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

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The comparison of the behaviors of the WCl_6-metal alkyl systems (metal alkyls are Bu_4Sn, Et_2Zn, Et_3Al, and BuLi) was carried out in the metathesis of 2-heptene in benzene. The WCl_6–Et_2Zn and the WCl_6–BuLi systems showed the sharp dependence of metathesis on the co-catalyst/WCl_6 ratio, whereas the WCl_6–Bu_4Sn and the WCl_6–Et_3Al systems did the dull one. The yield of the Friedel–Crafts products, heptylbenzenes, increased with a decrease in the co-catalyst/WCl_6 and the olefin/WCl_6 ratios, though the WCl_6–BuLi system barely catalyzed this side reaction. A proper amount of dicyclopentadiene, phenylacetylene, ethyl ether, ethanol, and esters repressed the Friedel–Crafts reaction, and the metathesis products were obtained in high yield and high selectivity in the metathesis of 2-heptene catalyzed by the WCl_6–Bu_4Sn system.

INTRODUCTION

It has been reported that the olefin metathesis reaction is catalyzed by the WCl_6, $MoCl_5$, and $ReCl_5$–R_4Sn (*1–4*), RMgX (*5–7*), RLi (*8*), R_nAlCl_{3-n} (R is alkyl or aryl) (*9–12*), $LiAlH_4$ (*13, 14*), and $NaBH_4$ (*13*) binary systems. Thus far a number of reaction mechanisms have been proposed for olefin metathesis (*15–19*), but now there seems to be a growing consensus that metal carbene and metallocyclobutane intermediates are contained in the reaction (*20–26*).

Several investigators have reported that the WCl_6–alkyl aluminum halide systems catalyzed other reactions such as the Friedel–Crafts reaction (*27–29*), the oligomerization and the polymerization (*12, 30*), and the double-bond migration (*10, 30, 31*). Such phenomena suggest that there is a close relationship between catalysts which promotes metathesis and those which aid the other reactions described above.

In this paper, the reactivities of the various WCl_6–co-catalyst recipes for the reaction and the effect of additives were investigated.

RESULTS AND DISCUSSION

Effect of the Co-catalyst/WCl_6 Ratio

The WCl_6–co-catalyst systems converted 2-heptene to 2-butene and 5-decene *in situ* in benzene. The simultaneous occurrence of the Friedel–Crafts reaction between benzene and 2-heptene was observed. The metathesis yield and the yield of the Friedel–Crafts products used here are defined as follows: Metathesis yield (mol%) = 100 × (2-butene + 5-decene)/2-heptene used; yield of the Friedel–Crafts products (mol%) = 100 × heptylbenzenes/2-heptene used.

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TABLE 1

Effect of Co-catalyst/WCl_6 Ratio[a]

Co-catalyst		Co-catalyst/WCl_6 ratio				
		0.5	1	2	3	4
Bu_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
BuLi	Metathesis	1	2	33	3	1
	F.C.	1	1	0	0	0

[a] The reaction of 2-heptene (1.4 mmol, 1.4 mol/liter) with WCl_6 (0.028 mmol, 0.028 mol/liter) and a co-catalyst was carried out in benzene at room temperature for 3 hr.

[b] Metathesis yield.

[c] Yield of the Friedel–Crafts products, heptylbenzenes.

The effect of the co-catalyst/WCl_6 ratio on the 2-heptene metathesis is shown in Table 1. In the WCl_6–Bu_4Sn and the WCl_6–Et_3Al systems, the good metathesis yield was obtained in the wide range of the co-catalyst/WCl_6 ratio, 2–4 and 0.5–3, respectively. In contrast, the sharp dependence of metathesis on the co-catalyst/WCl_6 ratio was observed in the WCl_6–Et_2Zn and the WCl_6–BuLi systems, and the good results were obtained only at the ratio, 1 and 2, respectively. This means that the latter systems require the strict conditions for the formation of the active catalytic species. Probably metal alkyls act as reducing agents and form the coordination sites of reactive groups such as an olefin and a carbene at the optimum co-catalyst/WCl_6 ratio on active species, W^{4+} for instance (*5–8*, *32*, *33*). On the other hand, these catalyst systems catalyzed the Friedel–Crafts reaction more intensively with a decrease in the co-catalyst/WCl_6 ratio, though the WCl_6–BuLi system barely did this reaction. The fact that the increase in the amount of the metal akyls decreased the yield of heptylbenzenes, suggests that the side reaction is mainly catalyzed by a W^{6+} 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 co-catalysts are not sufficient. The use of highly acidic co-catalyst metal species appears to increase the amount of the products of this side reaction. The deactivation of the catalyst for both meta-

TABLE 2

Effect of Olefin/WCl_6 Ratio[a]

Co-catalyst	$\frac{\text{Co-catalyst}}{WCl_6}$		Olefin/WCl_6 ratio				
			25	50	100	200	300
Bu_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
BuLi	2	Metathesis	32	23	6	1	1
		F.C.	0	0	0	0	0

[a] The reaction of 2-heptene with WCl_6 (0.028 mmol) and a co-catalyst was carried out in benzene at room temperature for 3 hr.

[b] Metathesis yield.

[c] Yield of the Friedel–Crafts products, namely heptylbenzenes.

TABLE 3

Effect of Adding Organic Compounds[a]

Additive	Additive/WCl_6	Metathesis[b]	F.C.[c]	Selectivity[d]
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] The reaction of 2-heptene (1.4 mmol, 0.77 mol/liter) with WCl_6 (0.069 mmol, 0.038 mol/liter), Bu_4Sn (0.069 mmol, 0.038 mol/liter), and an additive was carried out in benzene at room temperature for 3 hr.

[b] Metathesis yield.

[c] Yield of the Friedel–Crafts products, namely heptylbenzenes

[d] Selectivity (mol%) = 100 × (2-butene + 5-decene)/2-heptene consumed.

thesis and the Friedel–Crafts reaction at high co-catalyst/WCl_6 ratio is probably the result of over-reduction of tungsten.

Effect of the Olefin/WCl_6 Ratio

The results at the optimum co-catalyst/WCl_6 ratio in the *in situ* system are summarized in Table 2. The yield of the Friedel–Crafts products decreased with an increase in the amount of olefin, though the WCl_6–BuLi system did not catalyze this side reaction. The good metathesis yield was obtained at the optimum olefin/WCl_6 ratio.

The results of Table 1 suggest that in the WCl_6–Bu_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 co-catalyst/WCl_6 ratio whereas in the WCl_6–BuLi 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 trends of Table 2 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–BuLi system, good results were obtained at the olefin/WCl_6 ratio less than 50, and the metathesis yield decreased greatly at the olefin/WCl_6 ratio of 100. While in other catalyst systems, the good metathesis yield was obtained in wider range of the olefin/WCl_6 ratio as compared to the one in the WCl_6–BuLi system. The results of Tables 1 and 2 show that the nature of the co-catalyst metal affected the catalyst formation and/or the activity of the actual catalyst.

Effect of Adding Organic Compounds

In our previous paper (*34*), appropriate organic additives raised the selectivity to the metathesis of 1-octene by depressing the double bond migration and the polymerization at 80°C. In the metathesis of 2-heptene in benzene at room temperature, proper amounts of dicyclopentadiene, phenylacetylene, ethyl ether, ethanol, and esters depressed the Friedel–Crafts reaction, and the metathesis products were obtained in high yield and high selectivity (Table 3).

On the other hand, 2-nonyne and acetonitrile inhibited both the metathesis and the Friedel–Crafts reaction at the additive/WCl_6 ratio of 1, 2, 3, and 4. Mesitylene did not provide any effect at the same ratios. These additives, except mesitylene, probably form acid–base complexes with metal species. The infrared spectra study of esters was carried out. When WCl_6 and Bu_4Sn 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 1735 cm^{-1} decreased and the two new absorption peaks at 1673 and 1625 cm^{-1} appeared. When WCl_6 was added to the trichloroethylene solution of *n*-propyl acetate, the peak at 1735 cm^{-1} decreased and only one peak at 1658 cm^{-1} appeared. On the other hand, the addition of Bu_4Sn, Bu_3SnCl, or Bu_2SnCl_2 gave no new peak and the peak at 1735 cm^{-1} was unchanged, but the addition of $SnCl_4$ decreased the peak at 1735 cm^{-1} and gave a new peak at 1637 cm^{-1}. With respect to methyl oleate, the similar changes were observed. These ir analyses suggest that esters coordinate on the highly acidic metal species with carbonyl group. The results of Table 3 may be explained by the inference that only the metathesis catalyst survives after these additives poison the highly cationic species, such as W^{6+} responsible for the Friedel–Crafts reaction, more intensively than the active species, such as W^{4+} responsible for the metathesis. An excess amount of additive to the catalyst inhibited the metathesis also. This may be due to the reason that the coordination of additives on tungsten hinders the coordination of olefin. 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 olefin (*27*). The facts that dicyclopentadiene and phenylacetylene provided good results at the additive/WCl_6 ratio of 2–4 may be explained by the same inference, but also there seems to be the other factor (*35*). In the metathesis of 2-heptene or 1-octene catalyzed by the WCl_6–Bu_4Sn system in benzene at 80°C, the addition of 1–2 equimolar amounts of *n*-propyl acetate also provided the good metathesis yield and high selectivity, with extremely small amounts of the side reaction products from the Friedel–Crafts reaction, the double bond migration followed by the cross metathesis and the polymerization. The depression of the double bond migration and the polymerization also may be explained by the assumption that the additive poisons the highly cationic metal species, a W^{6+} species for instance, causing various cationic reactions more intensively than the active species of metathesis.

Finally, we believe that the positive charge on tungsten atom governs the course of the reaction, metathesis or other reactions, in these catalyst systems.

EXPERIMENTAL METHODS

Materials

Tungsten hexachloride was purified by the sublimation of more volatile contaminents, WO_2Cl_2 and $WOCl_4$, under nitrogen at about 200°C, leaving a residue of pure tungsten hexachloride. Triethylaluminum and butyllithium (both 15 w/v% *n*-hexane solution), diethylzinc (20 w/v% *n*-hexane solution), and tetrabutyltin (extra pure reagent) were purchased and used without purification. Benzene was distilled over sodium wire under nitrogen. Mixed 2-heptene (*cis* content 75%, extra pure reagent) was dried by sodium wire and distilled over sodium hydrogensulfite under nitrogen.

Procedure

A typical procedure for the metathesis of 2-heptene will now be described. The dried glass tube was sealed with a Neopren rubber cap. To the sealed tube, 2-heptene (1.4 mmol, 1.4 mol/liter), a benzene solution of WCl_6 (0.028 mmol, 0.028 mol/liter), and a benzene–hexane solution of Et_3Al (0.028 mmol, 0.028 mol/liter) were injected successively by means of hypodermic syringes. The tube was vibrated vigorously at room temperature for 3 hr and the products were analyzed by gas–liquid chromatography, which was performed with a Shimadzu GC-4APF or a JEOL GC-100 chromatograph, using a 1-m × 3-mm column packed with 10% SE30 on 80–100 mesh Chromosorb W. The identity of the Friedel–Crafts products, heptylbenzenes, was recognized by using the authentic sample prepared in the Friedel–Crafts reaction of 2-heptene with benzene by sulfuric acid and aluminum chloride catalysts.

The trends of the data in Tables 1 and 2 were confirmed by the repetition of runs, at least two times.

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