APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 232–235 **Materials, Nanoscience and Catalysis** **AOC**

Electrochemically reduced tungsten-based active species as catalysts for cross-metathesis reactions: cross-metathesis of non-functionalized olefins

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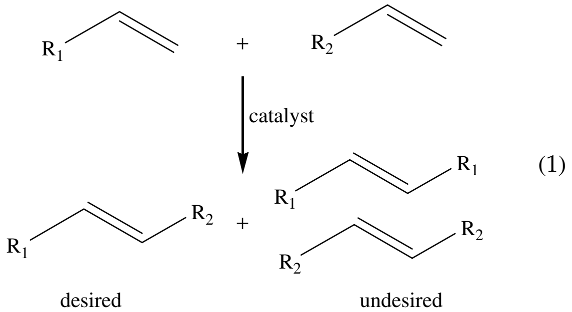
Received 26 November 2002; Accepted 17 January 2003

The electrochemical reduction of WCl_6 results in the formation of an active olefin (alkene) metathesis catalyst. The application of the WCl_6–e^-–Al–CH_2Cl_2 catalyst system to cross-metathesis reactions of non-functionalized acyclic olefins is reported. Undesirable reactions, such as double-bond shift isomerization and subsequent metathesis, were not observed in these reactions. Cross-metathesis of 7-tetradecene with an equimolar amount of 4-octene generated the desired cross-product, 4-undecene, in good yield. The reaction of 7-tetradecene with 2-octene, catalyzed by electrochemically reduced tungsten hexachloride, resulted in both self- and cross-metathesis products. The cross-metathesis products, 2-nonene and 6-tridecene, were formed in larger amounts than the self-metathesis products of 2-octene. The optimum catalyst/olefin ratio and reaction time were found to be 1:60 and 24 h, respectively. The cross-metathesis of symmetrical olefins with α-olefins was also studied under the predetermined conditions. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: cross-metathesis; metathesis catalyst; acyclic olefin; WCl_6; reduction

INTRODUCTION

Cross-metathesis reactions are a powerful tool for the synthesis of organic molecules. Intermolecular coupling between two different olefins is depicted in Eqn (1).



This reaction yields three unique products: one desired heterodimeric product and two undesired homodimeric products, each consisting of a mixture of olefin isomers.[1,2] A number of articles on cross-metathesis reactions between acyclic olefins have been reported.[3–7] Higher molecular weight olefins (feedstock for the manufacture of surfactants) can be obtained from lower molecular weight olefins by cross-metathesis reactions using both homogeneous and heterogeneous catalysts.[8] Tungsten-, molybdenum- and ruthenium-based catalysts are applied to various kinds of olefins in cross-metathesis reactions.[9–11]

We report here on the cross-metathesis reactions of non-functionalized acyclic olefins catalyzed by active tungsten species generated electrochemically. Systematic studies on the cross-metathesis reactions of acyclic olefins using different catalytic systems are scarce in the literature. Electrochemical reduction of WCl_6 and $MoCl_5$ results in the formation of stable and active olefin metathesis catalysts.[12,13] A careful analysis of the early products in olefin metathesis reactions with the WCl_6–e^-–Al–CH_2Cl_2 catalyst system suggested the *in situ* formation of $M{=}CH_2$ initiators, and this assumption was supported by applying ^{13}C NMR techniques to detect the carbenic structure. A WCl_6–Al–CH_2Cl_2 system that has been electrochemically reduced catalyzes the metathesis of α- and β-olefins[13] and polymerization of 1,9-decadiene[14] with good activity and selectivity. Electrochemical generation

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Contract/grant sponsor: The Scientific and Technical Research Council of Turkey; Contract/grant number: TBAG-2148 (102T039).

apparently stabilizes the higher oxidation state of the active species responsible for the metathesis reaction.[12,13]

EXPERIMENTAL

Chemicals

Dichloromethane (Merck) was washed with concentrated H_2SO_4, water and an aqueous solution of Na_2CO_3 (5 wt%), then dried over $CaCl_2$ and distilled from P_2O_5 under nitrogen.[15] Olefins were obtained from Aldrich, purified by distillation over CaH_2 and kept under nitrogen. WCl_6 (Aldrich) was purified by sublimation at 220 °C under nitrogen to remove more volatile WO_2Cl_2 and $WClO_4$ impurities.[16]

Electrochemical instrumentation

The electrochemical instrumentation consisted of an EGG-PAR Model 273 coupled with a PAR Model Universal Programmer. The measurements were carried out under a nitrogen atmosphere in a three-electrode cell having a jacket through which water from a constant-temperature bath was circulated. In the electrochemical experiments, the reference electrode consisted of AgCl coated on a silver wire in $CH_2Cl_2/0.1\ \text{N}$ tetra-*n*-butyl ammonium tetrafluoroborate ($TBABF_4$), which was separated from the electrolysis solution by a sintered glass disc. Experiments were carried out in an undivided cell with a macro working platinum foil electrode (2.0 cm^2) and an aluminum foil (2.0 cm^2) counter electrode. Electrolysis was carried out without a supporting electrode because of its deleterious effect on the catalyst system. For this reason, the distance between the platinum working and the aluminum counter electrode was kept constant and as small as possible (i.e. 2.0 mm) in order to keep solution resistance to a minimum.

Activation of catalyst

All electrochemical and catalytic work was done under a nitrogen atmosphere. WCl_6 (0.2 g, 0.50 mmol) was introduced into the electrochemical cell containing CH_2Cl_2 (25 ml) and a red solution was observed. The electrodes were introduced into the deep-red solution and reductive electrolysis at +0.9 V was applied to the solution for 3 h. The color of the solution darkened progressively. Aliquots from this catalytic solution were used in cross-metathesis reactions.

Synthesis and analysis

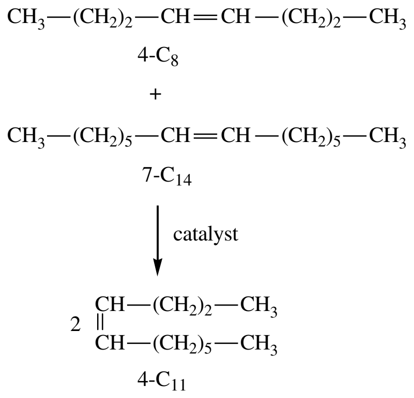
The metathesis experiments were carried out in a stirred glass vessel at room temperature. In a typical experiment, a certain amount of olefins was introduced into the reactor. 385 μl of the catalytic solution was taken with an automatic pipette from the electrochemical cell and added to the olefin in the glass vessel under a nitrogen atmosphere. Metathesis reactions were performed under different catalyst/olefin ratios and reaction times. The product mixtures obtained from the cross-metathesis experiments were analysed by gas chromatography (GC)–mass spectrometry (MS) techniques. GC analysis was performed with a Shimadzu GCMS-QP5050A using an Optima column, 5–1.0 μm (50 m × 0.32 mm), a temperature range of 80–250 °C (20 °C min^{-1}) and the carrier gas was helium at 1 ml min^{-1}.

n-Heptadecane ($C_{17}H_{36}$) was used as internal standard for the quantitative determination of the products. Optimum conditions for obtaining cross-metathesis products were determined.

RESULTS AND DISCUSSION

Cross-metathesis of 7-tetradecene with 4-octene

Cross-metathesis of 7-tetradecene with an equimolar amount of 4-octene in the presence of an electrochemically reduced catalyst at room temperature (Eqn (2)) resulted in the formation of the cross-metathesis product 4-undecene. Since the two olefins are symmetrical, no self-metathesis reactions can take place.



$$\begin{array}{c} CH_3-(CH_2)_2-CH=CH-(CH_2)_2-CH_3 \\ \text{4-C}_8 \\ + \\ CH_3-(CH_2)_5-CH=CH-(CH_2)_5-CH_3 \\ \text{7-C}_{14} \\ \Big\downarrow \text{catalyst} \\ 2\ \begin{array}{l} CH-(CH_2)_2-CH_3 \\ \| \\ CH-(CH_2)_5-CH_3 \end{array} \\ \text{4-C}_{11} \end{array} \qquad (2)$$

To optimize the reaction conditions, several experiments were carried out in which the olefin/catalyst ratio was varied. The results are shown in Table 1. The yield of 4-undecene increased significantly with an increase in olefin/catalyst ratio and gave a maximum yield of 59%.

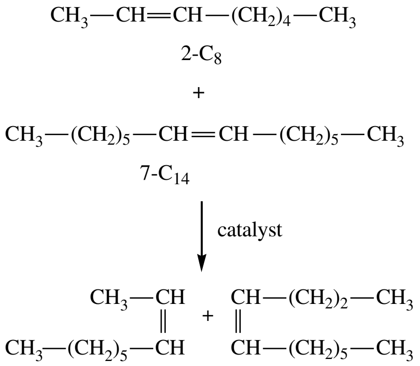
Table 1. The effect of olefin concentration on the yield of 4-undecene in the cross-metathesis of 7-tetradecene with 4-octene (reaction time: 24 h)

WCl_6/7-C_{14}/4-C_8	4-C_{11}, Yield[a] (%)
1 : 10 : 10	8
1 : 15 : 15	9
1 : 20 : 20	15
1 : 30 : 30	21
1 : 40 : 40	59
1 : 50 : 50	30

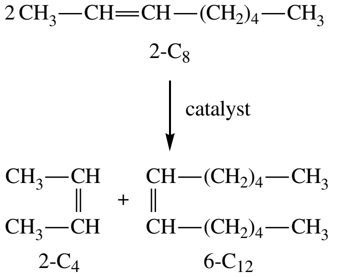
[a] Yield: ([4-C_{11}]/2 × [4-C_8]$_i$) × 100.

Cross-metathesis of 7-tetradecene with 2-octene

The reaction of 7-tetradecene with an equimolar amount of 2-octene, catalyzed by electrochemically reduced tungsten-based active species, resulted in both self- and cross-metathesis. The reaction products were two heterodimers (2-nonene and 6-tridecene) via cross-metathesis (Eqn (3)) and one homodimer (6-dodecene) via self-metathesis (Eqn (4)). No products from side reactions were observed.



$$\underset{2\text{-}C_8}{CH_3-CH=CH-(CH_2)_4-CH_3} + \underset{7\text{-}C_{14}}{CH_3-(CH_2)_5-CH=CH-(CH_2)_5-CH_3} \xrightarrow{\text{catalyst}} \begin{array}{c} CH_3-CH \\ \| \\ CH_3-(CH_2)_5-CH \end{array} + \begin{array}{c} CH-(CH_2)_2-CH_3 \\ \| \\ CH-(CH_2)_5-CH_3 \end{array} \quad (3)$$



$$2\,\underset{2\text{-}C_8}{CH_3-CH=CH-(CH_2)_4-CH_3} \xrightarrow{\text{catalyst}} \underset{2\text{-}C_4}{\begin{array}{c} CH_3-CH \\ \| \\ CH_3-CH \end{array}} + \underset{6\text{-}C_{12}}{\begin{array}{c} CH-(CH_2)_4-CH_3 \\ \| \\ CH-(CH_2)_4-CH_3 \end{array}} \quad (4)$$

Table 2 summarizes the effect of olefin concentration on the yields of cross- and self-metathesis products. The activity of the catalyst increased when the catalyst/olefins ratio was increased from 1:15:15 to 1:30:30, and decreased when this ratio was further increased up to 1:70:70. The optimum ratio obtained for this reaction was 1:30:30. Yields of 39% for the cross-metathesis products ($2\text{-}C_9$ and $6\text{-}C_{13}$) and 26% for the self-metathesis product ($6\text{-}C_{12}$) were obtained. The cross-metathesis products, 2-nonene and 6-tridecene, were formed in larger amounts than the self-metathesis products of 2-octene. In each case, the amounts of 6-tridecene produced were 1.33–1.65 times greater than those of 2-nonene. This is presumably due to the preferred formation of 2-butene relative to the formation of 2-nonene. When the catalyst/olefin ratio was increased to 1:70:70, the cross-metathesis products were much more preferred than the self-metathesis products, although the yield of both products decreased.

Table 2. The yield of products in the cross-metathesis of 7-tetradecene with an equimolar amount of 2-octene (reaction time: 24 h)

	Cross-metathesis			
$WCl_6/7\text{-}C_{14}/2\text{-}C_8$	yield Y_c (%)[a]	$[6\text{-}C_{13}]/[2\text{-}C_9]$	Self-metathesis yield Y_s (%)[b]	Y_c/Y_s
1:15:15	14	1.65	11	1.27
1:20:20	22	1.42	14	1.57
1:30:30	39	1.24	26	1.50
1:40:40	36	1.31	23	1.57
1:50:50	31	1.32	19	1.63
1:60:60	18	1.26	11	1.64
1:70:70	7	1.33	4	1.75

[a] Yield: $([2\text{-}C_9+6\text{-}C_{13}]/2 \times [2\text{-}C_8]_i) \times 100$.
[b] Yield: $(2\times [6\text{-}C_{12}]/[2\text{-}C_8]_i) \times 100$.

Figure 1 shows the changes in yield of reaction products during the course of reaction. The reaction proceeded at a moderate rate and reached an equilibrium within 24 h.

Cross-metathesis of symmetrical olefins with α-olefins

Metathesis reactions of symmetrical olefins with equimolar amounts of α-olefins were also studied under the pre-determined conditions. Cross-metathesis of 4-octene with the α-olefin 1-heptene, 1-nonene, 1-dodecene and 1-pentadecene leads to 1-pentene. The yield of cross-metathesis products was calculated according to the other cross-metathesis products, 4-decene, 4-dodecene, 4-pentadecene and 4-hexadecene (Table 3). The self-metathesis products of 1-heptene and 1-nonene ($6\text{-}C_{12}$, $8\text{-}C_{16}$) were observed, but those of 1-dodecene and 1-pentadecene ($11\text{-}C_{22}$, $14\text{-}C_{28}$) were not detected in the liquid products by GC–MS, because of their high boiling points. The WCl_6/symmetric olefin/α-olefin ratio changed the yield of the cross- and self-products greatly.

Table 3. The yield of products in the cross-metathesis of 4-octene with α-olefins (reaction time: 24 h)

		Product (yield (%))			
Substrates		Cross-metathesis[a]	Self-metathesis[a]	Cross-metathesis[b]	Self-metathesis[b]
$4\text{-}C_8$	$1\text{-}C_7$	$4\text{-}C_{10}$ (12)	$6\text{-}C_{12}$ (4)	$4\text{-}C_{10}$ (4)	$6\text{-}C_{12}$ (1)
$4\text{-}C_8$	$1\text{-}C_9$	$4\text{-}C_{12}$ (4)	$8\text{-}C_{16}$ (2)	$4\text{-}C_{12}$ (2)	$8\text{-}C_{16}$ (1)
$4\text{-}C_8$	$1\text{-}C_{12}$	$4\text{-}C_{15}$ (6)	Not detected	$4\text{-}C_{15}$ (31)	Not detected
$4\text{-}C_8$	$1\text{-}C_{15}$	$4\text{-}C_{18}$ (2)	Not detected	$4\text{-}C_{18}$ (6)	Not detected

[a] WCl_6/symmetric olefin/α-olefin: 1:40:40.
[b] WCl_6/symmetric olefin/α-olefin: 1:30:30.

Table 4. The yield of products in the cross-metathesis of 7-tetradecene with α-olefins (reaction time: 24 h)

Substrates		Product (yield (%))			
		Cross-metathesis[a]	Self-metathesis[a]	Cross-metathesis[b]	Self-metathesis[b]
7-C_{14}	1-C_7	1-C_8 (19) 6-C_{13} (27)	6-C_{12} (15)	1-C_8 (13) 6-C_{13} (23)	6-C_{12} (8)
7-C_{14}	1-C_9	1-C_8 (5) 7-C_{15} (27)	8-C_{16} (12)	1-C_8 (18) 7-C_{15} (26)	8-C_{16} (10)
7-C_{14}	1-C_{12}	1-C_8 (7) 7-C_{18} (19)	Not detected	1-C_8 (26) 7-C_{18} (23)	Not detected
7-C_{14}	1-C_{15}	1-C_8 (24)	Not detected	1-C_8 (50)	Not detected

[a] WCl_6/symmetric olefin/α-olefin: 1 : 40 : 40.
[b] WCl_6/symmetric olefin/α-olefin: 1 : 30 : 30.

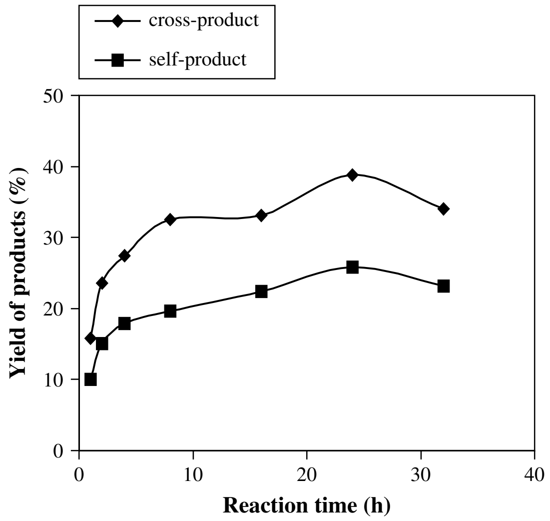


Figure 1. Effect of reaction time on the yield of the products in the cross-metathesis of 7-tetradecene with 2-octene (WCl_6/7-C_{14}/2-C_8 =1 : 30 : 30).

In the cross-metathesis of 7-tetradecene with 1-heptene and 1-nonene, three kinds of liquid product were produced (Table 4). The amounts of cross-metathesis products were larger than those of self-metathesis products. Higher olefins than C_{18} were not detected in the gas chromatograms. The changes in the olefin concentration affected the yield of products significantly. It is better to use much more catalyst in the cross-metathesis of symmetrical olefins with higher α-olefins. There were no side reactions in the cross-metathesis reactions, although most catalytic systems that use WCl_6 as precursor are inefficient for metathesis of α-olefins and give rise to side reactions.

CONCLUSIONS

The catalyst system WCl_6–e^-–Al–CH_2Cl_2 appeared to be very active and selective for cross-metathesis reactions of non-functionalized olefins. Undesirable reactions, such as double-bond shift isomerization and subsequent metathesis, were not observed in these reactions. C_{10}–C_{18} olefins can be obtained from lower molecular weight olefins in good yields by this electrochemically generated tungsten-based catalyst. Ongoing studies are aimed at the application of this catalyst to cross-metathesis of functionalized olefins.

Acknowledgements

The authors thank Professor J. C. Mol (University of Amsterdam) for helpful discussions. This work was supported by The Scientific and Technical Research Council of Turkey, project no. TBAG-2148 (102T039).

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