

Alkane activation on a multimetallic site*

Hiroharu Suzuki[†], Akiko Inagaki, Kouki Matsubara, and
Toshifumi Takemori

Department of Applied Chemistry, Graduate School of Science and Engineering,
Tokyo Institute of Technology and CREST, Japan Science and Technology
Corporation (JST), O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Abstract: Trinuclear polyhydrido complex of ruthenium effectively activates alkanes to cleave C–H bonds in a selective manner due to cooperative action of the metal centers. The reaction of $(\text{Cp}'\text{Ru})_3(\mu\text{-H})_3(\mu_3\text{-H})_2$ (**1**) ($\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$) with *n*-alkane at 170 °C leads to the formation of a trinuclear *closo*-ruthenacyclopentadiene complex as a result of a successive cleavage of six C–H bonds. Introduction of a μ_3 -sulfido ligand into the Ru_3 core of the trirutheniumpolyhydrido cluster significantly modifies the regioselectivity of the alkane C–H activation. Heating of a solution of $(\text{Cp}'\text{Ru})_3(\mu_3\text{-S})(\mu\text{-H})_3$ (**4**) in alkane exclusively gives a trinuclear μ_3 -alkylidyne complex via a selective C–H bond cleavage at the less-hindered terminus of alkane molecule.

INTRODUCTION

Activation of the carbon–hydrogen bonds of alkanes is of special importance because of its potential applicability to the functionalization of alkanes. The selective activation of alkane C–H bonds under mild conditions has, therefore, been one of the most challenging targets in recent organometallic chemistry and has been intensively studied using mononuclear hydride and carbonyl complexes as precursors to the active species [1]. Over the past ten years we have tackled the activation of organic substrates on multimetallic sites and demonstrated that a metal–polyhydride cluster effectively activates an organic substrate in a unique manner as a result of the cooperative action of the metal centers [2]. Here we report an unprecedented successive and regioselective cleavage of alkane C–H bonds mediated by a trirutheniumpentahydrido complex **1** and a trirutheniumtrihydrido complex **4**, which has a μ_3 -S ligand.

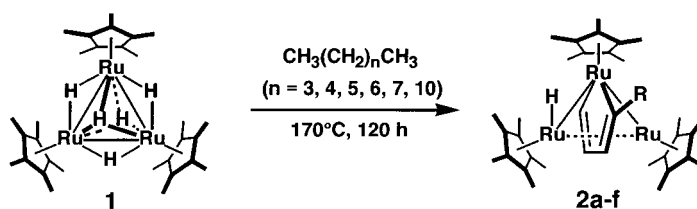
CARBON–HYDROGEN BOND ACTIVATION OF *N*-ALKANES BY A TRINUCLEAR RUTHENIUM PENTAHYDRIDE COMPLEX [3]

Heating a solution of **1** in hexane at 170 °C for 120 h resulted in the formation of a novel trinuclear *closo*-ruthenacyclopentadiene complex **2b** ($\text{R} = \text{C}_2\text{H}_5$) in a reasonable yield.

Complex **1** reacts with *n*-alkanes such as pentane, heptane, octane, nonane, and dodecane in a similar manner and leads to the formation of **2a** ($\text{R} = \text{CH}_3$), **2c** ($\text{R} = \text{CH}_2\text{CH}_2\text{CH}_3$), **2d** ($\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), **2e** ($\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), and **2f** ($\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), respectively, in good yields (Scheme 1). The structure of these compounds was inferred from spectroscopic data. Definitive proof for the structure was provided by an X-ray study on the single crystal of **2b**, and the result clearly establishes the structural identity of **2b**, as a trinuclear *closo*-ruthenacyclopentadiene in which the ruthenacycle bisects one of the Ru–Ru vectors.

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[†]Corresponding author



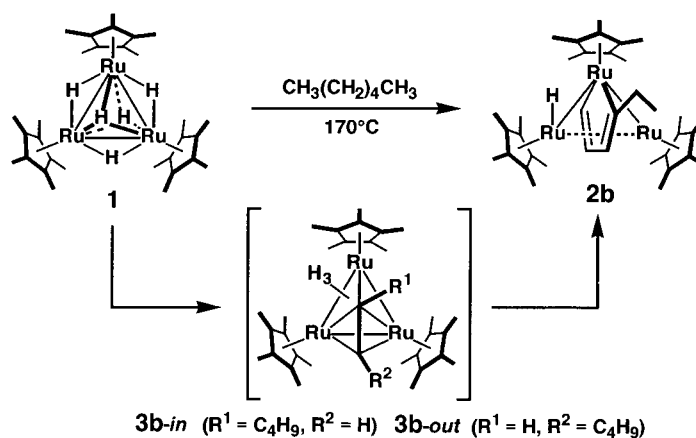
Scheme 1

It is clear that the carbon framework of 2-alkylruthenacyclopentadiene in **2** originates from the *n*-alkane used as the solvent. In this reaction, six C–H bonds of the alkanes are successively cleaved on the trimetallic site, and these results strongly suggest the applicability of transition-metal cluster complexes, especially polyhydridometal clusters, to the functionalization of alkanes.

The *n*-alkane molecule is most likely incorporated into the triangular reaction site from one of the methyl termini at the initial stage of the reaction. This was confirmed through the H/D exchange between the hydride ligands in **1** and the deuterated methyl group in octane-*d*₁₈ observed in the temperature range of 140–160 °C.

By monitoring the reaction by means of ¹H NMR spectroscopy, signals for several intermediates were observed and the intermediates finally converged into thermodynamically stable products **2**. When the reaction of **1** with hexane was monitored at 170 °C by ¹H NMR spectroscopy, formation of an equilibrated mixture of μ_3 -(Δ)-hexyne complexes, (Cp^{*}Ru)₃(μ -H)₃{ μ_3 -(Δ)-HCCC₄H₉} (**3-in**) and (Cp^{*}Ru)₃(μ -H)₃{ μ_3 -(Δ)-C₄H₉CCH} (**3-out**), was detected in a complex mixture of intermediates. Intermediacy of the alkyne complex **3** was confirmed by use of an authentic complex independently prepared by treatment of **1** with 1-hexyne (Scheme 2).

Pyrolysis of **3** in 1,3,5-trimethylcyclohexane at 170 °C gave **2b** in 65% yield. Pyrolysis of the authentic μ_3 -(Δ)-pentyne, μ_3 -(Δ)-heptyne, and μ_3 -(Δ)-octyne complexes also led to the formation of the corresponding *closo*-ruthenacyclopentadiene complexes, **2a**, **2c**, and **2d**, respectively.



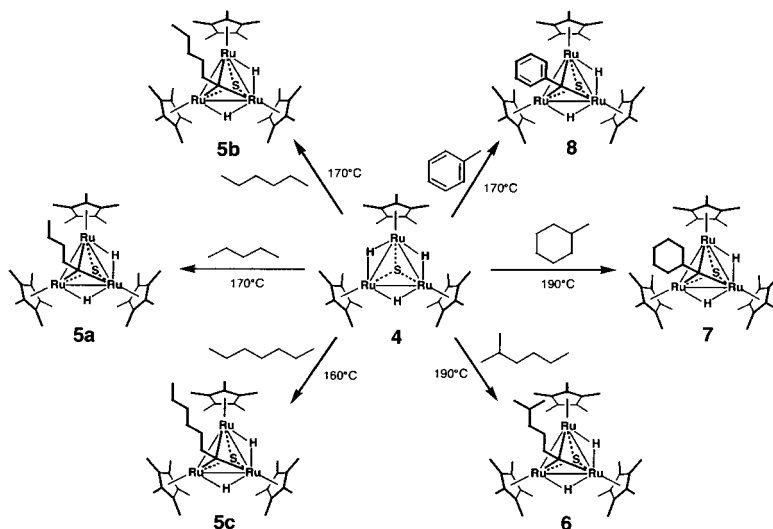
Scheme 2

REGIOSELECTIVE C–H BOND ACTIVATION OF ALKANES BY A TRINUCLEAR RUTHENIUM TRIHYDRIDE COMPLEX HAVING A μ_3 -SULFIDO LIGAND [4]

To modify the regioselectivity of the triruthenium cluster-mediated alkane C–H bond activation, we introduced a triply bridging sulfido ligand into the Ru₃ core by the reaction of **1** with thiophenol. The

μ_3 -sulfido group introduced from the backside of the trimetallic reaction site is expected to reinforce the Ru_3 framework and to prevent Ru–Ru bond cleavage in the course of the reaction.

Heating a solution of **4** in hexane at 170 °C for 107 h led to the quantitative formation of a μ_3 -hexylidyne complex $(\text{Cp}^*\text{Ru})_3(\mu_3\text{-S})(\mu\text{-H})_2\{\mu_3\text{-C}(\text{CH}_2)_4\text{CH}_3\}$ (**5b**) as a result of C–H bond cleavage at the terminal carbon, while the reaction of **1** with hexane afforded a *closo*-ruthenacyclopentadiene complex. The results of the reactions of **4** with a series of alkanes are summarized in Scheme 3.

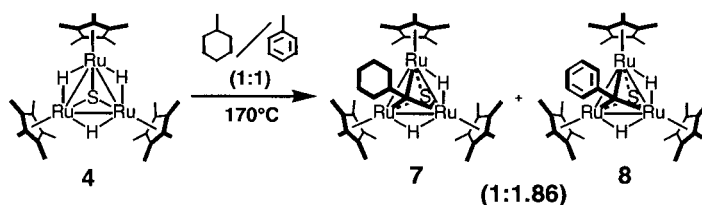


Scheme 3

A notable feature of the reaction is its regioselectivity that no insertion products into the secondary C–H bonds are detected in spite of the clear advantage over that of the primary C–H bonds judging from the bond dissociation energy, ca. 95 kcal/mol vs. ca. 98 kcal/mol. The steric repulsion between the substrates and the C_5Me_5 fence surrounding the reaction site would be responsible for highly primary-selective C–H bond activation because it impedes the access of the secondary C–H bonds to the metal center. In the reaction of **4** with 2-methylhexane, the C–H insertion reaction at the less-hindered methyl group exclusively took place to yield 4-methylhexylidyne complex **6** despite the statistical disadvantage.

Complex **4** is active toward cleavage of both aromatic and benzylic C–H bonds of toluene. When complex **4** was heated in toluene- d_8 at 130 °C, H/D exchange took place among the hydride ligands and aromatic C–D bonds of toluene- d_8 . However, a tolyl intermediate resulting from the aromatic C–D bond cleavage could not be detected, presumably because it is unstable due to the steric repulsion with the C_5Me_5 group. Heating a toluene solution of **4** at 170 °C, however, led to the exclusive formation of a thermally stable μ_3 -benzylidyne complex $(\text{Cp}^*\text{Ru})_3(\mu_3\text{-S})(\mu\text{-H})_2(\mu_3\text{-CC}_6\text{H}_5)$ (**8**) as a result of C–H bond cleavage at the benzylic carbon.

A competition experiment using a 1/1 mixture of toluene and methylcyclohexane was carried out to elucidate the mechanism. While the steric accessibility of the methyl group of these two substrates to the reaction site seems to be of similar extent, the C(methyl)–H bond dissociation energy of toluene (ca. 88 kcal/mol) is much smaller than that of methylcyclohexane (ca. 98 kcal/mol). From a thermodynamic point of view, the μ_3 -benzylidyne complex should be exclusively formed if the reaction proceeded via homolysis of the C–H bond. In spite of this, heating the solution of **4** in the mixed solvent at 170 °C for 142 h resulted in the formation of **7** and **8** in the ratio of 1:1.86. This result implies that a radical mechanism seems unlikely for these reactions.



Scheme 4

As mentioned above, we have realized selective activation of alkanes by using transition-metal polyhydrido cluster. We believe that alkane C–H bond activation on multimetallic sites is one of the promising approaches to the functionalization of alkanes.

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