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Preliminary Communication

Regiospecific Cp*Ru$^+$ mediated codimerization of conjugated dienes with non-conjugated 1,5-dienes and its application to catalytic cooligomerization

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Abstract

When Cp*RuCl(η^4-butadiene) (**1**; where Cp* = η^5-C$_5$Me$_5$) was treated with an excess of 1,5-hexadiene in the presence of silver trifluoromethanesulfonate (AgOTf) at or below ambient temperature, a 2-(3′-butenyl)-1,5-hexadiene complex of cationic ruthenium was obtained by regiospecific C4 homologation at the internal carbon atom of the non-conjugated diene. This stoichiometric C–C bonding was extended to the catalytic codimerization and stepwise oligomerization of butadiene with 1,5-hexadiene or 1-hexene.

Various metal complexes have been reported as actively catalyzing codimerization of butadiene with several alkenes [1], in particular, iron, cobalt, rhodium and nickel in combination with alkylaluminium chloride. Additionally, palladium complexes can induce selective codimerization of ethylene and butadiene to give *cis*- and *trans*-1,4-hexadienes via a metal hydride mechanism. Homogeneous nickel or palladium catalysts have frequently been reported to cause cotrimerization between two molecules of conjugated dienes and an alkene.

The catalytic activity of ruthenium complexes in such cooligomerizations of conjugated dienes, however, has not been investigated to such an extent [2], though Mitsudo and coworkers recently reported that several conjugated dienes codimerized with acrylic esters or amides by means of a Ru(0) cyclooctapolyene complex modified by N-methylpiperidine [3]. We report here a stoichiometric reaction of conjugated diene with 1,5-hexadiene which proceeds with unusual regiospecificity, and its application to catalytic cooligomerization.

When Cp*RuCl(η^4-butadiene) (**1**, 100 mg, 0.307 mmol) [4a] was treated with 1,5-hexadiene (182 μl, 1.54 mmol) in dichloromethane (45 ml) in the presence of a stoichiometric amount of AgOTf (1.84 ml of a 0.2 N acetone solution, 0.368 mmol) at −20°C, the mixture then being held at room temperature for 2 h, pale yellow microcrystals of [Cp*Ru{2-(3-buten-1-yl)-1,5-hexadiene}]OTf (**2a**; 153 mg) were isolated in 94% yield after filtration of silver salts and subsequent recrystallization (by dissolving the concentrated residue in the smallest possible volume of dichloromethane followed by addition of ether).

The symmetric triene ligand structure in **2a** is supported by the following spectroscopic results [5*]. There appeared four olefinic ^{1}H and ^{13}C resonances: δ 2.69 (2H, s), 2.90 (2H, d, J = 8.78 Hz), 3.37 (2H, m), and 3.74 (2H, d, J = 13.2 Hz) in ^{1}H NMR, as well as, 51.0 (t, J(C–H) = 158.5 Hz), 54.6 (t, J(C–H) = 156.5 Hz), 82.8 (d, J(C–H) = 156.5 Hz), and 126.6 ppm (s) in ^{13}C spectra in CDCl$_3$. It is notable that the triene, 2-(3-buten-1-yl)-1,5-hexadiene, ligand in **2a** is assembled by the C–C bond formation between an internal C2 atom of the 1,5-diene and a terminal carbon of the coordinated butadiene. This is quite different from reported catalytic processes, which have been known to provide linear dimers in most cases [1,3]. This unusual regiospecificity may be ascribed to the steric repulsion of the four-carbon alkenyl chain of 1,5-hexadiene with methyl substituents on the Cp* ligand, as depicted in Scheme 1. This view is supported by the fact that a less bulky Cp (η^5-C$_5$H$_5$) analogue, CpRuCl(η^4-butadiene), showed much lower C2 regioselectivity (below 56%) in the AgOTf induced reaction with 1,5-hexadiene under similar reaction conditions.

Similar ruthenium-mediated ligand coupling between **1** and 3-methyl-1,5-heptadiene gave [Cp*Ru{2-(2-hexen-5-yl)-1,5-hexadiene}]OTf (**2b**; in 95% yield), regioselectively [6*]. However, 2,5-dimethyl-1,5-hexadiene did not react with **1** at all under similar conditions, because this 1,5-diene has two methyl substituents at both C2 positions where the regiospecific C4 homologation of butadiene should occur.

When the reaction was carried out at higher temperatures in THF, the replacement of the butadiene

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* Reference number with asterisk indicates a note in the list of references.

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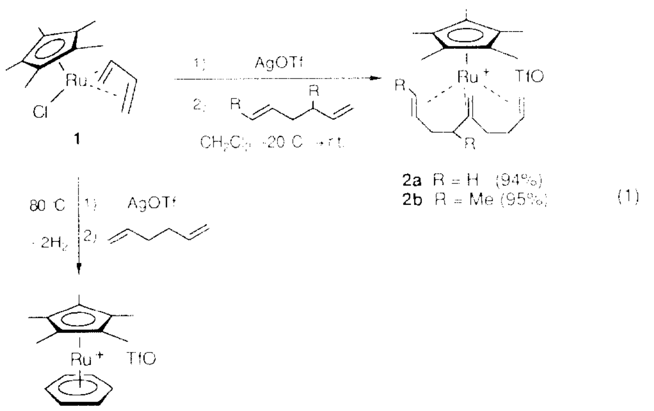

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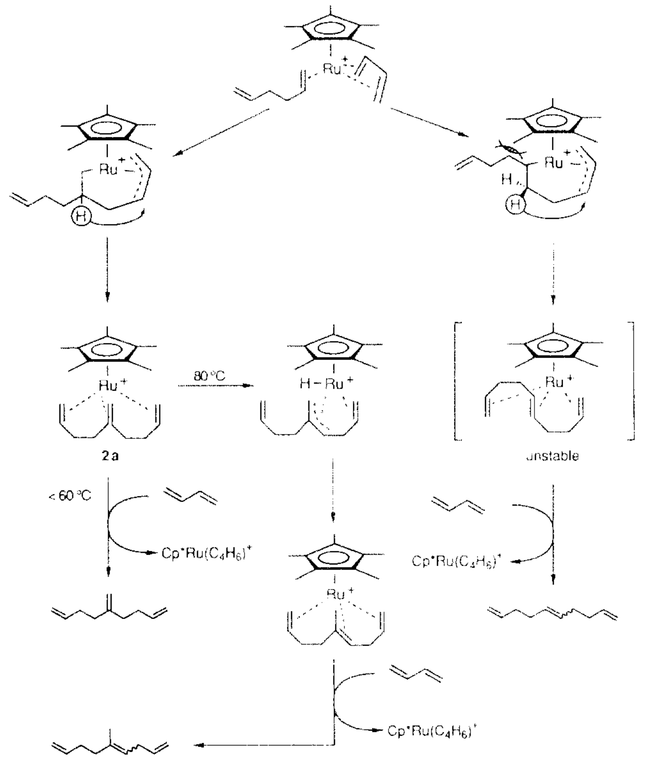
2a R = H (94%)
2b R = Me (95%)

(1)

ligand by 1,5-hexadiene occurred over 4 days at 90°C to give the previously known [Cp*Ru(η^6-benzene)]OTf [7*] in 38% yield. The formation of the arene complex is explained in terms of a Cp*Ru$^+$ induced dehydrogenative cyclization of 1,5-hexadiene.

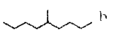
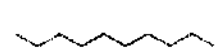
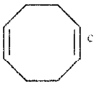
Such a particular regiospecificity, however, cannot be maintained under catalytic conditions, although the bond formation at the C2 position still takes precedence. When butadiene (23.5 mmol), 1,5-hexadiene (23.5 mmol), 1 mol% of **1**, and AgOTf (1 mol%), were heated in THF (5 ml) and ether (2 ml) in a pressure bottle at 50°C for 48 h, a mixture of 2-(3-buten-1-yl)-1,5-hexadiene, *trans*-1,5,9-decatriene, 1,5-cyclooctadiene, and higher cooligomers [8*] was obtained (939 mg; corresponding to 30% conversion based on charged butadiene). The codimer fraction, involving the former two trienes in 73 : 27 molar ratio, was 66 mol% of the total oligomer mixture based on the reacted butadiene. The recovered ruthenium fragment after the catalysis was identified as the cationic triene complex (**2a**). Consequently, the catalyst was restored as an active form. At higher temperatures, the most abundant codimer became *trans*- and *cis*-5-methyl-1,4,8-nonatrienes, double bond isomers of 2-(3-buten-1-yl)-1,5-hexadiene.



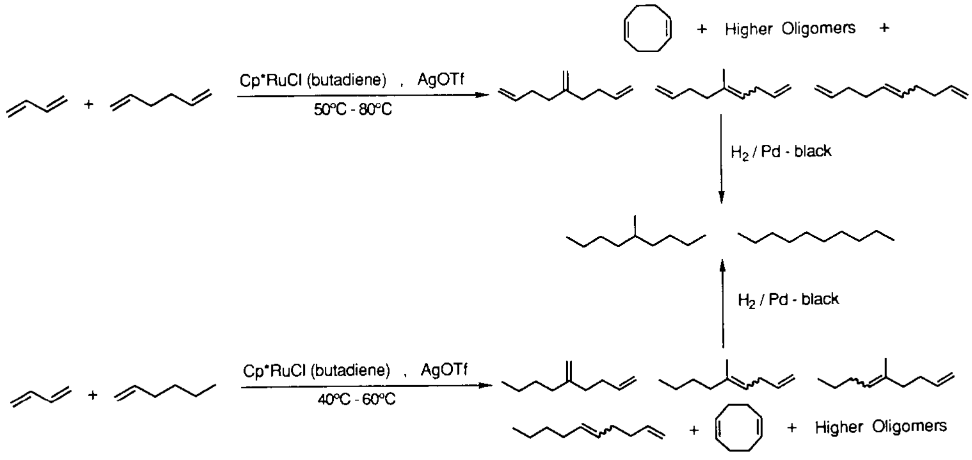
Scheme 1.

In order to determine accurately the regioselectivity of the first step C4 homologation, the triene mixture of the codimer was hydrogenated (1 atm; H_2) by means of a Pd black catalyst (Scheme 2). 5-Methylnonane (addition of butadiene at the C2 carbon of 1,5-hexadiene) and decane (the same addition but at the C1 carbon of the non-conjugated diene) were identified by vpc in the molar ratio of 48 : 18 at 50°C, respectively. Regioselectivity at different temperatures is summarized in Table

TABLE 1. Cooligomerization of alkene with butadiene [a]

Entry	Substrate	Temp. (°C)	Time (h)	Conversion (%)	Product Ratio (mol%)			
					 [b]	 [b]	 [c]	Higher oligomers
1	1,5-hexadiene	80	24	100	17	9	5	69
2	1,5-hexadiene	60	48	43	38	19	12	31
3	1,5-hexadiene	50	48	30	48	18	13	21
4	1-hexene	60	24	68	28	15	6	52
5	1-hexene	50	48	67	30	13	11	46
6	1-hexene	40	48	58	31	10	11	48

[a] Standard condition: alkene (23 mmol), butadiene (23 mmol), THF (5 ml), **1** (0.23 mmol) and AgOTf (0.28 mmol). [b] Determined from VPC of the hydrogenation products of crude cooligomers involving several polyene mixtures. [c] Yield of 1,5-cyclooctadiene was directly determined by VPC.



Scheme 2.

1 (runs 1–3), together with the amounts of 1,5-cyclooctadiene and higher oligomers [8*].

This type of catalytic codimerization and subsequent oligomerization of butadiene is not limited to 1,5-hexadiene. When 1-hexene was employed instead of 1,5-hexadiene under the catalyst, composed of Cp*RuCl(butadiene) and AgOTf, analogous insertion of butadiene was also found to occur at 40–60°C as shown in Table 1 (runs 4–6). In the codimer mixtures, 2-butyl-1,5-hexadiene, 5-methyl-1,4-nonadiene and 5-methyl-1,5-nonadiene were branched products, whereas *trans*-1,5-decadiene was the predominant linear product. The formation of 1,5-cyclooctadiene and of higher oligomers was also confirmed.

Selective formation of 1,5-cyclooctadiene with the same catalyst has already been reported by us [4a]. The suppression of its formation in the presence of 1,5-hexadiene or 1-hexene suggests that the coordinated butadiene forms a C–C bond with terminal alkenes more readily than the C–C bond is formed with the second butadiene molecule. In fact the Cp*Ru-mediated cyclodimerization of butadiene required a longer reaction time than the formation of **2a**.

The X-ray structure determination of the 2-(3-buten-1-yl)-1,5-hexadiene complex (**2a**), and catalytic oligomerization are now under active investigation.

Acknowledgments

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5 **2a**: Yellow microcrystals; Mp. 166–168°C (dec), Anal. Calcd. for $C_{21}H_{31}F_3O_3RuS \cdot 0.5\ H_2O$: C, 47.54; H, 6.08. Found: C, 47.50; H, 6.02%. ^1H NMR (270 MHz in $CDCl_3$): δ 1.48 (4H, m, CH_2), 1.62 (15H, s, CH_3 of Cp*), 1.99 (2H, dd, J = 13.65; 2.9 Hz, CH_2), 2.25 (2H, dd, J = 14.2, 2.9 Hz, CH_2), 2.69 (2H, s, central vinyl), 2.90 (2H, d, J = 8.8 Hz, *cis* vinyl), 3.37 (2H, ddd, J = 13.2; 8.8; 3.4 Hz, vinyl C2), 3.74 (2H, d, J = 13.2 Hz, *trans* vinyl). ^{13}C NMR (67.8 MHz in $CDCl_3$): 9.11 (q, J(C–H) = 129 Hz, Cp* CH_3), 26.4 and 29.6 (t, 129 Hz, two methylenes), 51.0 (t, J = 159 Hz, central vinyl), 54.6 (t, J = 156 Hz, terminal vinyl), 82.8 (d, 156 Hz, terminal vinyl –CH=), 98.6 (s, quarternary vinyl), 126.6 (s, Cp* ring).

6 **2b**: Brown powder, Mp. 142–143°C (dec). Anal. Calcd. for $C_{23}H_{35}F_3O_3RuS \cdot H_2O$: C, 48.66; H, 6.57. Found: C, 48.62; H, 6.24%. ^1H NMR (270 MHz in $CDCl_3$): δ 0.98 (3H, d, J = 6.4 Hz, –CH(CH_3)–), 1.30–1.44 (1H, m, –CH_2–), 1.44–1.56 (2H, m, –CH_2–), 1.56–1.61 (1H, m, –CH(CH$_3$)–), 1.64 (15H, s, Cp* CH_3), 1.88 (3H, d, J = 6.4 Hz, CH_3–CH=), 2.02–2.35 (1H, m, CH_2), 2.23–2.35 (1H, m, CH_2), 2.43 (1H, d, J = 9.3 Hz, H_2C=, *cis* vinyl), 2.53 (1H, dd, CH_2), 2.67 and 2.77 (each 1H, s, central H_2C= vinyl), 3.33 (1H, broad d, J = 12.7 Hz, –CH=CH(CH$_3$)), 3.51 (ddd, J = 13.2; 9.3 Hz, CH=CH$_2$), 3.98 (1H, d, J = 13.2 Hz, *trans* vinyl H_2C=), 4.21 (1H, m, (CH$_3$)HC=). ^{13}C NMR (67.8 MHz in $CDCl_3$): 9.83 (q, J(C–H) = 129 Hz, Cp* CH_3), 19.3 (q, 126 Hz) and 20.5 (q, 128 Hz) due to two methyl groups on the ligand, 24.5 (t, 128 Hz), 29.6 (t, 131 Hz), 38.2 (t, 125 Hz), due to methylene carbons, 34.4 (d, 123 Hz, –CH(CH$_3$)–), 52.1 (t, 160 Hz) and 57.0 (t, 160 Hz) due to terminal vinyl, 72.7 (d, 155 Hz), 81.2 (d, 153 Hz), and 84.2 (d, 147 Hz) due to vinyl methines, 99.1 (s, quarternary vinyl), 133.3 (s, Cp* ring).

7 [Cp*Ru(η^6-C_6H_6)]OTf: Anal. Calcd. for $C_{17}H_{21}F_3O_3RuS$: C, 44.05; H, 4.57. Found: C, 44.12; H, 4.57%. ^1H NMR (270 MHz in $CDCl_3$): δ 2.04 (15H, s, Cp* CH_3), 5.86 (6H, s, C_6H_6). ^{13}C NMR (67.8 MHz in $CDCl_3$): 10.8 (q, J(C–H) = 129 Hz, Cp* CH_3), 87.2 (d, 176 Hz, C_6H_6), 97.0 (s, Cp* ring).
The Cp* benzene complex has been reported: H. Suzuki, H. Omori, D.H. Lee, Y. Yoshida, Y. Moro-oka, *Organometallics*, *7*

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8 GC-MS measurements of a higher oligomer mixture indicated multiple insertion of butadiene molecules to take place ($m/e = [C_6H_{10}] + n[C_4H_6]$, as well as their fragment ions due to $M-CH_3$, $M-CH=CH_2$, and $M-CH_2CH=CH_2$). Sets of above four signals up to $n = 10$ were definitely detected. The formation of the higher oligomers revealed that further molecules of butadiene were inserted into either terminal vinyl groups of the codimers, 2-(3-buten-1-yl)-1,5-hexadiene, 5-methyl-1,4,8- nonatriene, or *trans*-1,5,9-decatriene. However, no oligomerization of 1,5-hexadiene itself took place under the same conditions.