catalysis. Any mechanisms thus far posturated require *cis* coordination vacancies on the metal. That $PhWCl_3$ prepared by the reduction of WCl_6 with Ph_4Sn[117] is active without any cocatalyst for olefin metathesis,[46] means (a) that Lewis acid cocatalysts are not essential components of the active catalysts and (b) that even noncarbenoid precursors can catalyze the olefin metathesis.

Figure 12 shows that the addition of metallic compounds considerably increased the activity of the WCl_6-nBuLi system. The addition of LiCl, NaCl, $BiCl_3$, $SnCl_2$ and $PbCl_2$ did not provide any effect. The following routes leading to powerful catalysts can be envisioned: (a) WCl_4 resulting from WCl_6-nBuLi is activated by additives, (b) nBu_4Sn, nBu_xAlBr_{3-x}etc., resulting from the reactions of nBuLi with nBu_3SnCl, $AlBr_3$ etc., give highly active catalysts. Menapace[118] reported the enhancement of the catalytic activity of the WCl_6-nBuLi system when $AlCl_3$ is added to it and proved that this benefit is not derived from the possible formation of $nBuAlCl_2$ from nBuLi and $AlCl_3$. The result of Fig. 12 suggests that the cocatalysts serve another function in addition to the one as reducing agents. The cocatalysts are converted to metal halides or organometal halides. These halides species may act as Lewis acids so as to accelerate the metathesis. This inference explains the fact that the

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* Calderon[9] has reported that a combination of WCl_6 with excess AlX_3 (X=Cl, Br; Al : W= 2-8 : 1) is a metathesis catalyst, and has proposed that the chlorides are removed from the tungsten not through reduction but *via* an acid-base equilibrium: $WCl_x + AlCl_3 \rightleftarrows WCl^+_{x-1} + AlCl_4^-$. However it is unlikely that the final systems contain W^V or W^{VI}. Since it is conceivable that olefins can insert into aluminum-halogen bonds similar to the well-known olefin-insertion into aluminum-hydrogen bonds, aluminum chloroalkyls produced may reduce WCl_6.

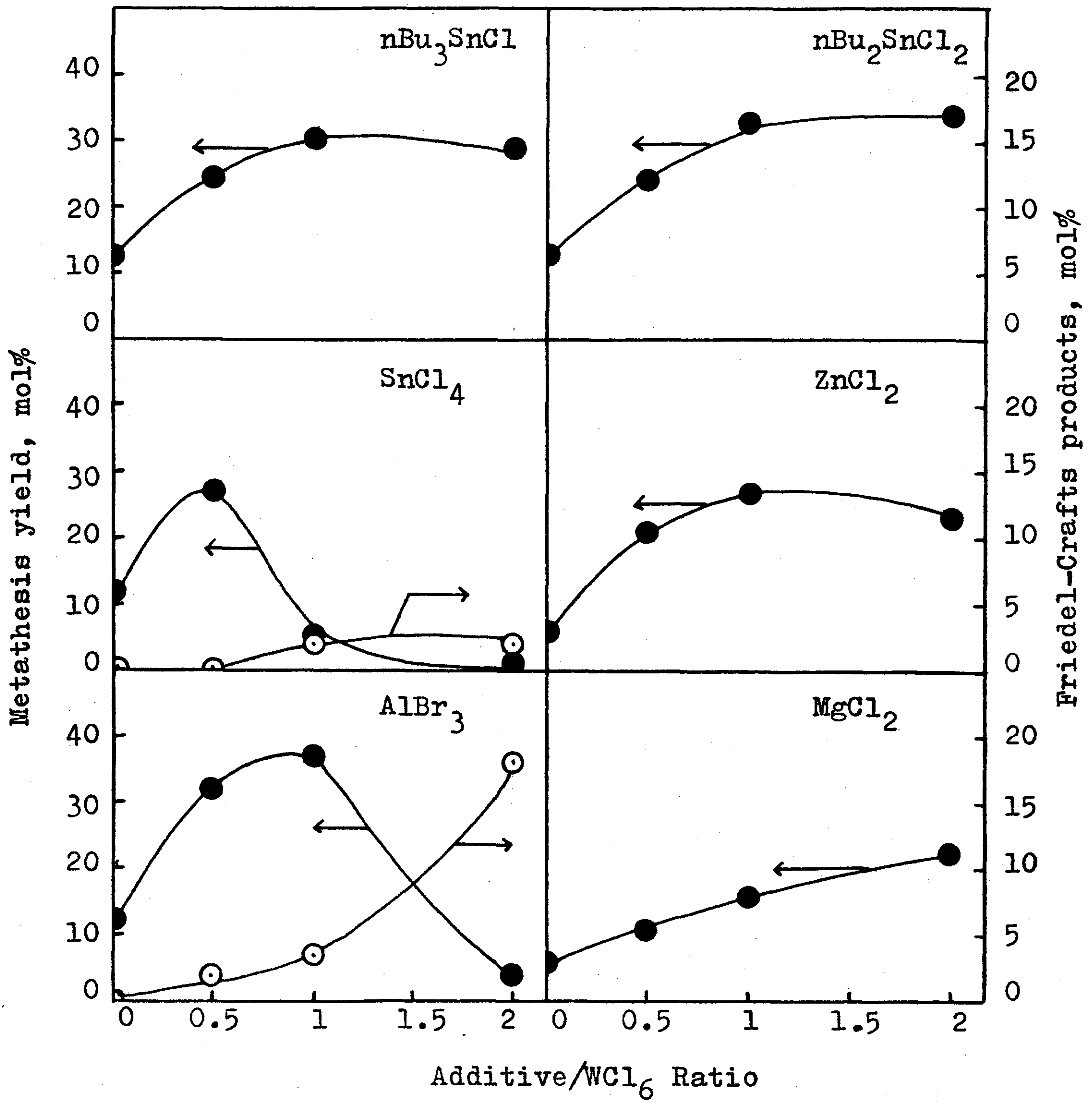
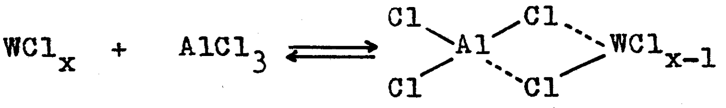


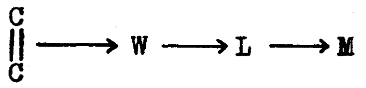
Fig.12. Effect of adding metallic compounds: WCl$_6$ 0.034 mol/l, nBuLi/W 2, 2-Heptene/W 25, Solvent Benzene, room temp., 2 hr. Yield(mol%) = 100 X (2-Butene + 5-Decene)/2-Heptene used.

optimum ranges of the olefin/WCl_6 ratio vary drastically with the nature of the cocatalyst metals (Table 14). Moreover, it has been reported that the combination of $AlCl_3$ with WCl_4,[9] $PhWCl_3$[46] or $W(CH_2Ph)_4$[50] leads to a powerful catalyst. As Calderon[9] has pointed out (Eq. 14 and 15), Lewis acids may associate with reduced tungsten. Lewis acids would reduce electron density on tungsten by attracting electrons from the ligands, as shown below. This phenomenon is related to the "*trans* effect" in which the susceptibility of a metal ligand toward substitution may be strongly influenced by the properties of the ligand *trans* to it. Menapace[118] has described that the enhancement of the activity of the WCl_6-nBuLi system by $AlCl_3$ is attributable to the rapid isomerization of *trans*-$WCl_4(\text{olefin})_2$ to *cis*-$WCl_4(\text{olefin})_2$ by acid-base equilibria (Eq. 15). Most recently, Gassman[48] has demonstrated that a metal-carbene complex formed as an intermediate in a metathesis reaction possesses a nucleophilic carbon, as depicted in (c).

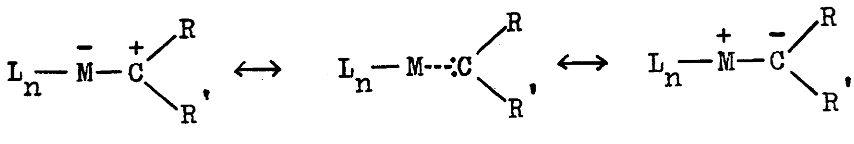


(14)

$$WCl_x + AlCl_3 \rightleftharpoons WCl^{+}_{x-1} + AlCl_4^{-} \qquad (15)$$



L= Ligand
M= Lewis Acid



(a) (b) (c)

Lewis acids may interact with tungsten through carbene bridges, as Muetterties[111] has pointed out.

Substantial supportive evidence exists for the non-pairwise chain mechanism, whereas relatively little is known about the origin of the metal-carbene intermediate, except the reports of Farona[40] and Muetterties.[111] We believe that potential routes to the formation of the initial carbene-metal entity exist in our catalyst systems, aside from the catalyst formation. Gassman[48] has demonstrated that metal-carbene intermediate can be generated from non-carbenoid precursor under metathesis reaction conditions. Pathways that olefins and catalyst metal lead to the formation of carbene-metal entities are speculated by several investigators.[102,119]

CHAPTER IV

EFFECT OF THE REACTION MEDIUM

1. Effect of the Reaction Medium on the Metathesis Yield

1-1. Effect of the Catalyst Concentration

Influence of the catalyst concentration on the final yield in the metathesis of 2-heptene with WCl_6-Et_3Al was examined in various solvents. The results are shown in Table 18. At a fixed level of the catalyst concentration, the metathesis yield was markedly affected by the solvents used. Additionally, the level of the catalyst concentration at which the final yield of the metathesis attained the equilibrium value, varied with the solvents. The polychlorinated aliphatic hydrocarbons, and polyhalogenated benzenes such as trichloroethylene, tetrachloroethylene, hexachloro-1,3-butadiene, hexachlorocyclopentadiene, 1,1,2,2-tetrachloroethane, o- and m-dichlorobenzene and 1,2,4-trichlorobenzene gave the good yield without the formation of the undesirable Friedel-Crafts products. By the judicious choice of solvents, the separation of the product from the reaction mixture can be performed more easily. Especially, the use of trichloroethylene, tetrachloroethylene, 1,1,2,2-tetrachloroethane, 1,2-dichloroethane, and 1,1,2-trichloroethane as solvents appears to increase the merit of the metathesis reaction in synthetic chemistry, since these solvents are inexpensive.

The data showed interesting trends as follows:

(a) In the more chlorinated benzene, the better result was obtained. It is noteworthy that 1,2,4-trichlorobenzene and o-dichlorobenzene gave the significantly good results.

1,2,4-trichlorobenzene ~ o-dichlorobenzene > m-dichlorobenzene > chlorobenzene ~ benzene

(b) Of the monohalogenated benzenes, bromobenzene gave the best metathesis yield. The metathesis did not proceed in iodobenzene.

bromobenzene > chlorobenzene ~ benzene > florobenzene

(c) In the chloroflorobenzenes, the metathesis yield was affected by the orientation of halogen atoms of solvent molecules.

Table 18. The Dependence of Metathesis Yield on Solvents at Various Catalyst Concentrations a)

Solvent	Metathesis % b)							
	Catalyst Concentration, mol/l X 10^2							
	0.4	0.7	1.0	1.3	1.6	1.8	2.0	2.2
benzene	1	7	15	22	33	33	33	33
(F.C.Products	0	1	1	4	6	4	5	5)
florobenzene	0	1	6	9	19	22	26	33
chlorobenzene	1	8	17	24	33	33	33	33
bromobenzene	6	25	33	33	33	33	33	33
Iodobenzene	0	0	0	0	0	0	0	0
o-dichlorobenzene	20	31	33	33	33	33	33	33
m-dichlorobenzene	3	13	33	33	33	33	33	33
1,2,4-trichlorobenzene	20	33	33	33	33	33	33	33
o-florochlorobenzene	0	0	0	0	0	3	12	17
m-florochlorobenzene	0	1	3	7	15	18	22	28
p-florochlorobenzene	1	2	5	12	27	30	33	33
cis-1,2-dichloroethylene	1	2	4	10	16	23	28	33
trans-1,2-dichloroethylene	1	2	3	5	12	17	24	29
trichloroethylene	1	1	7	16	33	33	33	33
tetrachloroethylene	1	5	19	27	33	33	33	33
1,2-dibromoethylene(mix)	0	0	0	0	0	0	0	1
hexachloro-1,3-butadiene	3	8	19	33	33	33	33	33
hexachlorocyclopentadiene	5	10	21	33	33	33	33	33
1,1-dichloroethane	0	0	1	2	3	4	5	9
1,2-dichloroethane	0	1	4	12	24	33	33	33
1,1,2-trichloroethane	0	0	0	3	8	11	15	21
1,1,2,2-tetrachloroethane	9	16	24	30	33	33	33	33
1,2-dibromoethane	0	0	0	1	1	1	2	2

a) The reactions of 2-heptene with WCl$_6$ and Et$_3$Al (mole ratio: 2-heptene/W = 100, Al/W=1) were carried out at room temperature for 5 hours.

b) 100 X 5-Decene/(2-Heptene + 5-Decene), mol%.

chlorobenzene ~ benzene > p-florochlorobenzene > florobenzene > m-florochlorobenzene > o-florochlorobenzene

(d) Many chlorinated ethylenes and chlorinated dienes provided the better results than benzene and chlorobenzene.

hexachloro-1,3-butadiene ~ hexachlorocyclopentadiene ~ tetrachloroethylene > chlorobenzene ~ benzene ~ trichloroethylene > *cis*-1,2-dichloroethylene > *trans*-1,2-dichloroethylene

(e) In chlorinated ethanes, the yield decreased in the following order.

1,1,2,2-tetrachloroethane > chlorobenzene ~ benzene > 1,2-dichloroethane > 1,1,2-trichloroethane > 1,1-dichloroethane

(f) In the mixed 1,2-dibromoethylene and 1,2-dibromoethane, the metathesis reaction hardly proceeded. In cyclohexane, n-pentane and n-hexane, the yield was low because of the poor solubility of WCl_6 in these alkanes. The good solubility of WCl_6 may be due to the affinity of WCl_6 with aromatic rings, double bonds or chlorines of solvent molecules. The coordination of aromatic molecules to tungsten carbonyl complexes[120] or halogenides (WCl_6 and WF_6)[121,122] has been reported. It was shown that, at least in the latter case, a rapid exchange process actually takes place.

In halogenated propenes such as 1,3-dichloropropene, 2,3-dichloropropene, 1,1-dichloropropene and 1,2,3-trichloropropene, the metathesis hardly proceeded.

The results show that the good yield was obtained in the solvents containing the groups such as $\mathrm{{}^{Cl}\diagdown C{=}C\diagup{}^{Cl}}$, $\mathrm{{}^{Cl}\diagdown C{-}C\diagup{}^{Cl}}$ and aromatic ring. The order of extent of the metathesis in monohalogenated benzenes parallels that of the Hammet-Brown substituent constant σ_p or σ_m, except iodobenzene. This suggests that the metathesis is affected by the π-donor ability of the aromatic molecule. The metathesis of 2-heptene with WCl_6-nBu_4Sn also showed the similar trends. The observed trends are independent of the dipole moment of solvent molecules.

Solvent molecules may be effective for forming and stabilizing active species. It is speculated from molecular radii and bond distances that $\mathrm{{}^{Cl}\diagdown C{=}C\diagup{}^{Cl}}$ and $\mathrm{{}^{Cl}\diagdown C{-}C\diagup{}^{Cl}}$ can fill the *cis*-vacancies of WCl_4 with chlorine atoms. Active WCl_4 containing *cis*-vacancies may be formed predominantly in the solvents containing such groups. Moreover, the catalyst deactivation may be retarded by the stabilization of the active species due to the interaction between tungsten species and $\mathrm{^{Cl}\diagdown C{=}C \diagup^{Cl}}$, $\mathrm{^{Cl}\diagdown C{-}C \diagup^{Cl}}$ or aromatic rings of solvent molecules.

The olefin exchange step which completes the catalytic cycle is important in the olefin metathesis. That is, an outstanding feature of certain metathesis catalysts is their capacity to promote rapid reactions at very low concentrations. Extremely fast rates are common, and these could not be realized if an efficient route did not exist for the exchange of incoming and outgoing olefin molecules on the active site on the metal. In this step, which may be viewed as either S_N1 or as S_N2, solvent molecules may affect this reaction by either the rapid competitive coordination to tungsten or by acting as a metal ligand. Alternatively, solvent molecules may affect this reaction in the transalkylidenation step.

After all, the metathesis yield seems to depend on both rates of olefin metathesis and catalyst deactivation. Good solvents act so as to increase the metathesis rate and so as to slow down the catalyst deactivation.

Table 19 suggests that the catalyst formation is not influenced by the solvents such as trichloroethylene and bromobenzene.

Table 19. Effect of Solvent on Catalyst Formation from WCl_6 - Ph_4Sn System [a]

Solvent	Sn/W	Products, mol X 10^5		Metathesis % [b]
		PhCl	Ph-Ph	
Trichloroethylene	0.5	1.3	0.6	8
	1	2.6	3.7	28
Bromobenzene	0.5	1.4	0.6	15
	1	2.8	3.6	33

a) The reactions of 2-heptene (1.2×10^{-3}mol, 0.8 mol/l) with WCl_6 (6.5×10^{-5}mol, 0.043 mol/l) and Ph_4Sn were carried out at room temperature for 5 hours.

b) 100 X 5-Decene/(2-Heptene + 5-Decene), mol%.

1-2. Optimum Reaction Conditions in Several Solvents

Figure 13 shows the effect of the cocatalyst/WCl_6 ratio on the 2-heptene metathesis with WCl_6-Et_3Al in several solvents. In 1,2,4-trichlorobenzene, the good metathesis yield was obtained without the Friedel-Crafts products even at low Al/W ratio, though in benzene the Friedel-Crafts reaction rapidly occurred and extremely decreased the selectivity of metathesis at low Al/W ratio. Moreover, 1,2,4-trichlorobenzene provided the wider optimum Et_3Al/WCl_6 ratio range as compared to benzene. In trichloroethylene and *cis*-1,2-dichloroethylene, the good yield was obtained at the Et_3Al/WCl_6 ratios more than one and the decrease of the yield was not observed even at the markedly high Al/W ratio. Davie[123] reported that the activity of an heterogeneous $Mo(CO)_6$-Al_2O_3 system is increased by

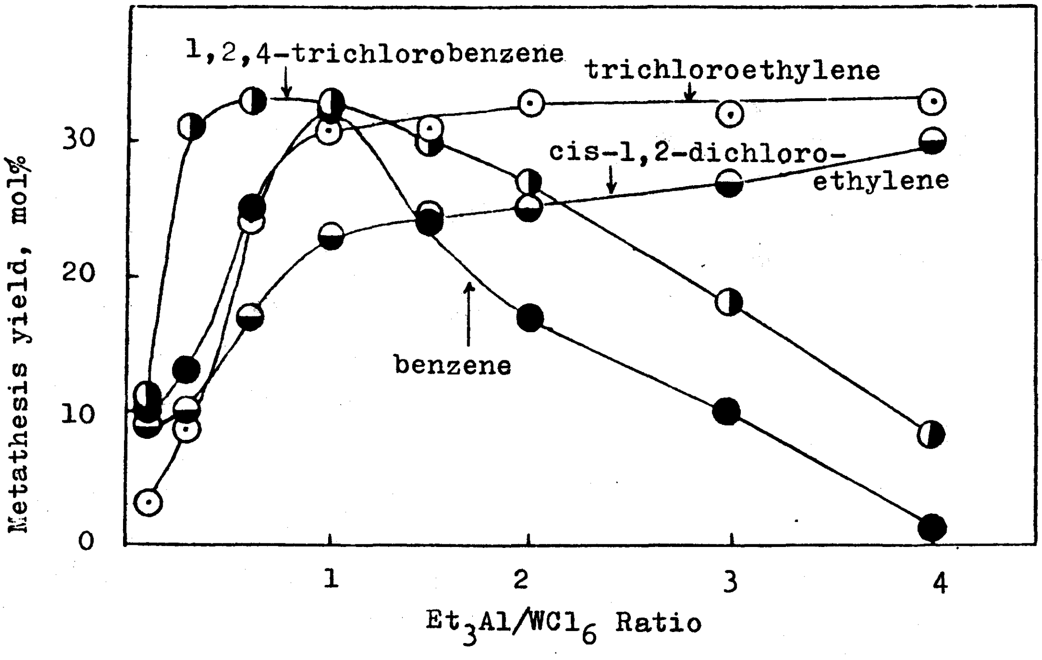


Fig.13. Effect of Et_3Al/WCl_6 ratio on the metathesis yield in several solvents: WCl_6 0.016 mol/l, 2-Heptene/W 100, room temp., 5 hr. Metathesis yield(mol%) = 100 X 5-Decene/(2-Heptene + 5-Decene).

treating the catalyst with a halogenated olefin. He obtained some evidence that the activating molecules are bonded to the catalyst, and suggested that the increase in activity caused by halogen-containing olefins is attributed to electron-withdrawing substituents reducing the strength of the back bonding from the molybdenum to the other ligands and thus enhancing their reactivity. Similarly in our homogeneous system, trichloroethylene and *cis*-1,2-dichloroethylene may activate the catalyst by coordinating on over-reduced tungsten with double bond.

As shown in Fig. 14, 1,2,4-trichlorobenzene especially gave a wide optimum olefin/WCl_6 ratio range. Generally, the solvent which gives a good yield appears to widen the optimum ranges of the cocatalyst/WCl_6 and the olefin/WCl_6 ratios.

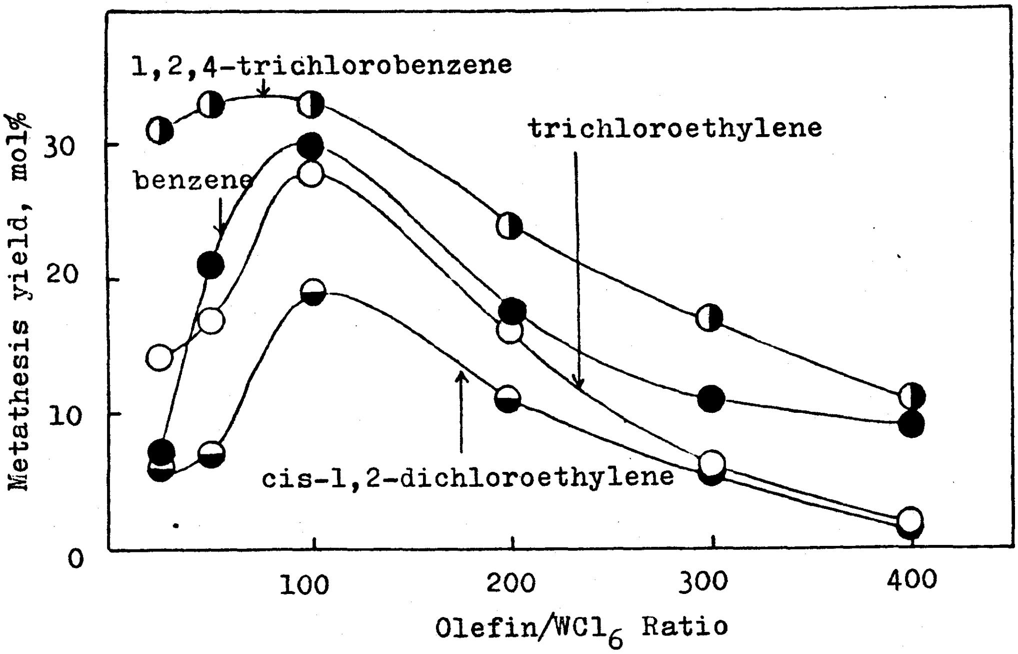


Fig.14. Effect of olefin/WCl_6 ratio on the metathesis yield in several solvents: WCl_6 0.016 mol/l, Et_3Al/W 1, Olefin 2-Heptene, room temp., 5 hr. Metathesis yield (mol%) = 100 X 5-Decene/(2-Heptene + 5-Decene).

2. Effect of Binary Solvent Systems

In the binary solvent systems of benzene-trichloroethylene, -1,2,4-trichlorobenzene, and -m-dichlorobenzene, the 2-heptene metathesis with the WCl_6-nBu_4Sn system was carried out. The best yield was observed at 40-45 volume% of the halogenated solvents (Fig. 15).

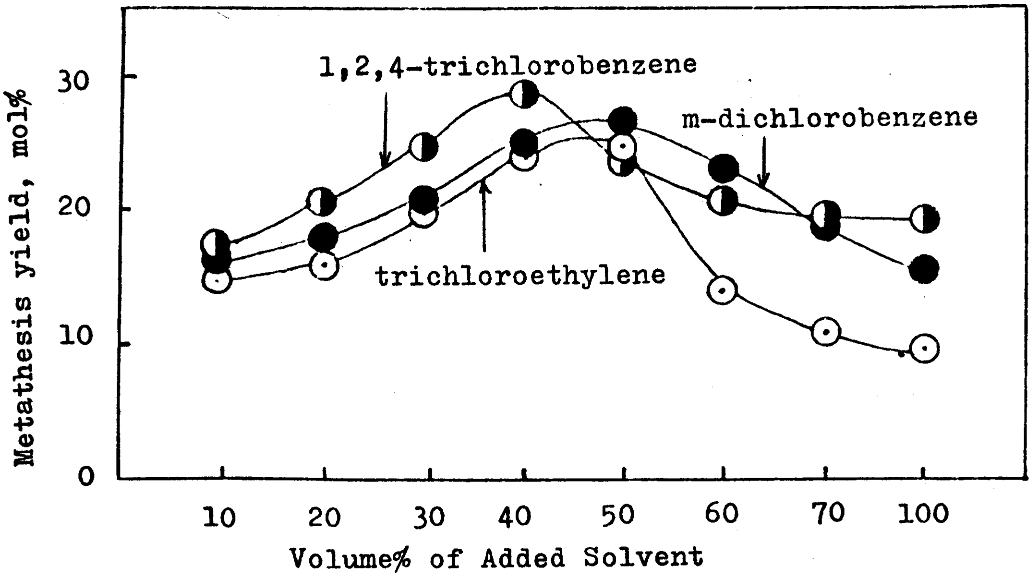


Fig.15. Effect of benzene-binary solvent systems: WCl_6 0.01 mol/l, 2-Heptene/W 100, nBu_4Sn/W 1, room temp., 5 hr. Metathesis yield (mol%)= 100 X 5-Decene/(2-Heptene + 5-Decene).

The result shows that a mixture of aromatic ring and ${}^{\mathrm{Cl}}\diagdown\mathrm{C{=}C}\diagup{}^{\mathrm{Cl}}$ components leads to the excellent medium for olefin metathesis. Again, it is assumed that these components of solvent molecules accelerate the olefin exchange or the transalkylidenation and/or slow down the deactivation of the catalyst.

3. Inhibitory Effect of Heteroatom Compounds

Table 20 shows that the addition of ether depressed the 2-heptene metathesis more intensively than the production of PhCl and PhPh species from WCl_6-Ph_4Sn. The result suggests that ether inhibits the metathesis by deactivating the active species produced rather than by depressing the catalyst formation. This assumption is also supported by the fact that the addition of ether to the medium stopped the reaction in the course of the metathesis.

Table 20. Effect of Ether on Catalyst Formation from WCl_6 - Ph_4Sn System [a)]

Et_2O/W	Products, mol X 10^5		Metathesis % [b)]
	PhCl	Ph-Ph	
0	1.1	3.4	31
0.3	1.1	3.1	29
0.6	1.1	2.7	21
1	0.7	2.3	1
2	0.4	1.1	0

a) WCl_6 0.046 mol/l (6.9 X 10^{-5}mol), 2-Heptene/W 20, Sn/W 1, Solvent Trichloroethylene, room temp., 5 hr.

b) 100 X 5-Decene/(2-Heptene + 5-Decene), mol%.

Other heteroatom compounds also inhibited the metathesis (Table 21). These compounds contain oxygen, sulfur, nitrogen and phosphorus atoms. The intensity of the inhibition of metathesis by ethers decreased in this order: THF > ethyl ether > furan > n-propyl ether > iso-propyl ether. Less-hindered ether inhibits the metathesis more strongly. The order of this effect roughly paralles the order of nucleophilicity of ether. Furan showed

Table 21. Retarding Effect of Additives [a)]

Additive	Metathesis % [b)] Additive/WCl_6 ratio								
	0.5	1	2	4	6	12	24	48	96
	33	25	7	0					
Et_2O	33	33	33	26	20	4	0		
	33	32	30	28	23	11	2	0	
nPr_2O	33	33	33	33	33	33	31 (33)	21 (33)	1 (33)
$isoPr_2O$	33	33	33	33	33	32	21 (30)	19 (27)	2 (20)
MeOH	31	21	6	0					
tBuOH	32	25	13 (30)	0					
PhOH	33	28	9	0					
MeCOOnPr	33	33	5 (33)	0					
MeCOOisoPr	33	32	1 (33)	0					
MeCOOPh	33	33	28	20	12	0 (30)			
MeCOnPr	33	20	4	0					
MeCOisoPr	30	18	13	0					
PhCOOH	4	0							
	31	19	2	0					
PhSH	33	33	10	5	0				
Et_3N	33	4	0						
nBu_3N	30	1	0						
Ph_3N	33	29	27	21	10 (33)	0			
nBu_3P	33	7	0						
Ph_3P	23	12	3 (11)	0					

a) The reactions of 2-heptene (1.4×10^{-3}mol, 1.03 mol/l) with WCl_6 (4.6×10^{-5}mol, 0.034 mol/l) and Bu_4Sn (4.6×10^{-5}mol, 0.034 mol/l) were carried out in 1,2,4-trichlorobenzeme at room temperature for 5 hours. Conversions indicated in ( ) were obtained from the reactions at 60 °C.

b) 100 X 5-Decene/(2-Heptene + 5-Decene), mol%.

the less inhibitory effect than tetrahydrofuran. This fact may be explained by the weaker nucleophilicity of furan as compared to that of tetrahydrofuran, due to the delocalization of the electron of oxygen into the double bond. The inhibitory effect of alcohols, esters and ketones resembles that of tetrahydrofuran. The fact that esters and ketones showed the similar inhibitory effect suggests their coordination to the catalyst with carbonyl group. Phenyl acetate showed the weaker inhibitory effect than the other carbonyl compounds. This may be due to the delocalization of the electron of carbonyl oxygen into phenyl ring. Benzoic acid inhibited the reaction most strongly. It may be due to the coordination with both oxygens of carbonyl and hydroxy groups to the catalyst and due to the function as protonic acid. Oxygen compounds showed the similar inhibitory effect to the corresponding sulfur compounds, *viz*: tetrahydrofuran *vs.* tetrahydrothiophene, and phenol *vs.* thiophenol. Nitrogen compounds also showed the similar inhibitory effect to the corresponding phosphorus compounds, *viz*: tri-n-butylamine *vs.* tri-n-butylphosphine. Triphenylamine showed the less inhibitory effect than the corresponding phosphine, exceptionally.

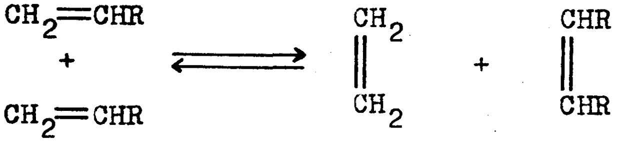
When the reactions were carried out at 60°C, the inhibitory effect extremely decreased. Heating may weaken the bonding between the catalyst and additives and may cause the competitive coordination of olefins, additives and solvents. The result means that heating enables the metathesis of unsaturated hydrocarbons containing functional groups.

CHAPTER V

METATHESIS OF 1-ALKENE

1. Effect of Additives on 1-Octene Metathesis with the Tungsten Hexachloride — Tetra-n-butyltin System

The metathesis of 1-alkene gives an ethylene and a symmetric internal alkene (Eq. 16).



$$\begin{matrix} CH_2{=}CHR \\ + \\ CH_2{=}CHR \end{matrix} \rightleftarrows \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + \begin{matrix} CHR \\ \| \\ CHR \end{matrix} \qquad (16)$$

Unfortunately this reaction is accompanied by the various side reactions[18,112] such as double bond migration, oligomerization/polymerization of olefins and the Friedel-Crafts alkylation, and the yield of the metathesis products is low, except several catalysts.[19,38,39,40] The depression of various side reactions and the improvement of the metathesis yield have been thus far important subjects in this reaction. These problems were resolved by using the modified WCl_6-nBu_4Sn catalysts and trichloroethylene as a solvent at elevated temperature as shown in Table 22. In the absence of additives, the metathesis of 1-octene with WCl_6-nBu_4Sn at room temperature afforded a mixture of alkenes ranging C_2 to C_{14} with low conversion. When the temperature was elevated up to 80°C, the amount of consumed 1-octene greatly increased, and the increase in the yield of alkenes ranging from C_9 to C_{14} was recognized. Probably a polymerization took place at the same time, since the amount of product alkenes was much less than that of the consumed 1-octene. At the same temperature, the addition of n-propyl acetate to the reaction system suppressed the formation of alkenes ranging from C_9 to C_{13} and from C_3 to C_7, and the polymerization, but 7-tetradecene and ethylene were formed in high yield and in high selectivity. The addition of ethyl acetate, n-butyl acetate and sec-butyl acetate also provided high yield of 7-tetradecene and high

Table 22. Effects of Additives in the Metathesis of 1-Octene [a]

Additive	Additive/ WCl_6	Distribution of alkenes, mol %[b]						Selectivity,[c] %
		C_8	C_9	C_{10}	C_{12}	C_{13}	C_{14}	
None[d,e]	0	87.8	1.4	0	0.2	0.5	1.4	23.0
None[e]	0	6.7	5.1	1.8	2.3	2.6	2.8	6.0
None[f]	0	14.7	7.2	2.0	4.0	4.7	5.1	12.1
n-Propyl acetate	4[e]	64.3	1.0	0.8	0.4	0.6	14.8	82.9
	4[g]	57.5	1.1	0.9	0.2	0.9	16.9	79.5
Ethyl acetate	4	68.2	0.4	0.8	0.2	0.3	14.1	88.7
n-Butyl acetate	4	69.2	0.5	0.7	0.2	0.3	13.7	89.0
sec-Butyl acetate	4	74.5	0.6	0.4	0.2	0.3	11.3	88.6
Acetonitrile	2	60.2	0.1	0	0.2	0.1	19.4	97.5
	4	73.5	0	0	0	0	13.2	100
Phenylacetylene	4	44.1	3.2	1.4	0.9	2.6	17.0	60.8
	8	44.8	2.3	1.5	0.7	1.7	16.1	58.5
Dicyclopentadiene	4	37.5	4.0	1.1	1.6	3.1	15.4	49.3
	8	51.7	1.6	0.5	1.6	1.2	15.4	64.0
Ethyl ether	4	30.8	6.3	1.6	1.6	3.9	12.1	34.8
	8	38.5	5.1	1.7	1.5	3.6	15.3	49.9
n-Propyl ether	4	22.1	7.5	1.5	2.0	4.7	9.9	25.4
	8	36.9	5.6	1.5	1.5	3.3	13.7	43.4
Tetrahydrofuran	4	73.4	0.8	0.5	0	2.7	9.4	70.4
	8	84.9	0	0	0	0	4.5	59.6
1-Propanol	1	43.7	8.2	2.1	1.2	3.8	10.6	37.7
	4	100	0	0	0	0	0	

[a] The mixture of 1-octene (1.2 M), WCl_6 (0.024 M), Bu_4Sn (0.048 M), and an additive was heated in trichloroethylene in the absence of air at 80 °C for 3 h. [b] Mole % of each alkene based on the amount of 1-octene used. The product alkenes lower than C_8 were not determined. [c] % selectivity = (moles of 7-tetradecene × 2) × 100/moles of 1-octene consumed. [d] The reaction was carried out at room temperature. [e] The reaction was carried out in the presence of air. [f] Detected octenes were composed of 1-octene (0.11 M), *trans*-2-octene (0.04 M), and *cis*-2-octene (0.02 M). Detected C_{14} components contained *cis*- and *trans*-7-tetradecene mainly, with several other components. 7-Tetradecene contained 21% cis isomer. [g] Detected octenes were composed of 1-octene (0.67 M), *trans*-2-octene (0.02 M), and trace of *cis*-2-octene. No other C_{14} component except 20% *cis*- and 80% *trans*-7-tetradecene was detected.

selectivity, respectively. The distribution of the alkenes ranging from C_8 to C_{14} was not influenced by the presence of air. In the 1-octene metathesis in the absence of additives, *cis-* and *trans*-2-octene, which are produced by the double bond migration, were detected by a capillary squalane column. Presumably, alkenes ranging from C_2 to C_{14} were formed not only by the self-metathesis of 1- and 2-octene and by the cross-metathesis of 2-octene with 1-octene but also by the successive reactions of product alkenes such as the isomerization of 1-heptene into 2-heptene and the self- and the cross-metathesis of 2-heptene. The $WCl_6 \cdot CH_3COOnPr/nBu_4Sn$ system reduced the amounts of *cis-* and *trans*-2-octene and the product alkenes ranging from C_9 to C_{13}. This fact indicates that the addition of n-propyl acetate suppresses the isomerization of 1-octene to 2-octene. Acetonitrile showed an excellent effect at the CH_3CN/WCl_6 ratio of 2. Phenylacetylene, dicyclopentadiene, ethyl ether, n-propyl ether and tetrahydrofuran were also found to be comparatively effective additives. Water, hydrochloric acid, benzoic acid, tri-n-butylamine, tri-n-butylphosphine, and tetrahydrothiophene were not effective ones. In the presence of such compounds, the catalytic activity was hardly recognized at the additive/WCl_6 ratios of 1 and 4. Water, hydrochloric acid, and benzoic acid might destroy the catalyst. However, the addition of 1-propanol gave 11% 7-tetradecene at the equimolar amount to tungsten. Tri-n-butylamine, tri-n-butylphosphine, and tetrahydrothiophene induced the yellow precipitations with a solution of WCl_6. Probably the stable acid-base tungsten complexes were formed.

2. Research for Optimum Reaction Conditions in the 1-Octene Metathesis with the Tungsten Hexachloride — n-Propyl Acetate — Tetra-n-butyltin System

Optimum reaction conditions were searched in the metathesis of 1-octene catalyzed by the $WCl_6 \cdot CH_3COOnPr/nBu_4Sn$ system. Figure 16 shows the effects of temperature and of the $CH_3COOnPr/WCl_6$ ratio on the yield and the selectivity. At room temperature, n-propyl acetate hindered the reaction at the $CH_3COOnPr/WCl_6$ ratio of 2, whereas at 60°C good yield and good selectivity were obtained at the same $CH_3COOnPr/WCl_6$ ratio, though the yield decreased sharply with the increase in the $CH_3COOnPr/WCl_6$ ratio. At 80°C, good

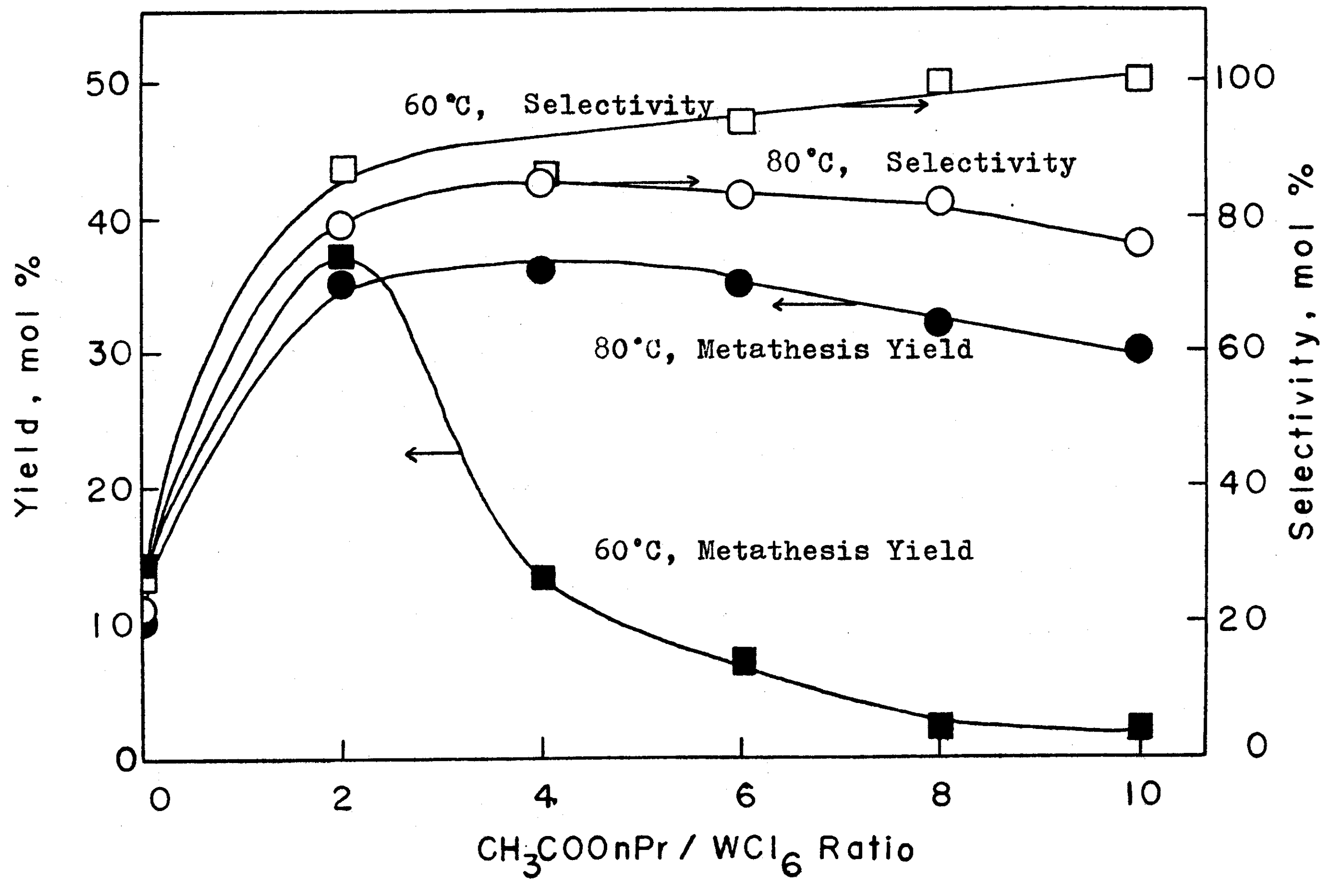


Fig.16. Effect of temperature and of the amount of n-propyl acetate: WCl_6 0.024 mol/l, 1-Octene/W 50, Bu_4Sn/W 2, Trichloroethylene Medium, 3 hr.

results were obtained at the $CH_3COOnPr/WCl_6$ ratio of 2-8, and 27% yield and 74% selectivity were obtained even at the $CH_3COOnPr/WCl_6$ ratio of 20. This result means that an excess amount of n-propyl acetate inhibits the metathesis and that heating promotes the metathesis and extremely widens the optimum range of the $CH_3COOnPr/WCl_6$ ratio.

Figure 17 shows the effect of the nBu_4Sn/WCl_6 ratio in the reaction at 80°C. Good yield and good selectivity were obtained at the nBu_4Sn/WCl_6 ratio of 2-8. The optimum range was extremely wider than that of the nBu_4Sn/WCl_6 ratio in the 2-heptene metathesis in benzene at room temperature. This result shows that the catalyst effective for the 1-alkene metathesis is easily prepared from WCl_6, nBu_4Sn and n-propyl acetate in trichloroethylene.

Figure 18 indicates that this system gives the markedly wide optimum range of the olefin/WCl_6 ratio such as 20-400. The yield decreased from 38 to 14% when the concentration of WCl_6 was changed from 0.024 mol/l to 0.008 mol/l at the 1-octene/WCl_6 ratio of 400. At 0.008 mol/l of the WCl_6 concentration, the yield of 14-9% and the selectivity of 99-93% were obtained at the 1-octene/WCl_6 ratio of 400-800. The result of Fig. 18 means again that this reaction does not require certain strict reaction conditions.

Table 23 shows that the metathesis yield is rarely influenced by the order in which reagents are combined in this system.

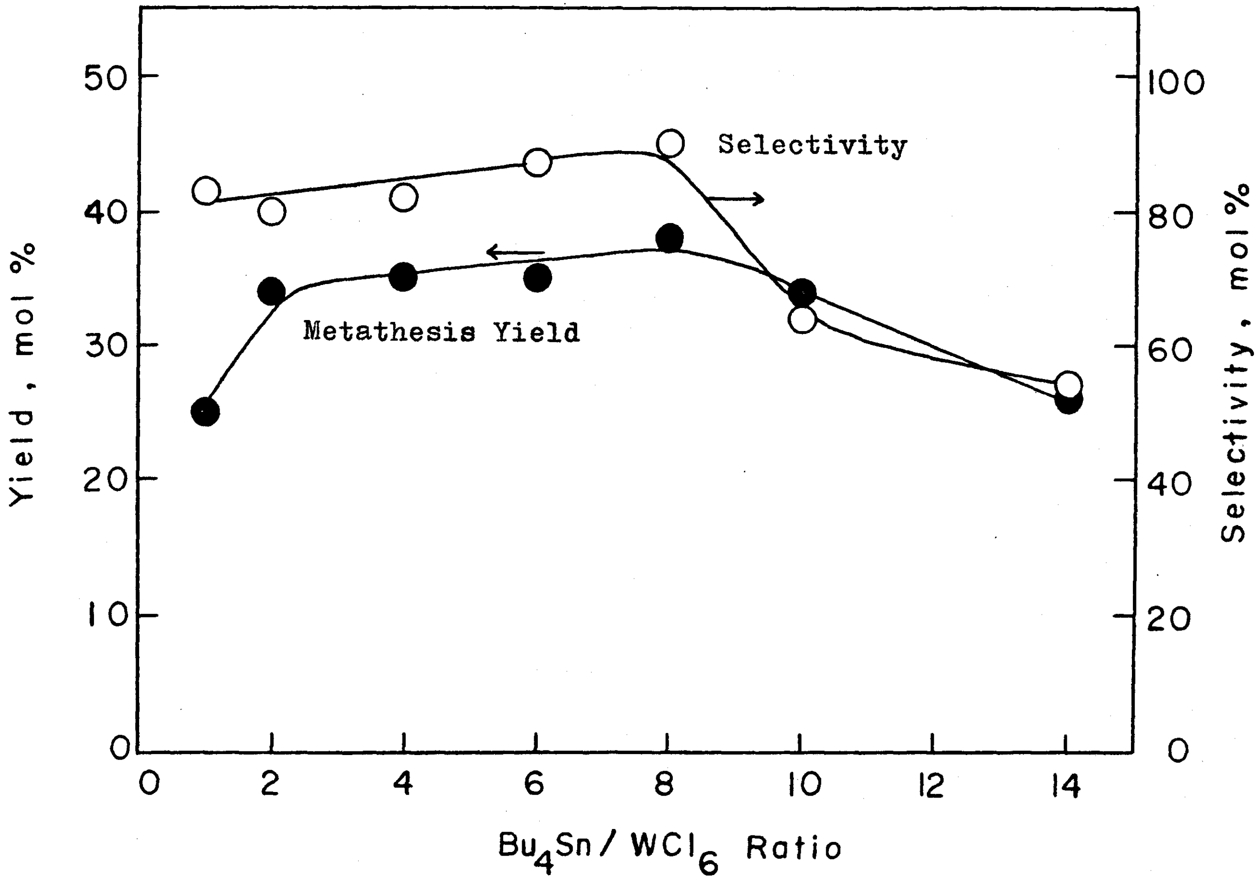


Fig.17. Effect of Bu_4Sn/WCl_6 ratio: WCl_6 0.024 mol/l, 1-Octene/W 50, Bu_4Sn/W 4, $CH_3COOnPr$/W 4, Trichloroethylene Medium, 80°C, 3 hr.

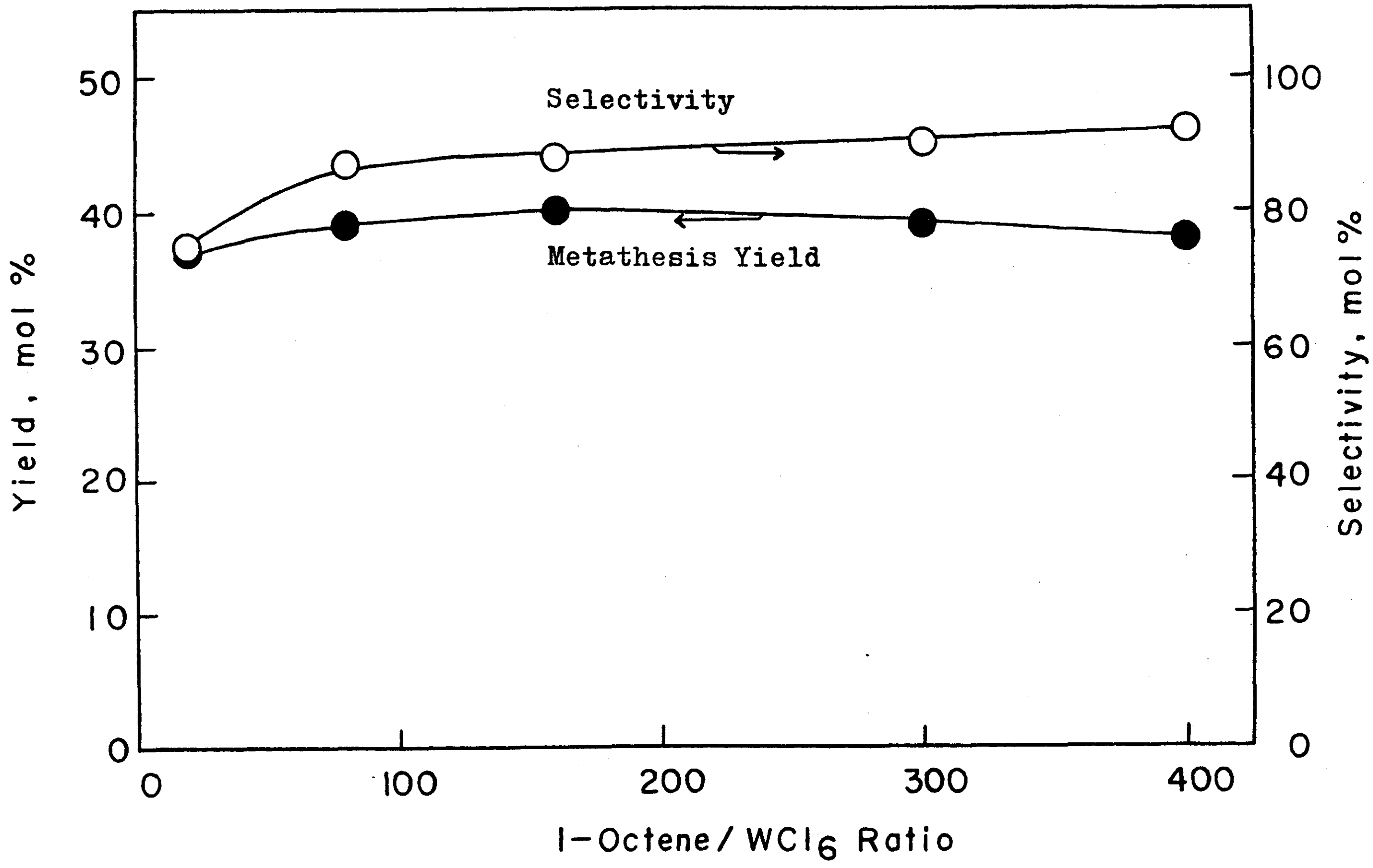


Fig.18. Effect of 1-Octene/WCl_6 ratio: WCl_6 0.024 mol/l, Bu_4Sn/W 2, $CH_3COOnPr/W$ 4, Trichloroethylene Medium, 80°C, 3 hr.

Table 23. Effect of the Order of Adding Reagents

Order a)	Metathesis yield b)	Selectivity c)
O - A - W - Sn	29	79
O - W - Sn - A	33	93
W - Sn - A - O	34	95
W - A - Sn - O	33	91

a) W: WCl_6 0.028 mol/l, Sn: nBu_4Sn Sn/W 2, O: 1-Octene O/W 50, A: $CH_3COOnPr$ A/W 4, Solvent Trichloroethylene, 80°C, 3 hr.

b) (7-Tetradecene X 2) X 100/1-Octene used,mol%.

c) (7-Tetradecene X 2) X 100/1-Octene consumed,mol%.

3. Metathesis of Various 1-Alkenes

The yield and the *cis*-isomer content of the reaction product from the metathesis of 1-alkene using the $WCl_6 \cdot CH_3COOnPr/nBu_4Sn$ or the $WCl_6 \cdot CH_3CN/nBu_4Sn$ catalyst system are shown in Table 24. Symmetric internal alkenes were obtained in good yield. The additives prevented the double bond migration and other cationic reactions, but permitted the geometric isomerization, for the ratio of *cis*-isomer in the product alkene approached its equilibrium value at the end of the reaction. This suggests that the *cis-trans* isomerization of product alkene in olefin metathesis proceeds by the successive metathesis rather than by a cationic mechanism.

Table 24. Metathesis of Various 1-Alkenes [a)]

Reactant	Product	Additive	Yield mol %	Cis-isomer content %
1-Pentene	4-Octene	(A)	38	22
		(B)	28	34
1-Hexene	5-Decene	(A)	41	20
		(B)	40	21
1-Heptene	6-Dodecene	(A)	32	33
		(B)	24	32
1-Octene	7-Tetradecene	(A)	43	19
		(B)	43	20
1-Decene	9-Octadecene	(A)	45	--
		(B)	44	--

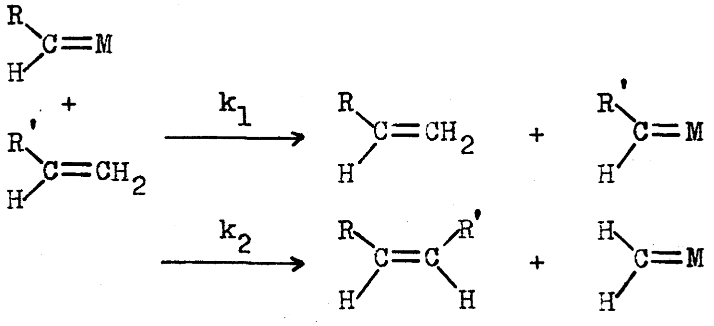
a) WCl_6 0.024 mol/l, 1-Alkene/W 60, nBu_4Sn/W 2, Solvent Trichloroethylene, 80°C, 3 hr. (A) $CH_3COOnPr$/W 4, (B) CH_3CN/W 2.

When the ethylene was removed from the reaction system by the liquefaction with liquid nitrogen in the metathesis of 1-octene catalyzed by the $WCl_6 \cdot CH_3COOnPr/nBu_4Sn$ system in trichloroethylene at 80°C for 5 hours, 59% yield and 94% selectivity were obtained. The reaction also proceeded without solvent. This process is remarkably effective one for the synthesis of the symmetric internal alkenes. This result apparently increases the merit of the metathesis reaction in synthetic chemistry. Additionally, these reaction systems remove difficulties in reproducing the level of catalytic activity in olefin metathesis reaction.

4. Interpretation of the Effect of Additives

The foregoing results concerning effects of organic additives (Tables 5,10,20 and 21, and Fig. 16) mean that the organic additives are essentially poisons. The excellent effects of additives in 1-alkene metathesis may be also explained by the inference that the additives poison the highly cationic metal species causing various side reactions more intensively than the active species catalyzing metathesis. The side reactions were extremely promoted at high temperature in the absence of additives, whereas even in benzene at 80°C, the metathesis of 2-heptene or 1-octene was catalyzed by the $WCl_6 \cdot CH_3COOnPr/nBu_4Sn$ system with high yield and high selectivity almost without the Friedel-Crafts products and other side reaction products. These results support the above inference.

According to Katz[56], the reason for the low yield in the metathesis of 1-alkenes is that the metal-carbene complexes combine with terminal alkenes selectively according to



(17)

(18)

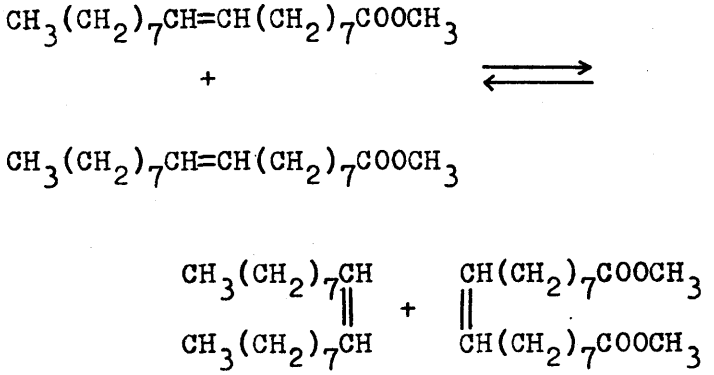
Eq. 17 rather than according to Eq. 18, that this selectivity varies with the catalysts, and that only a limited number of metatheses take place before the chain reactions terminate. The improvement of the metathesis yield in our systems may be explained by the inferences (a) that the increase in the number of productive metathesis (Eq. 18) due to heating forces the distribution of olefins to approach the statistical one before the reaction is stopped by the catalyst deactivation and/or (b) that the catalyst giving high k_2/k_1 ratio is produced from WCl_6, nBu_4Sn and additives at high temperature.

CHAPTER VI

METATHESIS OF METHYL OLEATE

1. The Reactivities of the Tungsten Hexachloride — Cocatalyst Systems

The metathesis of methyl oleate gives 9-octadecene and dimethyl 9-octadecenedioate (Eq. 19).



$$\begin{array}{c} CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 \\ + \\ CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 \end{array} \rightleftarrows \begin{array}{c} CH_3(CH_2)_7CH \\ \| \\ CH_3(CH_2)_7CH \end{array} + \begin{array}{c} CH(CH_2)_7COOCH_3 \\ \| \\ CH(CH_2)_7COOCH_3 \end{array} \qquad (19)$$

The unsaturated dicarboxylic acid ester is significant as raw material for the preparation of unsaturated polyesters and polyamides, as well as for the synthesis of certain flavoring agents, from technological view points.[63] The reactivities of the WCl_6-cocatalyst systems which were found to be effective for the 2-heptene metathesis were examined in this reaction, as shown in Table 25. Tetra-n-butyltin, tetraethyltin and triethylaluminum were found to be effective as cocatalysts with WCl_6 for this reaction. It is worth noting that nBu_4Sn is less toxic and easier to handle than Me_4Sn[60-63] and also less hazardous than Et_3B.[64]
In the WCl_6-Et_3Al system, the yield and the selectivity were low as compared to those in the WCl_6-Et_4Sn and WCl_6-nBu_4Sn systems, owing to the side reaction between methyl oleate and triethylaluminum. The WCl_6-Ph_4Sn, WCl_6-Ph_4Pb, and WCl_6-Ph_3Bi systems were inactive for this reaction under these reaction conditions. The presence of the considerable amount of ester groups may hinder the phenylation of WCl_6 by arylmetals and/or the reductive

Table 25. Reactivities of WCl_6–Cocatalyst Systems for Metathesis of Methyl Oleate [a]

Cocatalyst (M)		M/W ratio	Yield [b] mol %	Selectivity [c] mol %
Sn	Et_4Sn	2	39	81
		4	29	74
	Bu_4Sn	2	40	68
		4	40	66
	Bu_3SnCl	2	3	24
	Bu_2SnCl_2	2	0	--
	Ph_4Sn	2	1	17
		4	2	33
Al	Et_3Al	2	18	54
		4	17	41
Zn	Et_2Zn	2	2	23
		4	1	3
Pb	Ph_4Pb	2	3	25
		4	2	33
Bi	Ph_3Bi	1	1	14
		2	0	--

a) The mixture of methyl oleate (3×10^{-4} mol), WCl_6 (2×10^{-5} mol) and a cocatalyst was heated in chlorobenzene at 100 °C for 3 hours.

b) 100 X (9-Octadecene X 2)/Methyl Oleate used.

c) 100 X (9-Octadecene X 2)/Methyl Oleate consumed.

elimination of Ph and Cl from phenyltungsten intermediates. n-Butyllithium, lithium aluminum hydride, or sodium borohydride in conjunction with WCl_6 did not catalyze this reaction. Probably these reagents were consumed by the reactions with the ester. Diethylzinc did not form the active catalyst with WCl_6. On the other hand, the $WOCl_4$-nBu_4Sn system efficiently catalyzed this reaction.

2. Research for the Optimum Reaction Conditions

It is presumed that the optimum conditions for the metathesis of methyl oleate are different from those for the metathesis of alkene having no functional group, since methyl oleate contains ester group. The optimum reaction conditions for this reaction were searched using WCl_6-nBu_4Sn.

In the reactions at 100°C, good yield was obtained in the extremely wide range of Sn/W ratio, *viz*: 2-8 (Table 26). This optimum range agrees with the one in the metathesis of 1-octene catalyzed by the $WCl_6 \cdot CH_3COOnPr/nBu_4Sn$ system. The optimum methyl oleate/WCl_6 ratio was less than 30 under this reaction condition (Table 27). The yield significantly decreased with an increase in the methyl oleate/WCl_6 ratio. The fairly low optimum olefin/WCl_6 ratio is attributable to the poisoning effect of ester group. A lowering in temperature decreased the yield intensively (Table 28). This effect was observed more remarkably at the methyl oleate/WCl_6 ratio of 30 than at the ratio of 15. This result also shows that heating promotes the metathesis while the ester group inhibits this reaction. The best result was obtained at 100°C. The yield and the selectivity both decreased at 120°C. Over-heating may induce the catalyst decomposition and the side reactions.

3. Effect of Ester Group of Methyl Oleate

The addition of methyl oleate and methyl stearate provided a good metathesis yield by depressing the various side reactions such as double bond migration and oligomerization/

Table 26. Effect of nBu_4Sn/WCl_6 Ratio a)

Bu_4Sn/WCl_6 ratio	Yield mol %	Selectivity mol %
1	21	53
2	40	68
4	40	66
6	48	87
8	38	58
10	30	43

a) The mixture of methyl oleate (3×10^{-4}mol), WCl_6 (2×10^{-5}mol) and Bu_4Sn was heated in chlorobenzene at 100 °C for 3 hours.

Table 27. Effect of Methyl Oleate/WCl_6 Ratio a)

Methyl oleate/WCl_6 ratio	Yield mol %	Selectivity mol %
15	44	72
30	42	78
60	6	88
90	4	100
120	0	---

a) The mixture of methyl oleate, WCl_6 (2×10^{-5}mol) and Bu_4Sn (4×10^{-5}mol) was heated in chlorobenzene at 100 °C for 3 hours.

Table 28. Effect of Temperature[a)]

Reaction temp., °C	Methyl oleate / WCl_6 ratio 15 Yield	15 Selectivity	30 Yield	30 Selectivity
30	3	60	0	--
60	17	57	0	--
80	40	61	32	73
100	44	72	42	78
120	37	55	30	58

a) The mixture of methyl oleate, WCl_6 (2×10^{-5}mol) and Bu_4Sn (4×10^{-5}mol) was heated in chlorobenzene for 3 hours.

Table 29. Effect of Fatty Acid Esters on 1-Octene Metathesis a).

Additive	Yield b) mol %	Selectivity c) mol %
Methyl oleate	36	78
Methyl stearate	41	90
n-Propyl acetate	42	89
None	4	4

a) The mixture of 1-octene (1.5×10^{-3}mol), WCl_6 (2×10^{-5}mol), Bu_4Sn (4×10^{-5}mol) and an additive was heated in trichloroethylene at 100 °C for 3 hours.

b) Yield (mol %) = 100 X (7-Tetradecene X 2)/1-Octene used.

c) Selectivity (mol %) = 100 X (7-Tetradecene X 2)/1-Octene consumed.

polymerization of olefins in the metathesis of 1-octene at elevated temperature, similarly to the addition of alkyl acetates (Table 29). These additives also depressed the Friedel-Crafts reaction in the 2-heptene metathesis in benzene at high temperature. These facts indicate that in spite of the high reaction temperature, the relatively high selectivity is obtained in the metathesis of methyl oleate, owing to the existence of its ester group. After all, it is concluded that the action of ester group in methyl oleate molecule is essentially the same as those of esters as additives. The observed effects can be interpreted similarly to those of alkyl acetates in 1-alkene metathesis (Chapter V).

4. Cross Metathesis of Methyl Oleate and 1-Decene

It is too difficult to synthesize ω-unsaturated fatty acid esters. We found out that the cross metathesis of methyl oleate and 1-decene gave methyl 9-decenoate directly (Eq. 20).

$$\begin{gathered}\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3} \\ + \\ \mathrm{CH_3(CH_2)_7CH{=}CH_2}\end{gathered} \rightleftarrows \begin{gathered}\mathrm{H_2C{=}CH(CH_2)_7COOCH_3} \\ + \\ \mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3} \\ + \\ \mathrm{CH_3OCO(CH_2)_7CH{=}CH(CH_2)_7COOCH_3} \\ + \\ \mathrm{CH_2{=}CH_2}\end{gathered} \tag{20}$$

Glc analyses showed that compounds except those shown in Eq. 20 were barely formed. If the double bond migration of methyl 9-decenoate formed occurs, an exceedingly complex reaction mixture is obtained by the successive metathesis of isomers. Hence, the double bond migration of methyl 9-decenoate is depressed, probably owing to the existence of ester group. The results are summerized in Table 30. The yield of methyl 9-decenoate was maximal at the methyl oleate/1-decene ratio of 2-3. The increase in the concentration of 1-decene at the fixed concentration of methyl oleate led to the considerable increase in the yield of 9-octadecene, but the increase in the yield of methyl 9-decenoate was slight. This result suggests that the coordinating power of 1-decene is stronger than that of methyl oleate and/or that 1-decene is more reactive toward olefin metathesis than methyl oleate.

Table 30. Cross Metathesis of Methyl Oleate with 1-Decene a).

Reactant (10^5mol)		Distribution of reaction mixture (10^5mol) b)			
Methyl oleate	1-Decene	Methyl 9-decenoate	9-Octadecene	Methyl oleate	1-Decene
34	73	8	20	16	38
34	109	9	25	8	37
34	145	10	28	6	57
34	182	11	49	11	72
68	73	9	25	16	22
136	73	16	42	56	29
204	73	17	37	125	29
272	73	14	34	195	31

a) The mixture of methyl oleate, 1-decene, WCl_6 (4×10^{-5}mol) and Bu_4Sn (4×10^{-5}mol) was heated in trichloroethylene at 100 °C for 3 hours.

b) Dimethyl 9-octadecenedioate was produced, but not determined.

In conclusion, metathesis of functionally substituted alkenes requires judicious selection of reaction conditions, *viz*: (a) the use of the catalyst that is inert toward functional group, *e.g.* WCl_6-nBu_4Sn, (b) the most favourable catalyst composition, (c) an appropriate amount of substrate, and (d) a moderate reaction temperature.

EXPERIMENTAL

1. Chemicals

1-1. Catalysts

Tungsten hexachloride (Nakarai Chemicals, extra pure reagent) was purified by the preferential sublimation of more volatile contaminents, WO_2Cl_2 and $WOCl_4$, under nitrogen at about 200° C, leaving a residue of pure tungsten hexachloride. Tungsten oxytetrachloride (Soekawa Chemical, guaranteed reagent) was used without further purification.

Triethylaluminum (Tokyo Kasei, 15 W/V % n-hexane solution), n-butyllithium (Merk, 15 W/V % n-hexane solution), diethylzinc (Wako Pure Chemicals, 20 W/V % n-hexane solution), tetra-n-butyltin (Tokyo Kasei, extra pure reagent), triphenylbismuthine (Tokyo Kasei, extra pure reagent), tetraphenyllead (Tokyo Kasei, guaranteed reagent) and tetraphenyltin (Tokyo Kasei, extra pure reagent) were used without further purification.

The unsolvated n-butylmagnesium iodide was prepared according to the method given in the literature.[124] Twenty five g of n-butyl iodide in 100 ml benzene were added dropwise to 5g of dried magnesium turnings in three necked flask under nitrogen with vigorous stirring. Then the reaction mixture was refluxed for a day. The supernatant solution was stored in a sealed Schlenk tube. The concentration of the reagent was determined by titration with aqueous sodium hydroxide, after the addition of excess hydrochloric acid to the reagent.

The cyclopentadienylsodium was prepared according to a modification of the method given in the literature.[125,126] Sodium-dried benzene and a sodium-naphthalene dispersion containing 15 wt% sodium were used instead of xylene and sodium metal. The supernatant solution was stored in a sealed Schlenk tube. The concentration of the reagent was determined by titration with aqueous sodium hydroxide after the addition of excess hydrochloric acid to the reagent. The preparation and the analysis of phenylethynylsodium were carried out in a similar way.[127,128]

1-2. Reactant Olefins

Mixed 2-heptene (*cis*-content 75%, Tokyo Kasei, extra pure reagent), *trans*-2-pentene (99%, Tokyo Kasei, guaranteed reagent), and *cis*-2-pentene (95%, Tokyo Kasei, extra pure reagent) were dried by sodium wire and distilled over sodium hydrogensulfite under nitrogen. The purification of 1-pentene (Wako Pure Chemicals, guaranteed reagent), 1-hexene (Tokyo Kasei, guaranteed reagent), 1-heptene (Wako Pure Chemicals, extra pure reagent), 1-octene and 1-decene (Tokyo Kasei, extra pure reagents) was carried out by the distillation under nitrogen.

Methyl oleate was purified by the vacuum distillation (152-155°C/4mmHg) after the esterification of oleic acid, which was purified *via* the urea complex of the commercial oleic acid (Wako Pure Chemicals, extra pure reagent). Methyl oleate obtained was greater than 97% pure as determined by glc. The content of *trans* double bond was less than 3% by ir.

1-3. Solvents

Benzene was distilled over sodium wire under nitrogen, after thiophene-free benzene was refluxed over sodium wire for several hours. Halogenated hydrocarbons were distilled under nitrogen after dried over anhydrous calcium sulfate (Drielite), anhydrous potassium carbonate or anhydrous calcium chloride for two weeks.

2. Procedures

All reaction tubes (Pyrex) were dried at 150°C for 8 hours and cooled in the desiccator containing phosphorus pentoxide and anhydrous calcium sulfate (Drielite) as desiccants before use. After the dry tube was sealed with a neoprene rubber cap, an olefin, a solution of WCl_6 and a solution of the cocatalyst were successively injected by hypodermic syringes in this order. The tube was shaken vigorously at room temperature through the reaction periods. The reaction was stopped by injecting isopropanol. In the metathesis of 2-heptene with WCl_6-arymetals, 2-heptene and a solution of WCl_6 were injected into the tube successively after an arylmetal was placed in a dry glass tube. In the reaction at high temperature, the glass tube was sealed after air was evacuated. The tube was heated in the oil bath.

3. Analyses

Quantitative glc analyses were routinely performed on a JEOL-GC-1100 chromatograph, or a Shimadzu-GC-4APF chromatograph, using a 1m × 3mm column or a 1.5m × 3mm column packed with 10% SE30 on 80-100 mesh Chromosorb W. n-Undecane was used as an internal standard in order to determine the metathesis yield and the selectivity. Isomer content of olefin was obtained, using a 90m × 0.25 mm capillary column coated with squalane or a 1.5m × 3mm glass column packed with 10% silver nitrate-diethyleneglycol (1:4 W/W) on 80-100 mesh Celite 545. Alkyl- and chloroalkyl-tin compounds were analyzed using a 2m × 3mm column packed with 20% DC550 silicone fluid on 80-100 mesh Chromosorb W.[113]

Peaks in the chromatograms of the reaction mixtures were identified by comparison of retention times for known materials. In this qualitative glc analysis, the identification was confirmed, by using an additional polar column such as a 2m × 3mm column packed with 18% DEGS on 60-80 mesh Diasolid L or a 2m × 3mm column packed with 20% FFAP on 60-70 mesh Anakrom ABS. Methyl 9-decenoate was identified by the correlation through a linear relation of logarithms of retention time *vs.* the number of carbon atoms in the fatty acid chain.[129]

Authentic sample 5-decene was prepared according to the method described in the literature.[130] That is, 5-decyne prepared by the addition of n-butyl bromide and liquid ammonium solution of sodium amide to the liquid ammonium solution of sodium acetylide, was hydrogenated to 5-decene with hydrogen and palladium black: mass spectrum m/e 140 ($C_{10}H_{20}$); elementary analysis C 85.48, H 14.52 (Calc. C85.63, H 14.37); The capillary column chromatography showed that 5-decene prepared contains *cis-* isomer predominantly. Mixed 7-tetradecene (*trans* content 79% by ir) and other olefins as authentic samples were supplied by Tokyo Kasei. Diphenyldiacetylene was prepared for the identification of the product, by the method described in the literature.[131] The Friedel-Crafts products, heptylbenzenes, were prepared in the alkylation of benzene with 2-heptene by sulfuric acid and aluminum chloride catalysts.

Methyl 9-octadecenedioate and 9-octadecene were isolated and identified as follows. A mixture of methyl oleate (15mmol), WCl_6(0.5mmol), and nBu_4Sn (0.75mmol) was heated without solvent in the sealed glass tube at 100°C for 6 hours, after air was evacuated from the reaction tube. At the end of the reaction, the reaction mixture was dissolved in an excess of n-hexane. To this solution, an excess of strong ammonium hydroxide was added. Then, the mixture was stirred vigorously during which operation the metallic derivatives of the catalyst system were precipitated. After filtration of the precipitate, a bright yellow solution resulted. Methyl 9-octadecenedioate was crystallized from the solution at −20°C, and purified by the recrystallization from n-hexane: mp 29-30°C (lit.[62] mp32°C); mass spectrum m/e 340; elementary analysis C 67.28, H 9.98, O 22.74 (Calc. C70.55, H 10.66, O 18.79); nmr (CCl_4) δ 5.3 ($-\overset{H}{C}=\overset{H}{C}-$), 3.6 ($-OCH_3$), 2.25 ($-CH_2-COO$), 1.9 ($-C=C-CH_2-$), 1.25 ($-C-CH_2-C-$); ir ($CCl_4$) a strong absorption peak at 1735 cm^{-1} ($\nu_{C=0}$). The mother liquor was concentrated and saponified with potassium hydroxide ethanol solution. The soap formed was dissolved in an excess of water. The water layer was extracted with n-hexane. The n-hexane layer obtained was concentrated, whereafter 9-octadecene was distilled as main product: mass spectrum m/e 252 ($C_{18}H_{36}$); elementary analysis C 86.06, H 13.94 (Calc. C 85.63, H 14.37); nmr (CCl_4) δ 5.3 ($-\overset{H}{C}=\overset{H}{C}-$), 1.9 ($-CH_2-C=C-$), 1.26 ($-C-CH_2-C-$), 0.86 ($CH_3-$).

Infrared spectra study was performed with a Shimadzu IR-27B spectrophotometer. The nmr spectra were recorded on a JEOL-C-60HL spectrometer at 60 MHz with TMS as an internal standard. Mass spectra were obtained with a Hitachi RMS-4 mass spectrometer at 80 eV. Elementary analyses were carried out with a Perkin-Elmer 240 Elemental Analyzer or a Yanagimoto C.H.N. Corder.

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LIST OF PUBLICATIONS

1. Olefin Metathesis. I. Olefin Metathesis by Binary Catalyst Systems of WCl_6-Bu_4Sn.

   T. Takagi, K. Ichikawa, T. Hamaguchi, K. Fukuzumi, and M. Aoyama, *Yukagaku*, 24, 377 (1975).

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6. Metathesis of 1-Alkene.

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7. Olefin Metathesis and Side Reactions with the Binary Systems of WCl_6 and Metal Alkyls.

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8. Olefin Metathesis. IV. Metathesis of Methyl Oleate.

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9. Olefin Metathesis catalyzed by a Binary System of Tungsten Hexachloride and Triphenylbismuthine.

   K. Ichikawa, O. Watanabe, and K. Fukuzumi, *Transition Met. Chem.*, 1, 183 (1976).

ADDITIONS AND CORRECTIONS

page	uncorrected	corrected
p. 52, line 2	cocatalysts.	cocatalysts
p. 58, Table 18	lodobenzene	iodobenzene