18 *Organometallics* **2008,** *27,* 18–20

Introduction of a Methoxy Group into a Hydrocarbyl Ligand Derived from a Linear Alkane on a Triruthenium Cluster via Chemical Oxidation

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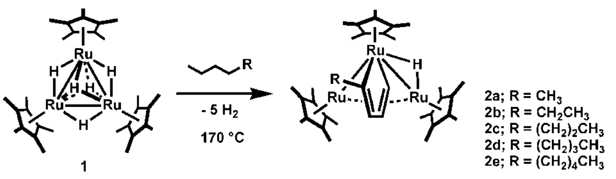
Received October 3, 2007

Summary: The two-electron oxidation of a closo-ruthenacyclopentadiene complex, $[(Cp^*Ru)_2\{Cp^*Ru(\mu_3\text{-}CMe{=}CHCH{=}CH-)\}(\mu\text{-}H)]$ (**2a**)*, derived from the reaction of a triruthenium complex,* $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (**1**)*, with n-pentane, resulted in the formation of a dicationic complex,* $[\{Cp^*Ru(\mu\text{-}H)\}_2\{Cp^*Ru(\mu_3\text{-}C(CH_2)CHCHCH-)\}]^{2+}$ (**7**)*, having an exo methylene group on the metallacycle moiety. The treatment of* **7** *with methanol resulted in the nucleophilic addition of a methoxy group to form a cationic closo-ruthenacyclopentadiene complex,* $[\{Cp^*Ru(\mu\text{-}H)\}_2\{Cp^*Ru(\mu_3\text{-}C(CH_2OMe){=}CHCH{=}CH-)\}]^+$ (**9a**)*, demonstrating the functionalization of a hydrocarbyl ligand originating from n-pentane.*

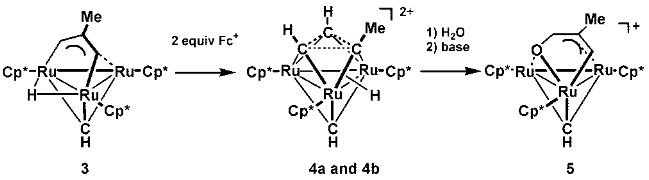
The regioselective activation of alkanes has been one of the most challenging objectives of organometallic chemistry in recent times, and it has been extensively studied.[1] One successful example of alkane activation is the catalytic borylation of alkanes performed by Hartwig and co-workers.[2] They showed that the borylation proceeds selectively at the terminal position of an alkane. Since the oxidative addition of a C−H bond occurs at the less crowded terminal position of the alkane, activation by the use of transition-metal complexes is of importance for the regioselective functionalization of alkanes at the terminal position. This is in strong contrast with the addition performed by heterogeneous catalysts and superacids, in which C−H bond activation occurs at internal positions.



(1)

We have reported the formation of the *closo*-ruthenacyclopentadiene complex **2** by the reaction of a triruthenium pentahydrido complex, $\{Cp^*Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (**1**; $Cp^* = \mu^5\text{-}C_5Me_5$), with linear alkanes (eq 1).[3] The most arresting feature of this reaction is that the C−H bond cleavage was achieved by a synergism inherent to the adjacent metal centers, and this induces the scission of a total of six C−H bonds of the linear alkane. This reaction clearly represents the high ability of a polyhydrido cluster toward C−H bond cleavage. Recently, we demonstrated the dehydrogenative coupling of pyridines catalyzed by bimetallic hydrido complexes as an example of such multimetallic activation.[4]

Scheme 1



It is important to investigate the reactivity of **2** in relation to the functionalization of an alkane. However, attempts to introduce a functional group on the metallacycle moiety of **2** by the reaction of nucleophiles were unsuccessful, due to its thermal stability and robustness toward air and moisture. We have shown that oxidation is a suitable method for the functionalization of a hydrocarbyl ligand on a multimetallic center: the μ_3-oxaruthenacyclopentadienyl complex **5** was obtained by the two-electron oxidation of the thermally stable μ_3-methylidyne μ_3-diruthenaallyl complex **3** (Scheme 1).[5] The nucleophilic attack of water at the μ_3-C_3 ring is facilitated by the electron deficiency arising from the dicationic nature of **4a**,**b**. Therefore, we applied this method to the *closo*-ruthenacyclo-

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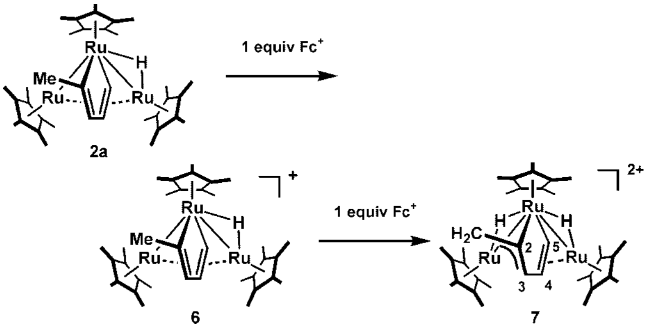
(6) THF (5 mL) and **2a** (51.3 mg, 0.0661 mmol) were charged in a reaction flask. After $[Cp_2Fe](PF_6)$ (43.0 mg, 0.130 mmol) was added to the solution at room temperature, the solution was stirred for 2 h. The color of the solution changed from red to purple, and a purple precipitate was formed. After the supernatant was removed, the residual solid was washed with 5 mL of pentane three times. The residual solid was then dried under reduced pressure, and 70.2 mg of a hexafluorophosphate salt of **7** was obtained as a purple solid (0.0659 mmol, 99%). ^{1}H NMR (400 MHz, 23 °C, acetone-d_6): δ −8.90 (br m, 2H, Ru *H*), 2.00 (s, 30H, C_5Me_5), 2.39 (s, 15H, C_5Me_5), 2.87 (br m, 2H, μ_3-C(C*H*$_2$)CHCHCH−), 5.09 (ddd, J_{H-H} = 4.0, 2.4, 1.0 Hz, 1H, μ_3-C(CH$_2$)CHCHC*H*−), 6.30 (dd, J_{H-H} = 4.0, 1.6 Hz, 1H, μ_3-C(CH$_2$)CHC*H*CH−), 6.80 (m, 1H, μ_3-C(CH$_2$)C*H*CHCH−). ^{13}C NMR (100 MHz, 23 °C, acetone-d_6): δ 10.9 (C_5Me_5), 11.5 (C_5Me_5), 40.9 (dd, J_{C-H} = 172.3, 171.6 Hz, μ_3-C(*C*H$_2$)CHCHCH−), 57.1 (dt, J_{C-H} = 199, 10 Hz, μ_3-C(CH$_2$)*C*HCHCH−), 70.3 (dt, J_{C-H} = 192, 6 Hz, μ_3-C(CH$_2$)CH*C*HCH−), 96.9 (C_5Me_5), 106.9 (C_5Me_5), 121.8 (d, J_{C-H} = 175 Hz, μ_3-C(CH$_2$)CHCH*C*H−), 147.1 (t, $^3J_{C-H}$ = 9 Hz, μ_3-*C*(CH$_2$)CHCHCH−).

10.1021/om7009914 CCC: $40.75

pentadiene complex **2a**, which is the product of the reaction of **1** with *n*-pentane, for the purpose of alkane functionalization.

The treatment of **2a** with 2 equiv of a hexafluorophosphate salt of the ferrocenium cation, $[Cp_2Fe]^+$ (Fc^+; Cp = μ^5-C_5H_5), in THF resulted in the quantitative formation of the dicationic dihydrido complex **7** (eq 2).[6] When the oxidation of **2a** was performed by using 1 equiv of Fc^+, a paramagnetic intermediate, $[(Cp^*Ru)_2\{Cp^*Ru(\mu_3\text{-CMe=CHCH=CH-})\}(\mu\text{-H})]^+$ (**6**), was obtained as a purple solid.[7] The dicationic complex **7** was also obtained from the one-electron oxidation of **6**.



(2)

The cyclic voltammogram of **2a** exhibited quasi-reversible and irreversible one-electron waves (see the Supporting Information): the quasi-reversible wave at $E_{1/2}$ = –765 mV (referenced to Fc/Fc+) indicates the formation of a chemically stable paramagnetic species, and the second irreversible anodic peak observed at E_{pa} = +175 mV suggests that skeletal rearrangement occurs at the second oxidation step. The reversibility of the first redox wave strongly implies that it involves electron transfer and the structure of **2a** remains unchanged at this step. In the ^{1}H NMR spectrum of **6**, three broad signals possibly assignable to the Cp* groups were observed to be inequivalent at δ 11.2 ($w_{1/2}$ = 108 Hz), 13.9 ($w_{1/2}$ = 98 Hz), and 24.5 ($w_{1/2}$ = 328 Hz).

The second irreversible wave shows that the structural transformation via a C−H bond cleavage of the methyl group of the ruthenacycle moiety occurs during the electron transfer. The resulting dihydrido complex **7** has a pseudo mirror plane containing the metallacycle moiety. Consequently, the ^{1}H signals for the Cp* groups were observed as a set of two peaks with intensity ratios of 2:1 at δ 2.00 and 2.39, respectively.

The ^{1}H signals of the exomethylene group were observed at around δ 2.87 as unresolved multiplets, and the methylene carbon resonated at δ 40.9 as a doublet of doublets (J_{C-H} = 172.3 and 171.6 Hz). The four ^{13}C signals arising from the ruthenacycle moiety were observed at δ 147.1 (t, J_{C-H} = 9 Hz, C^2), 121.8 (d, J_{C-H} = 175 Hz, C^5), 70.3 (dt, J_{C-H} = 192 and 6 Hz, C^4), and 57.1 (dt, J_{C-H} = 199 and 10 Hz, C^3). The long-range coupling observed between the methine carbons (C^3 and C^4) and the methylene protons implies that the conjugation of the π-electrons spreads over the five carbon atoms of the ruthenacycle moiety.

Scheme 2

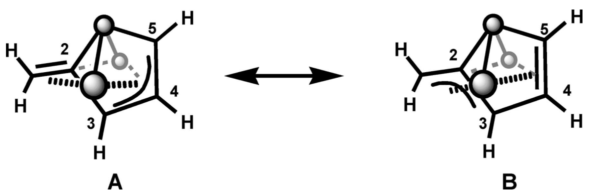
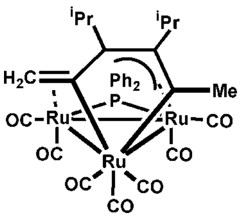
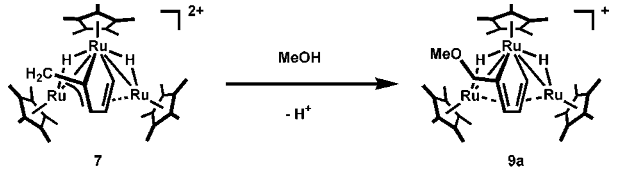


Chart 1



Although the structure of **7** was not corroborated by an X-ray diffraction study, due to the lack of a suitable single crystal, the metallacycle of **7** is depicted as a resonance hybrid between the two extremes **A** and **B** (Scheme 2). The exo methylene group is coordinated to the two peripheral ruthenium atoms as a part of the pentadienyl ligand. The ^{13}C signal of the exo methylene carbon appeared at a relatively higher magnetic field (δ 40.9), which is consistent with the pentadienyl structure. Carty and co-workers have elucidated a μ_3-η^3:η^2 coordination mode of a five-membered metallacycle having an exo methylene group in the triruthenium complex **8** (Chart 1).[8]

Complex **7** underwent nucleophilic addition at the sterically less hindered exo methylene group. The treatment of **7** with methanol at ambient temperature resulted in the formation of the cationic *closo*-ruthenacyclopentadiene complex **9a** in 58% yield (eq 3).[9] During the reaction, the charge reduces from +2 to +1 by the elimination of HPF_6. By the use of sodium methoxide, the yield of **9a** increased up to 84%.



(3)

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(7) THF (5 mL) and **2a** (21.5 mg, 0.0277 mmol) were charged in a reaction flask. After $[Cp_2Fe](PF_6)$ (9.0 mg, 0.0272 mmol) was added to the solution at room temperature, the solution was stirred for 2 h. The color of the solution changed from red to purple, and a purple precipitate was formed. After the supernatant was removed, the residual solid was washed with 5 mL of THF three times. The residual solid was then dried under reduced pressure, and 3.2 mg of a hexafluorophosphate salt of **6** was obtained as a purple solid (3.50 μmol, 13%). ^{1}H NMR (400 MHz, 23 °C, acetone-d_6): δ 11.18 (br s, $w_{1/2}$ = 108 Hz), 13.88 (br s, $w_{1/2}$ = 98 Hz), 24.51 (br s, $w_{1/2}$ = 328 Hz).

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(9) Methanol (5 mL) and a hexafluorophosphate salt of **7** (32.3 mg, 0.0303 mmol) were charged in a reaction flask. The solution was stirred for 2 h at room temperature, and then the solvent was evaporated under reduced pressure. ^{1}H NMR analysis of the residual solid showed exclusive formation of **9a**, and the yield was estimated at 58% by comparing the intensity with that of remaining **7**. ^{1}H NMR (400 MHz, 23 °C, acetone-d_6): δ −7.99 (br, 2H, Ru*H*), 1.90 (s, 30H, C_5Me_5), 2.13 (s, 15H, C_5Me_5), 2.93 (br m, 2H, μ_3-C(CH_2OMe)=CHCH=CH−), 3.01 (s, 3H, μ_3-C(CH$_2$O*Me*)=CHCH=CH−), 3.55 (d, J_{H-H} = 4.8 Hz, 1H, μ_3-C(CH$_2$OMe)=CHCH=C*H*−), 5.15 (dd, J_{H-H} = 4.8, 2.0 Hz, 1H, μ_3-C(CH$_2$OMe)=CHC*H*=CH−), 5.38 (br m, 1H, μ_3-C(CH$_2$OMe)=C*H*CH=CH−). ^{13}C NMR (100 MHz, 23 °C, acetone-d_6): δ 11.0 (C_5Me_5), 11.9 (C_5Me_5), 57.4 (q, J_{C-H} = 139 Hz, μ_3-C(CH$_2$O*Me*)=CHCH=CH−), 66.5 (d, J_{C-H} = 185 Hz, μ_3-C(CH$_2$OMe)=CH*C*H=CH−), 67.2 (d, J_{C-H} = 185 Hz, μ_3-C(CH$_2$OMe)=*C*HCH=CH−), 79.7 (d, J_{C-H} = 143 Hz, μ_3-C(*C*H$_2$OMe)=CHCH=CH−), 91.5 (C_5Me$_5$), 95.9 (C_5Me$_5$), 101.9 (s, μ_3-*C*(CH$_2$OMe)=CHCH=CH−), 109.7 (d, J_{C-H} = 161 Hz, μ_3-C(CH$_2$OMe)=CHCH=*C*H−).

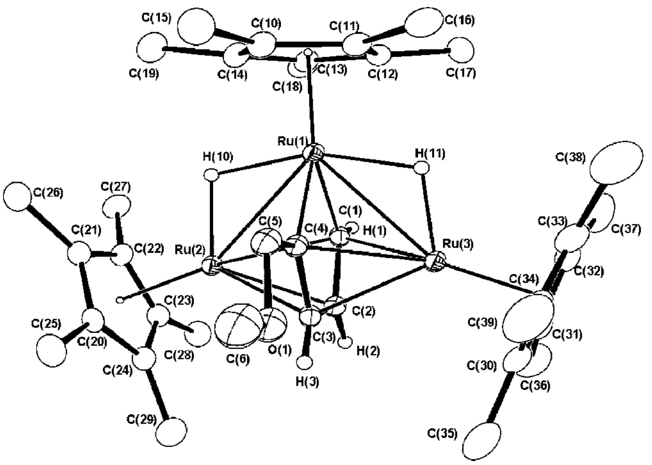

Figure 1. Molecular structure and labeling scheme of a cationic moiety of **9a** with thermal ellipsoids at the 30% probability level. An anionic moiety (PF_6^-) and solvent molecule (benzene) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(2), 2.7676(4); Ru(1)−Ru(3), 2.7897(4); Ru(1)−C(1), 2.095(3); Ru(1)−C(4), 2.097(3); C(1)−C(2), 1.438(5); C(2)−C(3), 1.471(5), C(3)−C(4), 1.437(5); O(1)−C(5), 1.412(4); O(1)−C(6), 1.435(5); Ru(2)−Ru(1)−Ru(3), 83.942(11); C(1)−Ru(1)−C(4), 76.97(13); Ru(1)−C(1)−C(2), 118.8(2); C(1)−C(2)−C(3), 112.4(3); C(2)−C(3)−C(4), 114.3(3); Ru(1)−C(4)−C(3), 117.6(2).

The molecular structure of **9a** was determined by an X-ray diffraction study.[10] A perspective view of **9a** is shown in Figure 1, along with the relevant bond lengths and angles. Figure 1 clearly shows incorporation of a methoxy group at the exomethylene carbon of **7**.

The structural parameters of **9a** are similar to those of a reported cationic *closo*-ruthenacyclopentadiene analogue, $[\{Cp^*Ru(\mu\text{-}H)\}_2\{Cp^*Ru(\mu_3\text{-}CH{=}CMeCH{=}CH)\}]^+$ (**9b**):[11] the Ru−Ru bond lengths (Ru(1)−Ru(2) = 2.7676(4) Å and Ru(1)−Ru(3) = 2.7897(4) Å) are nearly equal to those of **9b** (2.7612(10) and 2.7669(10) Å). The distance between C(5) and O(1) (1.412(4) Å) corresponds to a normal C−O single-bond length.

In the ^1H NMR spectrum of **9a**, signals of the methyl and methylene groups next to the oxygen atom were observed at δ 3.01 and 2.93, respectively. ^{13}C signals of the ruthenacyclopentadiene moiety appeared at δ 109.7 (d, J_{C-H} = 161 Hz, C^5), 101.9 (s, C^2), 67.2 (d, J_{C-H} = 185 Hz, C^3), and 66.5 (d, J_{C-H} = 185 Hz, C^4). These chemical shifts and J_{C-H} values are similar to those of **9b**.[11] To the best of our knowledge, this is the first example of the functionalization of the *closo*-ruthenacyclopentadiene complex.[12]

The formation of **9a** by the reaction of **7** with methanol corresponds to the introduction of a methoxy group at the terminal position of *n*-pentane on the cluster. Whereas C−O bond formation via the direct scission of the alkane C−H bond and the methanol O−H bond is a thermodynamically unfavorable process, the highly electrophilic nature of the dicationic species **7** enables the attack of methanol at the carbon atom. The subsequent deprotonation process as well as reconstruction of the ruthenacyclopentadiene skeleton probably makes this reaction thermodynamically favorable.

In summary, we have shown the introduction of a methoxy group into the hydrocarbyl ligand derived from *n*-pentane via C−H bond activation on the triruthenium cluster. Complex **2a** was formed by the reaction of **1** with *n*-pentane, and therefore, the results obtained in this study represent an important step for the functionalization of alkane mediated by cluster complexes.

Acknowledgment. This work was supported by Grants Nos. 18105002 (Scientific Research (S)) and 19550058 (Scientific Research (C)) from the Japan Society of the Promotion of Science and Grant No. 18064007 (Priority Area “Synergy of Elements”) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: Text, tables, and figures giving synthetic details for compounds **6**, **7**, and **9a** and X-ray crystallographic data fo r**9a**; these X-ray data are also given as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] Crystal data for **9a**: $C_{36}H_{55}F_6OPRu_3 \cdot C_6H_6$, fw = 1030.09, monoclinic, space group $P2_1/c$ (No. 14), a = 15.0409(5) Å, b = 12.3066(5) Å, c = 23.1384(8) Å Å, β = 98.7570(12) °, V = 4233.0(3) $Å^3$, Z = 4, D_{calcd} = 1.616 g/cm^3, temperature–120 °C, μ(Mo Kα) = 11.52 cm^{-1}, R1 = 0.0374, wR2 = 0.0776 for 8073 reflections with $I > 2\sigma(I)$. Hydrogen atoms attached to the ruthenium atoms were located by sequential difference Fourier synthesis and refined isotropically.

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