Regioselective C−H Bond Activation of Alkanes by a Trinuclear Ruthenium Trihydride Complex Having a μ_3-Sulfido Ligand

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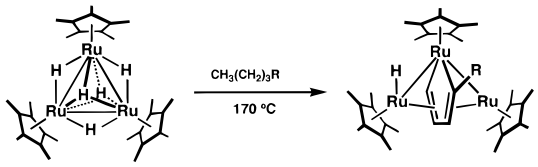
Activation of an alkane C−H bond mediated by late transition metal complexes has been the focus of recent studies in organometallic chemistry,[1] and Bergman and co-workers have recently obtained an outstanding result that alkane C−H bond is activated without prior photochemical excitation by use of a highly electron-deficient Ir(III) complex.[2] We have adopted a different approach using a transition metal polyhydride cluster in the alkane activation. We have recently discovered that trinuclear ruthenium pentahydride $\{(C_5Me_5)Ru\}_3(\mu\text{-H})_3(\mu_3\text{-H})_2$ effectively activates C−H bonds of *n*-alkanes in a thermal reaction to form *closo*-ruthenacyclopentadiene complexes.[3] In this reaction, there was concomitant cleavage of one of the Ru−Ru bonds with the successive cleavage of six C−H bonds of the alkane. As the next



stage in our study of the alkane activation, we aimed to activate alkane C−H bonds regioselectively at a primary carbon atom. To modify the regioselectivity of the triruthenium cluster-mediated alkane C−H bond activation, we introduced a triply bridging sulfido ligand into the Ru_3 core by the reaction of $\{(C_5Me_5)Ru\}_3(\mu\text{-H})_3(\mu_3\text{-H})_2$ with 1 equiv of thiophenol.[4] The μ_3-S 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. As a result, we found that a triruthenium hydride cluster having a μ_3-sulfido ligand, $\{(C_5Me_5)Ru\}_3(\mu_3\text{-S})(\mu\text{-H})_3$ (**1**), effectively activated alkanes in a thermal reaction. Here we describe the regioselective intermolecular C−H bond activation of alkanes at the terminal carbon leading to the exclusive formation of μ_3-alkylidyne complexes.

Heating a solution of **1** in hexane at 170 °C for 107 h led to the quantitative formation of a μ_3-hexylidyne complex $\{(C_5Me_5)Ru\}_3(\mu_3\text{-S})(\mu\text{-H})_2\{\mu_3\text{-C}(CH_2)_4CH_3\}$ (**2**) as a result of C−H bond cleavage at the terminal carbon (Scheme 1). Removal of the solvent under reduced pressure followed by purification by means of column chromatography on alumina gave **2** in 66% yield as a dark brown crystalline solid. Complex **2** was assigned as a μ_3-hexylidyne complex on the basis of the resonances for the alkylidyne carbon observed in the remarkably low field (δ 315.6) and those for four methylenes and a methyl carbon of the C_5 chain bound to the alkylidyne carbon in the range of δ 57.1−14.9 in the ^{13}C NMR spectrum. Despite the lack of a 3-fold symmetry axis in **2**, the resonance signals for three C_5Me_5 groups were observed to be equivalent both in the ^1H (δ 1.93) and ^{13}C NMR (δ 12.3) spectra measured at room temperature. This indicated that the three C_5Me_5 groups were in a time-averaged environment due to rapid exchange of two hydride ligands among three bridging coordination sites. The structure of **2** determined by X-ray crystallography is fully consistent with the NMR data.

The results of the reactions of **1** with a series of alkanes are summarized in Scheme 1. Reactions of **1** with pentane and heptane similarly proceeded to produce the corresponding μ_3-alkylidyne complex $\{(C_5Me_5)Ru\}_3(\mu_3\text{-S})(\mu\text{-H})_2\{\mu_3\text{-C}(CH_2)_3CH_3\}$ (**3**) and $\{(C_5Me_5)Ru\}_3(\mu_3\text{-S})(\mu\text{-H})_2\{\mu_3\text{-C}(CH_2)_5CH_3\}$ (**4**), respectively. In both reactions, no insertion products into the secondary C−H bonds were detected although cleavage of the secondary C−H bonds has a 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.[5] 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.

Steric repulsion-originated selectivity was also examined through the reaction of **1** with 2-methylhexane. When a solution of **1** in 2-methylhexane was heated at 190 °C for 4 days, μ_3-5-methylhexylidyne complex **5** was exclusively formed as a result of C−H activation at the less hindered terminus. The C−H insertion product at the hindered methyl groups, the μ_3-2-methylhexylidyne complex, was not detected despite the statistical advantage of C−H bond cleavage at the hindered methyl groups over the less hindered one.

Whereas the reaction of **1** with cyclohexane at 190 °C for 2 weeks resulted in the recovery of the starting materials, cleavage of the primary C−H bonds took place in the reaction with methylcyclohexane under milder conditions (190 °C, 5 days) to form the corresponding μ_3-cyclohexylmethylidyne complex $\{(C_5Me_5)Ru\}_3(\mu_3\text{-S})(\mu\text{-H})_2(\mu_3\text{-CC}_6H_{11})$ (**6**) selectively. An X-ray analysis of **6** clearly establishes the μ_3-cyclohexylmethylidyne structure. An ORTEP drawing of **6** is shown in Figure 1, along with a list of selected bond lengths and angles.

Complex **1** is active toward cleavage of both aromatic and benzylic C−H bonds of toluene. When complex **1** was heated in

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(4) Treatment of $\{(C_5Me_5)Ru\}_3(\mu\text{-H})_3(\mu_3\text{-H})_2$ (**1**) with 1 equiv of thiophenol in tetrahydrofuran at −78 °C yielded μ_3-sulfido cluster $\{(C_5Me_5)Ru\}_3(\mu\text{-H})_3(\mu_3\text{-S})$ quantitatively via oxidative addition of C−S bond followed by elimination of benzene. Matsubara, K.; Tanaka, M.; Suzuki, H., to be published.

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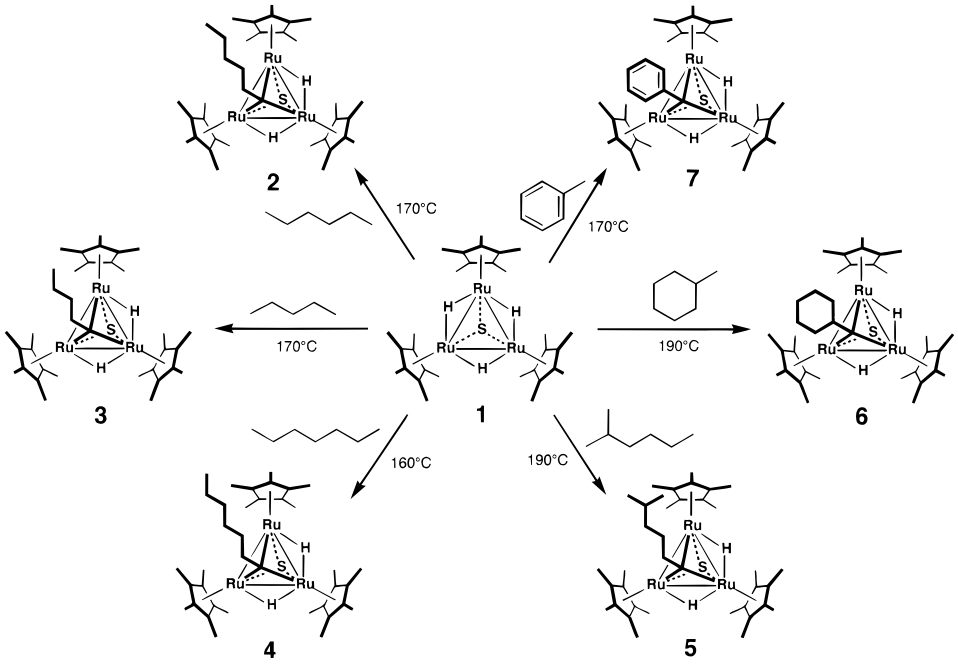
Scheme 1



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. Monitoring of the reaction by means of ^{1}H NMR spectroscopy showed that cleavage of the benzylic C−H bonds of toluene did not occur at 130 °C. Heating a toluene solution of **1** at 170 °C, however, led to the exclusive formation of a thermally stable μ_3-benzylidyne complex $\{(C_5Me_5)Ru\}_3(\mu_3\text{-}S)(\mu\text{-}H)_2(\mu_3\text{-}CC_6H_5)$ (**7**) as a result of C−H bond cleavage at the benzylic carbon. Complex **6** and **7** are characterized by means of ^{1}H and ^{13}C spectroscopy and their structures were definitely determined by X-ray crystallography.

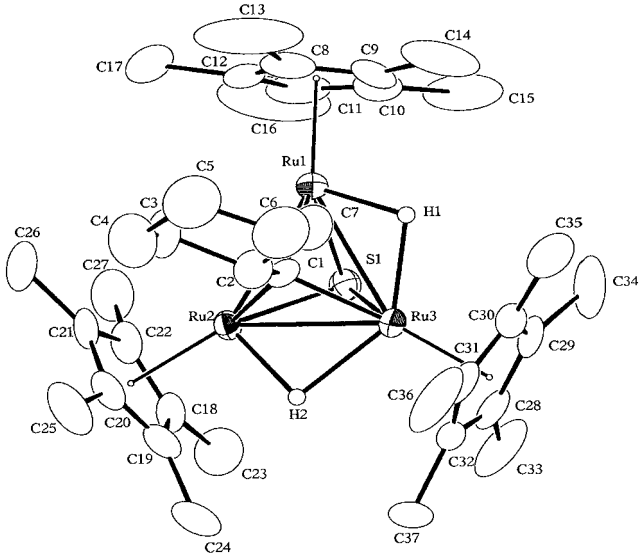
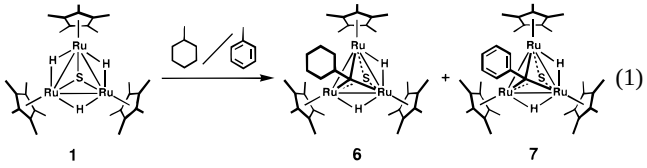


Figure 1. Molecular structure of $\{(C_5Me_5)Ru\}_3(\mu_3\text{-}S)(\mu\text{-}H)_2(\mu_3\text{-}CC_6H_{11})$ (**6**), with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg) are as follows: Ru(1)−Ru(2) 2.758(1), Ru(1)−Ru(3) 2.757(1), Ru(2)−Ru(3) 2.764(1), Ru(1)−S(1) 2.273(3), Ru(2)−S(1) 2.267(3), Ru(3)−S(1) 2.269(3), Ru(1)−C(1) 2.057(9), Ru(2)−C(1) 2.065(9), Ru(3)−C(1) 2.062(9), C(1)−C(2) 1.46(1), C(2)−C(3) 1.54(1), C(3)−C(4) 1.53(2), C(4)−C(5) 1.48(2), C(5)−C(6) 1.50(2), C(6)−C(7) 1.52(2), C(7)−C(2) 1.50(1); Ru(2)−Ru(1)−Ru(3) 60.15(3), Ru(1)−Ru(2)−Ru(3) 59.92(4), Ru(1)−Ru(3)−Ru(2), 59.93(3), Ru(1)−S(1)−Ru(2) 74.80(8), Ru(1)−S(1)−Ru(3) 74.75(9), Ru(2)−S(1)−Ru(3) 75.08(9), Ru(1)−C(1)−Ru(2) 84.0(3), Ru(1)−C(1)−Ru(3) 84.0(3), Ru(2)−C(1)−Ru(3) 84.1(3), Ru(1)−C(1)−C(2) 130.7(7), Ru(2)−C(1)−C(2) 129.5(7), Ru(3)−C(1)−C(2) 128.0(7).

The results summarized in Scheme 1 are in sharp contrast to those attained by using $\{(C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$, where cleavage of six alkane C−H bonds takes place to give trinuclear *closo*-ruthenacyclopentadiene complexes.[3]

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 energy of toluene (ca. 88 kcal/mol) is much smaller than that of methylcyclohexane (ca. 98 kcal/mol).[5] From the viewpoint of thermodynamics, the μ_3-benzylidyne complex should be exclusively formed if the reaction proceeded via homolysis of the C−H bond. Despite this, as shown in eq 1, heating the solution of **1** in the mixed solvent at 170 °C for 142 h resulted in the formation of **6** and **7** in the ratio of 1:1.86. This result strongly indicates that a radical mechanism seems unlikely for these reactions.



Experiments designed to elucidate the mechanism of alkane C−H activation mediated by μ_3-sulfido complex **1** are under way and the results will be reported in due course.

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Supporting Information Available: Table of ^{1}H and ^{13}C NMR spectral assignments of **2**−**7** and ORTEP diagram, text describing X-ray procedures, tables of X-ray data, positional and thermal parameters, and distances and angles for **6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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