

N-Chelate Ruthenium Carbene Complexes in Olefin Metathesis and Isomerization

N. M. Shcheglova^a, V. D. Kolesnik^a, R. V. Ashirov^a, and E. A. Krasnokutskaya^b

^a SIBUR Tomskneftekhim Chemical Research and Development Center,
ul. Kuzovlevskii trakt 2, build. 270, Tomsk 634067 Russia, P.O. Box 1548
e-mail: Shcheglova2006@rambler.ru

^b National Research Tomsk Polytechnic University, pr. Lenina 30, Tomsk, 634050 Russia

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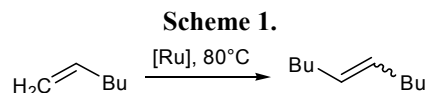
Abstract—The catalytic activity of *N*-chelate ruthenium carbene complexes in the metathesis of hex-1-ene has been studied in comparison to the second generation Grubbs catalyst.

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Olefin metathesis in the presence of ruthenium carbene complexes has found wide application in the synthesis of organic compounds and polymers [1]. In some cases, the reaction is accompanied by isomerization [2] involving double bond migration. Undesirable isomerization may be avoided by appropriate variation of the catalyst structure [3, 4].

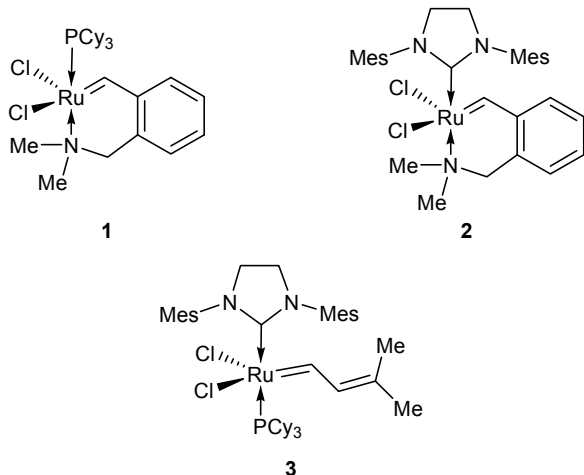
The catalytic activity of recently reported complexes **1** [5] and **2** [6] containing an *N*-chelating benzylidene ligand has been studied only in ring-opening metathesis polymerization and ring-closing metathesis [5, 6]. The behavior of these complexes in cross metathesis was not described, and their effect on the isomerization during metathesis was not studied; these issues were the subjects of the present study. As model substrate we used hex-1-ene (Scheme 1). The catalytic

activities of complexes **1** and **2** were compared with the activity of complex **3** which is a well known second generation Grubbs catalyst [1, 7, 8].



The reaction was carried out either under solvent-free conditions or in 1,2-dichloroethane in the presence of 0.01 mol % of complex **1** or **2** at 80°C. The product composition was determined by gas chromatography (see table). Complex **1** turned out to be the least active in the metathesis of hex-1-ene, but it was more selective than **3**. The catalytic activity of **2** approached that of complex **3**; however, it also favored isomerization, and the selectivity was about 30%. We failed to suppress isomerization and obtain pure dec-5-ene using a chlorinated solvent [1, 9].

The presence of an *N*-chelating ligand in complexes **1** and **2** is expected to endow them with higher thermal stability compared to complex **3** [10]. In fact, these complexes were stable on heating the reaction mixture to 150°C. The reaction catalyzed by complex **2** gave a mixture of C₂–C₂₉ olefins (see figure). Analogous set of olefins is obtained in the large-scale Shell higher olefin process (SHOP) for the manufacture of synthetic oils [11]; this process includes three steps: oligomerization of ethylene, isomerization, and metathesis. Each step is catalyzed by its own catalyst. The use of complex **2** could considerably enhance the efficiency of this process (one step instead of three).



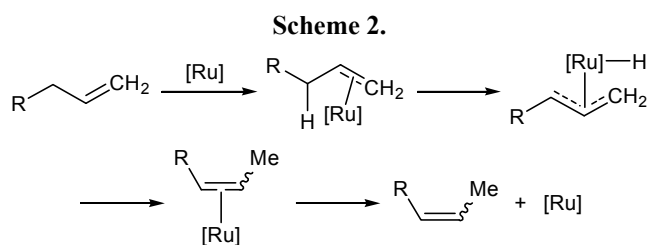
Metathesis of hex-1-ene catalyzed by complexes **1–3**^a

Catalyst	Time, h	Olefin, wt %						Conversion of hex-1-ene, %	Fraction of dec-5-ene in C ₁₀ alkenes, %
		C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁		
1	19.0	58.0	0.2	0.1	0.3	41.4	0.0	42	99
	24.0	26.4	0.6	0.1	0.6	72.2	0.1	74	98
3	0.2	27.1	0.7	0.6	5.6	63.9	2.1	73	85
2	0.7	31.3	12.2	9.6	25.6	21.0	0.3	69	32
	17.0	21.9	1.8	0.7	5.4	69.7	0.5	78	81 ^b

^a Amount of the catalyst 0.01 mol %; temperature 80°C.

^b In 1,2-dichloroethane (a 2 M substrate solution).

It was reported previously [3] that ruthenium carbene complexes are capable of abstracting a proton from the allylic position (Scheme 2), which leads to migration of the double bond. The olefins thus formed undergo metathesis to give a mixture of new olefins, and the latter isomerize again; as a result, the set of olefins extends.



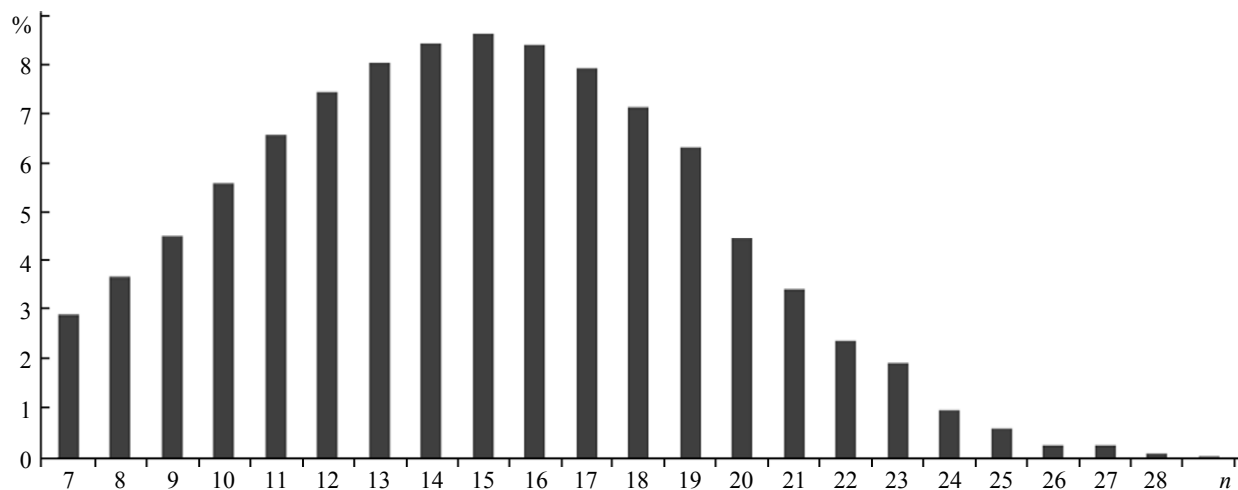
Presumably, analogous processes take place in the presence of complex **2**. The ability to induce isomerization is likely to depend on the basicity of the ruthenium complex, which is determined by the ligand

environment. Probably, the ligand composition of complex **1** does not allow profound isomerization of the double bond.

Thus, the catalytic activity of complexes **1** and **2** in the cross metathesis of hex-1-ene is comparable with the activity of the second generation Grubbs catalyst; however the metathesis of hex-1-ene in the presence of complex **2** is accompanied by strong isomerization with formation of C₂–C₂₉ olefin mixture.

EXPERIMENTAL

The products were analyzed by GLC using an Agilent 7890A gas chromatograph equipped with a flame ionization detector (HP-1 column, 30 m). Complexes **1–3** were synthesized according to the procedures described in [5–7], respectively; the syntheses were carried out under argon in an MBraun glove box.



Concentrations of C_nH_{2n} olefins in the reaction mixture obtained by heating hex-1-ene in the presence of 0.01 mol % of complex **2** (40 min at 80°C and 3 h at 150°C). Lower olefins (C₂–C₆) were not analyzed.

Metathesis of hex-1-ene. A solution of 0.012 mmol of complex **1–3** in 10 g of hex-1-ene was heated at 80°C on an oil bath until the mixture no longer boiled. The product mixture was analyzed by GLC.

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