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Preliminary communication

Oligomerization of butadiene with (η-C_5R_5)Ru^{II} complexes; stoichiometric and catalytic chemistry *

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Abstract

Treatment of (η-C_5R_5)Ru(η-butadiene)X; (R = H, Me; X = Br, Cl) with butadiene, in the presence of silver triflate, yielded cationic complexes with 1,3,7-octatriene ligands, produced from the C–C bond formation at both the terminal carbon atoms of two molecules of butadiene. In the pentamethylcyclopentadienyl system the octatriene ligand was cyclodimerized to 1,5-cyclooctadiene when treated with carbon monoxide. The ligand structure was elucidated by NMR spectroscopy. Catalytic reactions on these systems have also been studied.

There have been a number of studies on catalytic oligomerization of conjugated dienes by use of a wide range of transition-metal complexes [1]. In these reactions, regio- and stereo-selective formation of the desired products was crucially important. We report here stoichiometric and catalytic oligomerization of butadiene with high selectivity by use of "(η-C_5R_5)Ru^+" species.

The complex (η-C_5R_5)Ru(η-butadiene)Br (**1**, **2a**) was easily prepared by reducing (η-C_5R_5)$RuBr_2$(η-C_3H_5) [2], with a 4–6 fold excess of triethylaluminium, in the presence of butadiene under mild conditions (eq. 1, Yield: Cp, R = H, 83%; Cp*, R = Me, 97.8%). Alternatively Cp*Ru(η-butadiene)Cl (**2b**) was also prepared directly from the treatment of $[Cp^*RuCl_2]_n$ [3] with butadiene in the presence of zinc powder in methanol at 0°C (71% yield, eq. 2). These Cp*Ru(η-butadiene)X complexes **2** showed similar *exo*-conformations to those reported by Fagan *et al.* [4], as evidenced by their ^1H and ^{13}C NMR spectra.

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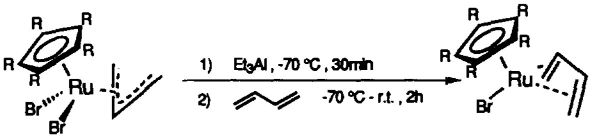
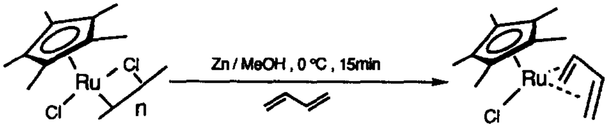
* Dedicated to Professor Akio Yamamoto upon his retirement from Tokyo Institute of Technology and in honour of his contributions to organometallic chemistry.



(1)

1 R = H 83%
2a R = Me 98%



(2)

2b 72 %

When CpRu(η-butadiene)Br (**1**, 30 mg, 0.1 mmol) was treated with an excess of butadiene (0.5 mmol) and silver triflate (0.12 mmol) in dichloromethane (8 mL) at -30°C for 1 h, pale yellow [CpRu(C_4H_6)$_2$]OTf (**3**, OTf = trifluoromethanesulfonate) was obtained in 78% yield. Similarly, the treatment of Cp*Ru(η-butadiene)Br (**2a**) with butadiene and silver triflate gave the 1,3,7-octatriene complex **4** (95% yield) that was thermally more labile around room temperature than its cyclopentadienyl analogue **3**.

The structure of the octatriene ligands in these complexes was carefully examined by ^{1}H and ^{13}C NMR spectroscopy [5*]. On the bases of the relative intensities of signals to the Cp or Cp* ligands, and supported by ^{13}C NMR spectra, it could be concluded that the coordinated ligands in both complexes have the C_8H_{12} composition. Existence of eight olefinic and four methylenic proton signals strongly indicated the ligand to be 1,3,7-octatriene, formed by C–C bond formation at both the terminal carbon atoms of two butadiene molecules, followed by regioselective hydrogen atom migration.

This Cp* octatriene complex (**4**) converted into the 1,5-cyclooctadiene complex (**5**) upon exposure to carbon monoxide (1 atm). [Cp*Ru$^+$(η-COD)CO]OTf (**5**) (COD = 1,5-cyclooctadiene) was identified by comparing spectral data with those of the authentic product independently prepared by the reaction of Cp*Ru(η-COD)Cl and CO in the presence of AgOTf [6*]. Thus, 1,5-cyclooctadiene, coordinated to ruthenium was formally generated by [π4 + π4] cycloaddition between two butadiene molecules (Scheme 1).

However, the octatriene ligand of the Cp complex **3** could not be cyclized in the presence of carbon monoxide (1 atm) into the 1,5-COD ligand. This indicates that the octatriene ligand in **4** has a different configuration from that in **3**.

In fact, the ^{1}H NMR of **4** appeared as a triplet signal at δ 3.30 ($J = 8.3$), assignable to the proton at C_3. Identical proton coupling constants of J_{2-3} and J_{3-4} strongly suggest that the olefinic geometry at the C_3–C_4 bond has (Z) configuration.

In contrast, the ^{1}H NMR spectra of **3** showed a double doublet signal of proton attached to the C_3 carbon at δ 2.95 ($J_{2-3} = 7.9$; $J_{3-4} = 11.6$ Hz). This suggests the 1,3,7-octatriene ligand in **3** being the more thermodynamically stable (E) isomer around the C_3–C_4 bond. In the case of **3**, the configuration puts the terminal

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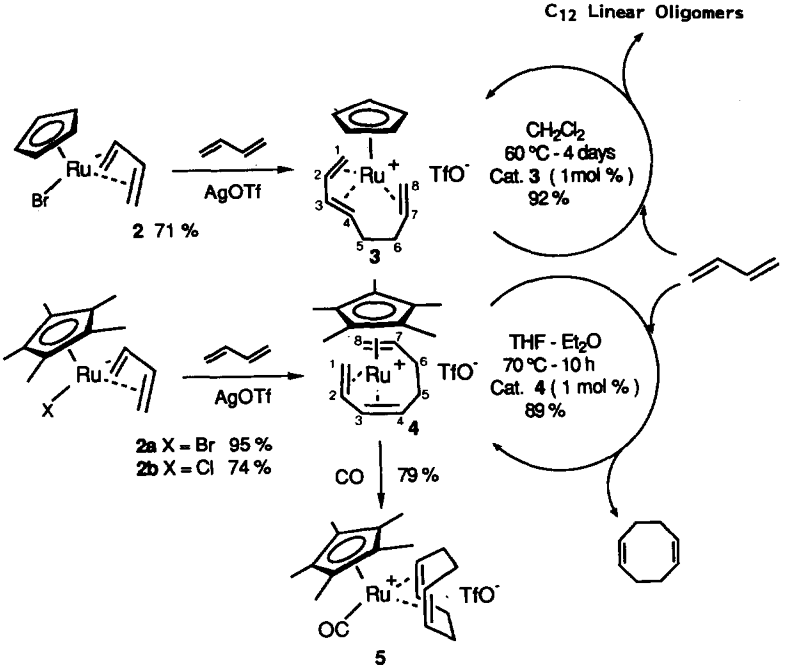
* Reference number with asterisk indicates a note in the list of references.



Scheme 1

carbon atoms (C_1 and C_8) too far from each other to induce the second step C–C bond formation to the 1,5-COD ligand.

Catalytic oligomerization of butadiene was studied by using these cationic complexes as catalyst. Results are included in Scheme 1. In the Cp* system, the best result was obtained when 1 mol% of $[Cp^*Ru(\eta\text{-}C_4H_6)]OTf$ and butadiene in THF were used at 70°C for 10 h; 1,5-cyclooctadiene was selectively obtained (89%; Ru based yield was 4440%).

On the other hand, the catalytic reaction with 1 mol% of $[CpRu(1\text{-}4;\ 7\text{-}8\text{-}\eta\text{-}C_8H_{12})]TfO$ (**3**), at 60°C for 4 days in dichloromethane, resulted in the formation of linear trimer products (C12 over 92% selectivity), contaminated with a little C8 and C16 linear oligomers. The linear trimers were a 55:45 mixture of 1,5,7,11-dodecatetraene and its 1,3,7,11-isomer.

The first step involved was the treatment of butadiene complexes **3** and **4** with silver triflate, generating a cationic coordinatively unsaturated intermediate, at which the coordination of the second butadiene took place. Two coordinated butadiene molecules induced the C–C bond formation between the terminal carbon atoms to give bis(allyl)Ru^{IV} intermediates. Rapid hydride migration in the bis(allyl) complex gave 1,3,7-octatriene Ru^{II} complexes. In the case of the Cp system, further insertion of butadiene between the diene part of the (*E*)-1,3,7-octatriene ligand in **3** and the third molecule of butadiene took place.

Alternatively, as the distance between C1 and C8 in the (*Z*)-1,3,7-octatriene ligand in the Cp* system (**4**) is extremely close, the coordination of further butadiene induced spontaneous cyclization of the (*Z*)-octatriene ligand, and the 1,5-COD is freed to regenerate the active $[Cp^*Ru(\eta\text{-}C_4H_6)]^+$ species.

References and notes

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5 Spectral data. [CpRu(η-C_8H_{12})]TfO: ^{1}H-NMR (270 MHz, acetone-d_6): 1.39 (1H, m), 2.04 (1H, m), 2.53 (1H, d), 2.64–2.78 (1H, m), 2.86–2.99 (1H, m), 2.95 (1H, dd), 3.92 (1H, d), 4.01 (1H, d), 4.05 (1H, d), 4.71 (1H, m), 5.70 (5H, s). ^{13}C-NMR (67.8 MHz, acetone-d_6): 29.7, 40.8, 50.3, 56.6, 81.6, 83.6, 85.5, 91.5 (ring), 98.1. Elemental analysis. Found: C, 38.96; H, 3.91. $C_{14}H_{17}F_3SO_3Ru$ calcd.: C, 39.71; H, 4.05%. Melting point 152–153°C (dec.).

[Cp*Ru(η-C_8H_{12})]TfO: ^{1}H-NMR (270 MHz, $CDCl_3$): 1.77 (15H, s), 2.01 (2H, d), 2.52 (1H, d), 2.71 (1H, m), 3.01 (2H, m), 3.30 (1H, t), 3.33 (1H, m), 3.85 (1H, m), 4.26 (1H, m), 4.27 (1H, d), 5.01 (1H, m). ^{13}C-NMR (67.8 MHz, $CDCl_3$, -10°C): 9.65, 37.2, 38.7, 62.5, 67.7, 90.2, 90.3, 98.1, 102.1, 105.0.

6 Pale yellow crystals in 62% yield. Spectral data: [Cp*Ru(η-1,5-COD)CO]TfO: ^{1}H-NMR (270 MHz, acetone-d_6): 1.94 (15H, s), 2.29 (4H, m), 2.58 (4H, m), 4.25 (2H, m), 4.47 (2H, m). ^{13}C-NMR (67.8 MHz, acetone-d_6): 10.3, 29.6, 30.5, 89.0, 93.4, 100.9, 206.8.