750 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(3), 750—753 (1976) [Vol. 49, No. 3

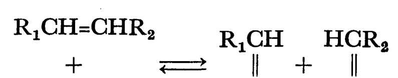
Cyclopentadienylsodium and Phenylethynylsodium as Cocatalysts in Olefin Metathesis

Kazuaki Ichikawa, Toru Takagi,* and Kazuo Fukuzumi
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464

(Received August 29, 1975)

Cyclopentadienylsodium and phenylethynylsodium are effective cocatalysts with WCl_6 in the homogeneous olefin metathesis. The optimum mole ratios of C_5H_5Na and PhC≡CNa to WCl_6 ranged more widely—from 1.5 to 3.0 and from 1.5 to 2.5 respectively—than that of BuLi to WCl_6. The formation of the Friedel-Crafts products was extremely small—such as 1—%, if the cocatalyst/WCl_6 ratio was about 2. The new catalyst systems were less poisoned by ether than the other catalyst systems and were hardly deactivated in the course of the reaction. The characteristics of these catalyst systems were discussed.

In olefin metathesis, the alkylidene moieties of olefins are redistributed as follows:



$$\begin{array}{c} R_1CH{=}CHR_2 \\ + \\ R_3CH{=}CHR_4 \end{array} \rightleftarrows \begin{array}{c} R_1CH \\ \| \\ R_3CH \end{array} + \begin{array}{c} HCR_2 \\ \| \\ HCR_4 \end{array}$$

For the homogeneous metathesis, binary catalyst systems, such as WCl_6, $MoCl_5$ or $ReCl_5$–R_4Sn,[1] RMgX,[2] RLi,[3] or $R_{3-n}AlCl_n$,[4] in which R is an alkyl or an aryl group, have been used *in situ*. Also, hydridic agents, such as lithium aluminum hydride and sodium borohydride, have been used as cocatalysts with WCl_6.[5] This reaction is unique and useful, but it has the faults that the catalysts are unstable and easily deactivated.

This study of cyclopentadienylsodium and phenylethynylsodium as cocatalysts was carried out in order to improve these faults and in order to investigate the scope and the limitations of the cocatalysts.

Results and Discussion

Dependence of Conversion on the Cocatalyst/WCl_6 Ratio. The dependence of the conversion on the Na/W mole ratio in the metathesis with catalyst systems of WCl_6–C_5H_5Na and WCl_6–PhC≡CNa is shown in Table 1. Good conversions were obtained at a Na/W ratio near 2 in both cases. Wang and Menapace have reported that the optimization at Li/W=2 strongly suggests a W^{IV} catalytic intermediate in the metathesis with a binary catalytic system of WCl_6 and *n*-BuLi.[3]

In the WCl_6–PhC≡CNa system the formation of diphenyldiacetylene was confirmed by GLC analysis. This fact suggests that the active catalyst species, $W^{IV}Cl_4$, forms as follows:

$$WCl_6 + 2PhC{\equiv}CNa \xrightarrow{-2NaCl}$$
$$(PhC{\equiv}C)_2WCl_4 \longrightarrow WCl_4 + PhC{\equiv}C{-}C{\equiv}CPh$$

In the NMR study, when WCl_6 was added to the C_5H_5Na benzene solution, the proton signal of $C_5H_5^-$ (1.7 ppm to high fields of the benzene reference, a singlet) disappeared and a new peak assignable to the vinyl protons of cyclopentadiene (about 0.85 ppm to high fields of the benzene reference, 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≡CNa system.

Table 1. Effect of cocatalyst/WCl_6 ratio[a]

Cocatalyst (M)	M/W ratio	Products, mol%[b] C_4	C_7	C_{10}	F.C.[c]
C_5H_5Na	0.5	3	93	3	1
	1	11	76	12	1
	1.5	18	63	18	1
	2	25	49	25	1
	3	20	59	20	1
	4	12	76	12	0
PhC≡CNa	0.5	3	61	3	33
	1	6	84	6	4
	1.5	18	62	18	2
	2	20	58	21	1
	3	10	76	11	3
	4	2	95	3	0
BuLi	0.5	1	78	1	20
	1	4	87	4	5
	1.5	10	77	11	2
	2	20	59	20	1
	3	4	91	4	1
	4	0	100	0	0

a) The reactions of 2-heptene (1.2 mol/l) with WCl_6 (2.4×10^{-2} mol/l) and the listed cocatalysts were carried out in benzene at room temperature for 15 h. b) Mol% of each product to the total amounts of 2-butene, 2-heptene, 5-decene, and Friedel-Crafts products. c) Friedel-Crafts products.

In Fig. 1 the conversions are plotted against the cocatalyst/WCl_6 mole ratio. The optimum ranges of the cocatalyst/WCl_6 ratio decreased as follows:

$$C_5H_5Na,\ 1.5\text{—}3.0 > PhC{\equiv}CNa,\ 1.5\text{—}2.5 > BuLi,\ 2$$

In the WCl_6–BuLi system, the sharp decrease in the conversion at Li/W>2 suggests that the Bu^- from BuLi easily displaces more than two Cl^- on WCl_6 because of the strong nucleophilicity of the carbanion, that is, the $W^{IV}Cl_4$ formed is easily attacked further by the excess BuLi to be destroyed. On the other hand, the wide optimum range of the Na/W ratio in the WCl_6–C_5H_5Na system suggests that $C_5H_5^-$ from C_5H_5Na does not destroy the active W^{V} species to any considerable extent, because of the weaker nucleophilicity of the carbanion. As the optimum range of the Na/W ratio

---

* Present address: Faculty of Fisheries, Hokkaido University, Minato-cho, Hakodate 040.

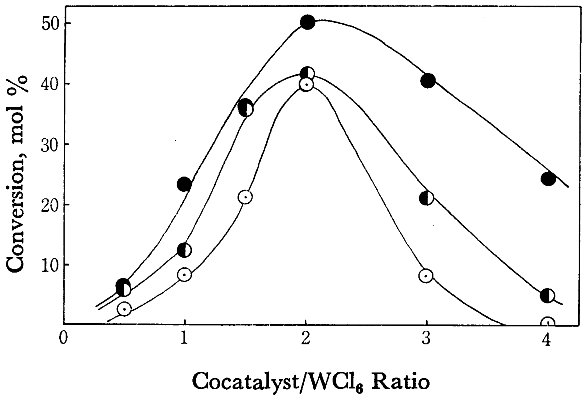


Fig. 1. Plot of conversion *vs.* cocatalyst/WCl_6 ratio. Cocatalyst: ● C_5H_5Na, ◐ $PhC{\equiv}CNa$, ○ BuLi. Conversion is mol % to 2-butene+5-decene.

in the WCl_6–$PhC{\equiv}CNa$ system lies in between that in WCl_6–C_5H_5Na and that in WCl_6–BuLi, the nucleophilicity of $PhC{\equiv}C^-$ may be stronger than that of $C_5H_5^-$ and weaker than that of Bu^-. 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–BuLi system in the region of cocatalyst/$WCl_6<2$ may be explained by either one or both of the following reasons: (1) the slower deactivation of the WCl_6–C_5H_5Na and WCl_6–$PhC{\equiv}CNa$ systems than the WCl_6–BuLi system, as will be described later, and (2) BuLi reacts completely and irreversibly with water, but C_5H_5Na and $PhC{\equiv}CNa$ 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 amounts of water are inferred to exist in the solvent and 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–BuLi system in the cocatalyst/$WCl_6 \geqq 2$ region may be attributable to the slower deactivation of these catalyst systems and the weaker nucleophilicity of the carbanions of the cocatalysts.

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

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.

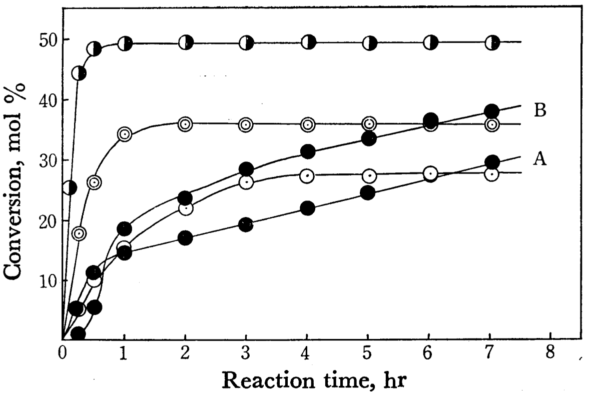


Fig. 2. Plot of conversion *vs.* reaction time. The reactions of 2-heptene (0.6 mol/l) with WCl_6 (2.4×10^{-2} mol/l) and cocatalysts were carried out in 1,2,4-trichlorobenzene at room temperature.
Cocatalyst: ● C_5H_5Na,Na/W=2, A: Preformed system, B: *In situ* system, ○ BuLi, Li/W=2, ◎ Bu_4Sn,Sn/W=1, ◑ Et_3Al,Al/W=1.
Conversion is mol % to 2-butene+5-decene.

Dependence of Conversion on the Reaction time. Figure 2 shows the dependence of the conversion on the reaction time in the metathesis of 2-heptene with a catalyst system of WCl_6–C_5H_5Na, together with the reaction by the WCl_6–BuLi, WCl_6–Bu_4Sn, or WCl_6–Et_3Al system. The catalyst from WCl_6–C_5H_5Na required preformation periods to reach its maximum activity toward metathesis. In Curve A of Fig. 2, 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–BuLi, WCl_6–Bu_4Sn, and WCl_6–Et_3Al do not require the preformation periods. These facts suggest that, in the WCl_6–C_5H_5Na system, the catalyst formation, that is, the nucleophilic attack of carbanion on WCl_6 and/or the reductive elimination of carbanion from R_2WCl_4, proceeded more slowly than in WCl_6–BuLi, WCl_6–Bu_4Sn, or WCl_6–Et_3Al. Moreover, Fig. 2 shows that the initial rates increased in the following order:

$$C_5H_5Na \sim BuLi < Bu_4Sn < Et_3Al.$$

The fact that alkali salts of carbanions afford the active metathesis catalysts with WCl_6 suggests that the central metals of the cocatalysts need not be Lewis acids. However, the order of the initial rates suggests that the reduced tungsten component was activated by the presence of acidic aluminum and tin species. Aluminum capable of binding to tungsten through Cl bridges might be a constituent of the catalyst and might modify the distribution of the electron density of the reduced tungsten component and/or might accelerate the formation of an active *cis* intermediate, *cis*-WCl_4-$(Olefin)_2$.⁶⁾ Also, the possibility of Sn–W coordination bond formation in the WCl_6–Bu_4Sn system can not be denied, since several compounds containing tin-transition metal bonds have been reported.⁷⁾ Tin might function as the electron modifier of the reduced tungsten component.

Table 2. Friedel-Crafts products[a]

Cocatalyst (M)	M/W ratio	Olefin/W ratio	Products, mol%[b]			
			C_4	C_7	C_{10}	F.C.[c]
C_5H_5Na	2	100	25	49	25	1
$PhC\equiv CNa$	2	100	25	49	25	1
Bu_4Sn	1	100	20	52	21	7
Et_3Al	1	100	23	46	23	8

a) The reactions of 2-heptene with WCl_6 (2.4×10^{-2} mol/l) and the listed cocatalysts were carried out in benzene at room temperature for 15 h. b) Mol% of each product to the total amounts of 2-butene, 2-heptene, 5-decene and Friedel-Crafts products. c) Friedel-Crafts products.

Friedel-Crafts Products. The yield of the Friedel-Crafts products was 1% in the metathesis of 2-heptene by WCl_6–C_5H_5Na and by WCl_6–$PhC\equiv CNa$, whereas it was 7—8% in the metathesis reaction of 2-heptene by WCl_6–Bu_4Sn and by WCl_6–Et_3Al, as is shown in Table 2. These facts, that the WCl_6–acidic cocatalyst system favors the Friedel-Crafts reaction more than the WCl_6-basic cocatalyst system, may be attributable to the influence of aluminum and tin on the reduced tungsten component through the W–Cl–Al or W–Sn bond.

Stability of Catalysts. In the olefin metathesis, the conversion of olefin should attain the equilibrium conversion, 50%. The failure to reach the equilibrium value results from catalytic deactivation, as has been described in our previous paper.[1,2] As is shown in Fig. 2, when BuLi or Bu_4Sn was used as a cocatalyst, the conversion leveled off within 3 h. On the other hand, in the WCl_6–C_5H_5Na system, the increase in conversion continued and the equilibrium conversion was reached. This result and those shown in Table 3 show that the deactivation of the WCl_6–C_5H_5Na system proceeded more slowly than those of the WCl_6–BuLi and WCl_6–Bu_4Sn systems.

The deactivation of the metathesis catalyst not only has been reported in the literature but has also been observed in our laboratory by the addition of heteroatom compounds, such as water, alcohols, ethers, carbonyl compounds, carboxylic acids, esters, amines, nitriles, amides, phosphines, thiophene and thiophenol, as has previously been reported.

Table 3. 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) The reactions of 2-heptene (0.6 mol/l) with WCl_6 (2.4×10^{-2} mol/l) and the listed cocatalysts were carried out in 1,2,4-trichlorobenzene at room temperature for 15 h. 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 h 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.

Table 4. 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
$PhC\equiv CNa$	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) The reactions of 2-heptene (1.2 mol/l) with WCl_6 (2.4×10^{-2} mol/l) and the listed cocatalysts were carried out in benzene at room temperature for 15h. b) Mol% of each product to the total amounts of 2-butene, 2-heptene, 5-decene and Friedel-Crafts products. c) Friedel-Crafts products.

In the metathesis using C_5H_5Na or $PhC\equiv CNa$ with WCl_6, also, the effect of ether on the conversion was investigated; the results are shown in Table 4. The fact that the WCl_6–C_5H_5Na and WCl_6–$PhC\equiv CNa$ systems were less poisoned by ether than the WCl_6–BuLi and WCl_6–Bu_4Sn systems 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: (1) the coordination of the inhibitor at its heteroatom to tungsten, which interrupts the formation of active intermediates, such as diolefin complexes; (2) the decomposition of the bimetallic catalyst system by the coordination of the basic inhibitor to the cocatalyst metal,[6] though no evidence for the formation of the tungsten-lithium or sodium binary complex has been reported in the olefin metathesis, and (3) the decomposition of the cocatalysts by a reaction with ether, such as a Wittig rearrangement.

The WCl_6–Bu_4Sn and WCl_6–BuLi systems showed the optimum conversion 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 $PhC\equiv CNa$ 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.

Experimental

Materials. The cyclopentadienylsodium was prepared according to a modification of the method given in the literature.[8] 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.[9] The triethylaluminum and butyllithium (both 15 w/v % hexane solutions) and tetrabutyltin (extra pure reagent) were purchased and used without further purification. The tungsten hexachloride was purified by the sublimation of the more volatile contaminants, WO_2Cl_2 and $WOCl_4$, under nitrogen at about 200 °C, leaving a residue of pure tungsten hexachloride. The benzene was distilled over sodium wire under nitrogen. After having been dried over anhydrous calcium sulfate (Drielite), 1,2,4-trichlorobenzene was distilled under nitrogen. The mixed 2-heptene (*cis* content, 75%; Tokyo Kasei; 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. To a dried glass tube sealed with a neopren rubber cap, 2-heptene (0.28 ml, 2.4×10^{-3} mol, 1.2 mol/l), a benzene solution of WCl_6 (4.8×10^{-5} mol, 2.4×10^{-2} mol/l), and a benzene solution of C_5H_5Na (9.6×10^{-5} mol, 4.8×10^{-2} mol/l) were injected, in this order, by means of hypodermic syringes. The total volume of the reaction mixture was 2.0 ml. The reaction mixture was oscillated vigorously at room temperature for 15 h, and then analyzed by gas-liquid chromatography, which was performed with a Shimadzu-GC-4APF or a JEOL-GC-1100 chromatograph, using an 1 m×3 mm column packed with 10% SE30 on 80—100 mesh Chromosorb W.

The Friedel-Crafts products were identified by gas-liquid chromatography using authentic samples which had been prepared by the alkylation of benzene with olefin catalyzed by sulfuric acid and aluminum chloride respectively. The identity of diphenyldiacetylene was determined by gas-liquid chromatography using an authentic sample prepared according to the method given in the literature.[10]

The NMR spectra were obtained by means of a Japan Electron Optics Lab. JEOL 60 HL apparatus operating at 60 MHz.

References

1) J. A. Moulijin and C. Boelhouwer, *Chem. Commun.*, **1971**, 1170; P. B. van Dam, M. C. Mittelmeijer, and C. Boelhouwer, *ibid.*, **1972**, 1221; *Fette Seifen Anstrichmittel*, **76**, 264 (1974); T. Takagi, K. Ichikawa, T. Hamaguchi, K. Fukuzumi, and M. Aoyama, *Yukagaku*, **24**, 377 (1975).

2) T. Takagi, T. Hamaguchi, K. Fukuzumi, and M. Aoyama, *Chem. Commun.*, **1972**, 839; P. A. Raven and E. J. Warton, *Chem. Ind.*, **1972**, 292; T. Takagi, K. Ichikawa, K. Fukuzumi, and T. Hamaguchi, *Yukagaku*, **24**, 518 (1975).

3) J. L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).

4) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, 3327 (1967); N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, **90**, 4133 (1968); E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *J. Amer. Chem. Soc.*, **92**, 528 (1970); N. Calderon, *Accounts Chem. Res.*, **5**, 127 (1972); A. Uchida, Y. Mukai, Y. Hamano, and S. Matsuda, *Ind. Eng. Chem. Prod. Res. Develop.*, **10**, 369 (1971).

5) J. Chatt, R. J. Haines, and G. J. Leigh, *Chem. Comm.*, **1972**, 1202; S. A. Matlin and P. G. Sammes, *ibid.*, **1974**, 173.

6) L. Bencze and L. Marko, *J. Organometal. Chem.*, **69**, C19 (1974); J. L. Wang, H. R. Menapace, and M. Brown, *J. Catal.*, **26**, 455 (1972); M. Hidai, T. Tatsumi, and Y. Uchida, This Bulletin, **47**, 3177 (1974).

7) N. A. D. Carey and H. C. Clark, *Inorg. Chem.*, **7**, 94 (1968).

8) G. Wilkinson, "Organic Syntheses," Coll. Vol. IV, p. 473 (1973); R. B. Moffett, "Organic Syntheses," Coll. Vol. IV, p. 238 (1963).

9) T. F. Rutledge, *J. Org. Chem.*, **22**, 649 (1957); H. Gilman and R. V. Young, *ibid.*, **1**, 315 (1936).

10) I. D. Campbell and G. Eglinton, "Organic Syntheses," Coll. Vol. V, p. 517 (1973).