Letter

A convenient catalyst system employing $RuCl_3$ or $RuBr_3$ for metathesis of acyclic olefins

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Abstract

A convenient ruthenium catalyst system for olefin metathesis was developed that is effective for metathesis of acyclic olefins. The catalyst system is comprised of $RuCl_3$ or $RuBr_3$ hydrate, a phosphine, and an alkyne which are simply combined with the olefin reactant and heated to moderate temperatures, preferably in the presence of H_2 to obtain highest activity. Catalyst components are readily available and no syntheses of ruthenium complexes are required. The system was found to be particularly active and selective for metathesis of acyclic alpha-olefins. The most effective phosphines identified were PCy_3, $P(i\text{-}Pr)_3$, $PH(t\text{-}Bu)_2$, and $PMe(t\text{-}Bu)_2$. Of the alkynes tested, 2-butyne-1,4-diol diacetate yielded the most active system for alpha-olefin metathesis. Self-metathesis reactions of 1-octene utilizing PCy_3 and 2-butyne-1,4-diol diacetate proceeded with initial turnover rates of about 1000 min^{-1} and total turnover numbers of 50,000–100,000 after 2 h at 80–90°C. The catalyst system was also demonstrated effective for metathesis of methyl oleate. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Olefin metathesis; Catalyst; Ruthenium trichloride; Ruthenium tribromide; Acyclic olefins

1. Introduction

Ruthenium catalysts for olefin metathesis, such as the carbene complexes developed by Grubbs et al. [1–4], are currently of great interest because they are very tolerant of polar functional groups. As a result, ruthenium catalysts are quite resistant to poisoning by polar impurities (such as water) and are able to effect metathesis of olefins containing various types of functional groups, including hydroxyl, amine, carboxylic acid and ester moieties [5–13].

Simple $RuCl_3$ hydrate was reported in the 1960s to be an effective catalyst for ring-opening metathesis of highly-strained cyclic olefins such as norbornene, but it does not catalyze metathesis of acyclic olefins [7,14]. It was not until the 1990s that ruthenium catalysts were developed with the ability to metathesize acyclic as well as cyclic olefins. The most prominent and well-studied of these are the $RuCl_2$-$(=CHR)(PR'_3)_2$ complexes of Grubbs et al., which have highest activity when $R' =$ cyclohexyl or isopropyl. Recently, Herrmann et

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al. replaced the phosphine ligands of these complexes with *N*-heterocyclic carbene ligands, yielding catalysts active for ring-closing metathesis of acyclic dienes [15]. Fürstner et al. reported cationic ruthenium allenylidene complexes, $[Ru=C=C=CR_2(PR'_3)Cl(arene)]PF_6$, R′ = cyclohexyl or isopropyl, that are active for metathesis of acyclic dienes containing O- or N-functional groups [16].

The reported syntheses of the Grubbs catalysts [3,4,17–20] and the catalysts of Herrmann and Fürstner et al. involve multistep procedures starting from $RuCl_3$. As a result, these catalysts are expensive and not readily available. We now report a very convenient ruthenium catalyst system effective for metathesis of acyclic olefins that employs $RuCl_3$ or $RuBr_3$ directly. This catalyst system is comprised of $RuCl_3$ or $RuBr_3$ hydrate, a phosphine, and an alkyne which are simply combined with the olefin reactant and heated to moderate temperatures, preferably with H_2 present. The catalyst components are readily available and no syntheses of ruthenium complexes are required. We report herein that this catalyst system is very active and selective for metathesis of acyclic alpha-olefins and is also able to metathesize methyl oleate, an acyclic functional olefin.

2. Experimental

1-Octene (98%, Aldrich) and 1-tetradecene (79%, Amoco) were passed through basic alumina and stored under N_2. Methyl oleate (99%, Aldrich), ethanol (200-proof), other alcohols, chlorobenzene and heptane (HPLC grades), $RuCl_3$ hydrate (40.3 wt.% Ru, Colonial Metals) and $RuBr_3$ hydrate (25.9 wt.% Ru, Strem) were used as obtained. Tricyclohexylphosphine (97%), di-*tert*-butylmethylphosphine (98%), and triisopropylphosphine (98% purity, 10 wt.% solution in hexane) were obtained from Strem. Di-*tert*-butylphosphine (98%), phenylacetylene, diphenylacetylene, 1-decyne, 3-hexyne, and H_2 (99.99%) were obtained from Aldrich. 2-Butyne-1,4-diol diacetate (BDD) was obtained from Narchem; propargyl acetate from Farchan. Stock solutions of RuX_3 hydrates, phosphines, and alkynes were utilized in reactions. Stock solutions of $RuCl_3$ hydrate (0.03–0.04 M) and $RuBr_3$ hydrate (0.005 M) in alcohols were prepared and stirred at room temperature overnight prior to use. Stock solutions of phosphines (5–50 mg/ml chlorobenzene or heptane) and alkynes (5–50 mg/ml chlorobenzene) were prepared and stored under N_2.

Reactions were performed in dried glass 100-ml round-bottom flasks equipped with a magnetic stirbar and water-cooled reflux condenser. An oil bubbler connected to the condenser outlet provided for escape of evolved gases (ethylene) and H_2. Reaction vessels were purged with N_2 and charged with olefin and stock solutions of RuX_3, phosphine, and alkyne at room temperature using gas-tight syringes. In a representative 1-octene metathesis experiment, 1-octene (40 ml, 255 mmol), 0.60 ml of 0.0066 M PCy_3/heptane (4.0 μmol PCy_3), 0.54 ml of 0.071 M BDD/chlorobenzene (38 μmol BDD), 0.40 ml chlorobenzene (GC internal standard), and 50 μl of 0.032 M $RuCl_3$ hydrate/ethanol (1.6 μmol Ru) were charged. After stirring, a small aliquot (0.5–1 ml) of solution was removed for GC analysis ('before reaction' sample). The flask was then immersed in an oil bath at the desired reaction temperature and a flow of H_2 was begun. H_2 was bubbled (sparged) through the solution at 1 atm at 25–50 sccm. Hydrogen delivery lines were thoroughly purged with H_2 beforehand to avoid introducing air. The solution was stirred and H_2 flow was maintained during the entire experiment. Small aliquots of reaction solution were removed periodically for GC analysis.

GC analyses were performed using an HP-5890 FID GC with a DB-1 capillary column.

$$2 \quad CH_2=CH-R \xrightarrow[\text{Metathesis Catalyst}]{-\ CH_2=CH_2} R-CH=CH-R$$
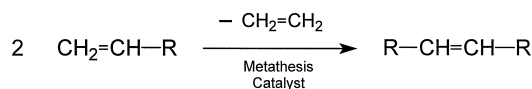
Scheme 1.

Table 1
1-Octene metathesis reactions utilizing RuX_3 hydrate, PCy_3, and 2-butyne-1,4-diol diacetate (BDD) catalyst components under 1 atm H_2

RuX_3 X =	Octene/Ru mole ratio	Temp. (°C)	1-Octene conversion		1-Octene turnover number[a]		$C_{14}^=$ product selectivity[b]	
			30 min	2 h	30 min	2 h	30 min	2 h
Cl	160,000	80	19%	37%	30,000	59,000	90%	90%
Cl	160,000	90	23%	43%	37,000	69,000	90%	> 90%
Br	160,000	80	14%	46%	22,000	74,000	90%	> 90%
Br	320,000	90	11%	34%	35,000	110,000	> 90%	> 90%

[a] Defined as total moles of 1-octene converted per mole Ru.
[b] Defined as 100%(observed wt.% tetradecene selectivity)/(87.5%), where 87.5% is the theoretical maximum wt.% tetradecene product selectivity based upon reaction stoichiometry.

For 1-octene reactions, conversions and tetradecene product selectivities were calculated using chlorobenzene as an internal standard since there was no detectable consumption or evaporative loss of chlorobenzene. For 1-tetradecene reactions, C_{14} vinylidene olefin isomers ($RR'C = CH_2$) present in the tetradecene reagent were employed as the internal standard since they appeared completely inert (not consumed or produced) in all experiments.

3. Results and discussion

Metathesis reactions of alpha-olefins (Scheme 1) were carried out very effectively by combining the olefin reactant with the following three catalyst components under 1 atmosphere H_2:
1. $RuCl_3$ hydrate or $RuBr_3$ hydrate dissolved in alcohol,
2. phosphine (PCy_3, P^iPr_3, PH^tBu_2, or PMe^tBu_2),
3. alkyne (e.g., 2-butyne-1,4-diol diacetate or propargyl acetate).

This catalyst system performed well in the temperature range of about 60–90°C. Table 1 presents the results of 1-octene self-metathesis reactions (Scheme 1, R = *n*-hexyl) utilizing $RuCl_3$ hydrate or $RuBr_3$ hydrate in ethanol, PCy_3, and 2-butyne-1,4-diol diacetate (BDD) in a 1:2.5:24 molar proportion (Ru/P/BDD). These experiments were carried out using a slow continuous sparge of H_2 through the reaction solutions, which consisted primarily of octene with very small amounts of solvents (ethanol, chlorobenzene, heptane from the catalyst component stock solutions). As the results in Table 1 indicate, turnover rates of about 1000 min^{-1} were observed during the first half-hour of reaction, and total turnover numbers of 50,000–100,000 were

Table 2
Effects of H_2 atmosphere and the amount of alkyne (BDD) employed in 1-octene metathesis reactions at 80°C utilizing $RuCl_3$ hydrate in ethanol, PCy_3, and BDD catalyst components[a]

Atmosphere employed (1 atm)	BDD/ Ru mole ratio	1-Octene conversion		$C_{14}^=$ product selectivity[b]		Extent of 1-octene isomerization[c]	
		30 min	2 h	30 min	2 h	30 min	2 h
N_2	24	2%	8%	90%	80%	low	low
H_2	24	17%	30%	90%	90%	very low	very low
H_2	6	16%	45%	80%	30%	low	high
H_2	0	5%	29%	10%	5%	high	very high

[a] 160,000:2.5:1 mole ratio of 1-octene/PCy_3/Ru employed.
[b] Defined as in Table 1.
[c] Relative to 1-octene metathesis.

Table 3
1-Tetradecene metathesis reactions utilizing different alkyne catalyst components[a]

Alkyne employed in catalyst system	1-Tetradecene conversion	$C_{26}^=$ product selectivity (wt.%)	Extent of 1-tetradecene isomerization[b]
$AcOCH_2C≡CCH_2OAc$ (BDD)	31%	95%	none detected
$HC≡CCH_2OAc$ (propargyl acetate)	23%	95%	none detected
1-Decyne	14%	90%	low
3-Hexyne	18%	10%	high
Phenylacetylene	4%	15%	high
Diphenylacetylene	5%	5%	high

[a]90°C for 2 h under H_2 using $RuBr_3$ hydrate (1-hexanol stock solution) and a 125,000:2.5:24:1 mole ratio of 1-tetradecene:PCy_3:alkyne:Ru.
[b]Relative to 1-tetradecene metathesis.

obtained after 2 h. The metathesis reactions proceeded cleanly, yielding internal tetradecene product in at least 90% of theoretical selectivity. The only side reaction observed was a small amount of isomerization of 1-octene to internal octenes; GC analyses indicated less than 5% of 1-octene isomerized after 2 h. Hydrogenation of octene was apparently insignificant (not detected by GC) and there was no evidence of octene polymerization.

The effects of H_2 and alkyne (BDD) on the performance of the catalyst system were significant, as shown in the results in Table 2 for a series of 1-octene experiments. Metathesis activity was several times greater when 1 atm H_2 (continuous sparge) was employed instead of N_2. The presence of the alkyne was critical, as the dominant reaction obtained with little or no alkyne (BDD) present was isomerization of 1-octene to internal octenes, not metathesis. With alkyne present, isomerization tended to increase relative to metathesis with increasing reaction time and with increasing reaction temperature.

1-Octene metathesis reactions were performed as above but with stock solutions of $RuCl_3$ hydrate dissolved in alcohols other than ethanol. Isopropanol, 1-butanol, 2-butanol, and 1-hexanol yielded essentially the same results as ethanol, but methanol yielded a less active catalyst system.

Various alkynes were tested as catalyst components. Table 3 presents the results of six 1-tetradecene self-metathesis reactions (Scheme 1, R = *n*-dodecyl) in which different alkynes were evaluated in a $RuBr_3$/PCy_3/H_2 catalyst system. The type of alkyne employed affected catalyst activity and selectivity. 2-Butyne-1,4-diol diacetate (BDD), an internal alkyne, yielded the most active system. In contrast, the predominant reaction observed with the other internal alkynes (3-hexyne and diphenylacetylene) was isomerization of 1-tetradecene to internal tetradecenes. Of the 1-alkynes examined, propargyl acetate yielded better metathesis activity and selectivity than 1-decyne, while phenylacetylene yielded primarily isomerization.

Four phosphines were found to generate highly active metathesis systems: PCy_3, P(*i*-Pr)$_3$, PH(*t*-Bu)$_2$, and PMe(*t*-Bu)$_2$, all sterically
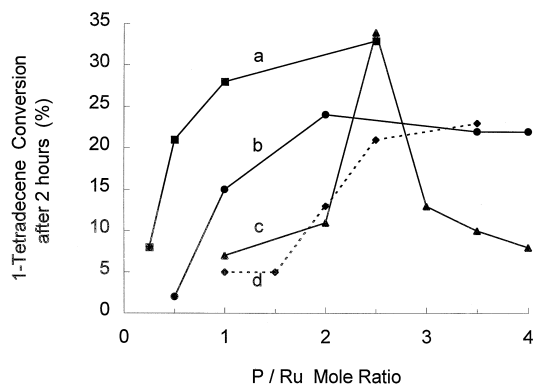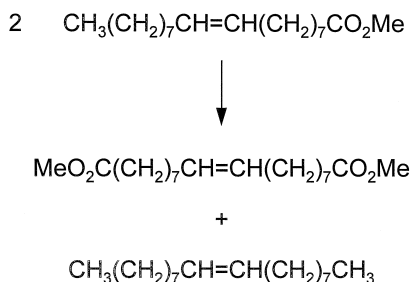

Fig. 1. 1-Tetradecene self-metathesis experiments using various phosphines: (a) PH(*t*-Bu)$_2$ (■); (b) P(*i*-Pr)$_3$ (●); (c) PMe(*t*-Bu)$_2$ (▲); (d) PCy$_3$ (♦, dashed line); 2-h reaction times at 90°C (80°C for PCy$_3$ experiments).

$$2 \quad CH_3(CH_2)_7CH=CH(CH_2)_7CO_2Me$$

$$\downarrow$$

$$MeO_2C(CH_2)_7CH=CH(CH_2)_7CO_2Me$$

$$+$$

$$CH_3(CH_2)_7CH=CH(CH_2)_7CH_3$$

Scheme 2.

bulky and strongly basic phosphines. PPh_3, $P(t\text{-}Bu)_3$, and trioctylphosphine yielded much lower metathesis activity. This is similar to the results of Grubbs et al. [1–4,21], Noels et al. [12,13], and Fürstner et al. [16], who reported that PCy_3 and $P(i\text{-}Pr)_3$ were the most effective phosphine ligands for their metathesis catalysts. Fig. 1 shows results of 20 1-tetradecene metathesis experiments with varying amounts of phosphines. These were performed under H_2 at 90°C (80°C for PCy_3) using $RuBr_3$/1-hexanol and a 125,000:24:1 mole ratio of 1-tetradecene:BDD:Ru. The metathesis reactions proceeded cleanly, with little or no 1-tetradecene isomerization observed. For $PH(t\text{-}Bu)_2$, significant metathesis activity was seen even at P/Ru ratios less than 1.

The catalyst system was also able to effect metathesis of the internal acyclic functional olefin, methyl oleate (Scheme 2), a reaction catalyzed by the ruthenium complex of Grubbs et al. [22] and by a number of W, Mo, and Re catalysts [23]. Experiments were performed under H_2 using $RuCl_3$/ethanol (0.08 M) and a 5000:24:2.5:1 mole ratio of methyl oleate/alkyne/PCy_3/Ru. Methyl oleate conversions of 13–17% (turnover numbers of 650–850) were obtained after 4 h at 80–90°C using the alkynes BDD, 1-decyne, or 3-hexyne. The metathesis reactions proceeded cleanly; the major products observed by GC were approximately equimolar amounts of the diester (dimethyl 9-octadecen-1,18-dioate) and internal octadecene.

Acknowledgements

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