Selective Carbon−Carbon Bond Cleavage of Cyclopentadiene on a Trinuclear Ruthenium Pentahydride Complex

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Carbon−carbon bond cleavage by a transition metal complex is of special interest in its applications to important industrial processes such as petroleum refining, alkane skeletal rearrangements, and cracking. The activation of C−C bonds by soluble transition metal complexes has, therefore, been the focus of many recent studies in the field of organometallic chemistry.[1] Most of the reported examples of C−C bond cleavage by transition metal complexes involve intramolecular ligand activation, activated systems such as alkylated cyclopentadienes, or highly strained systems such as cyclopropane or cubane. Recently, Milstein et al. have reported the selective activation of a C−C bond by a rhodium complex having diphosphinomesitylene with its C−C bond favorably oriented toward the rhodium center.[2]

During investigations on the activation of substrates on a multinuclear complex,[3] we were successfully able to synthesize a novel unsaturated trinuclear pentahydride complex of ruthenium $[(C_5Me_5)Ru]_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**1**) in which the three metal centers were tightly bound by the bridging hydrides.[4] In the reaction field provided by **1** which is surrounded by three C_5Me_5 groups, it seems likely that the three metal centers cooperate in the activation of the substrates. Here we report an unprecedented type of selective carbon−carbon bond cleavage of cyclopentadiene by a trinuclear pentahydride complex of ruthenium.

The reaction of **1** with 5 equiv of cyclopentadiene in tetrahydrofuran at ambient temperature for 12 h leads to the formation of the trinuclear 2-methylruthenacyclopentadiene $[(C_5Me_5)Ru(\mu\text{-}H)]_3[\mu_3\text{-}\eta^4\text{-}C(Me)=CHCH=CH]$ (**3**) as a result of the $C(sp^2)-C(sp^3)$ cleavage of the cyclopentadiene (eq 1).[5] It is noteworthy that the C−H bond cleavage of the methylene group of cyclopentadiene is completely suppressed. Removal of the solvent under reduced pressure followed by washing of the residual solid with methanol gave **3** in a 99.5% yield as a dark purple crystalline solid. Complex **3** is soluble in diethyl ether and *n*-hexane and very soluble in toluene while it is sparingly soluble in polar solvents such as methanol or acetone. Single crystals of **3** suitable for an X-ray diffraction study were obtained from a mixed solvent of tetrahydrofuran and methanol at −20 °C.

1 **2** **3**

Complex **3** was characterized on the basis of the ^1H and ^{13}C NMR spectra as well as the $^1H-^1H$ COSY and $^1H-^{13}C$ HSC spectra.[6] The ^1H NMR spectrum exhibited characteristic signals for three methine protons, H1, H2, and H3, at δ 6.85, 3.36, and 3.09 ppm, respectively. A resonance due to the methyl group attached to the α-carbon (C4) of the ruthenacycle appeared at δ 2.02. The gated ^{13}C NMR spectrum showed three doublets at δ 61.6 (J = 152.6 Hz, C2), 64.7 (J = 150.8 Hz, C3), and 166.4 (J = 154.3 Hz, C1) as well as a singlet signal at δ 170.5 (C4) for the carbons of the ruthenacycle. Shifts of δ 166.4 and 170.5 ppm were comparable to those for the α-carbon of the $\mu\text{-}\sigma,\pi$-vinylic ligands.[3b,c,h,7]

Definitive proof of the structure of **3** was provided by X-ray crystallography.[8] The structure shown in Figure 1 clearly depicts the formation of a five-membered ruthenacycle. The ruthenacyclopentadiene skeleton is disordered between two orientations (65.6:34.4). Two double bonds, C(1)=C(2) and C(3)=C(4), are bound to Ru2 and Ru1, respectively, in an η^2 fashion.

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(5) Experimental details for **3**: A 50 mL Schlenk tube was charged with 87.2 mg (0.122 mmol) of **1** and 15 mL of THF; 47.5 μL (0.611 mmol) of freshly distilled cyclopentadiene was added, and the reaction mixture was stirred at room temperature for 12 h. Removal of the solvent under reduced pressure followed by washing of the residual solid with methanol gave 94.5 mg of **3** (0.121 mmol, 99.5%) as a dark purple crystalline solid.

(6) **3**: ^1H NMR (THF-d_8, 400 MHz) δ −21.98 (m, 1H, Ru*H*Ru), −19.02 (m, 1H, Ru*H*Ru), −18.76 (m, 1H, Ru*H*Ru), 1.73 (s, 15H, C_5Me_5), 1.74 (s, 15H, C_5Me_5), 1.76 (s, 15H, C_5Me_5), 2.02 (s, 3H, RuC(*Me*)=CH), 3.09 (dd, J = 3.0 and 1.9 Hz, 1H, RuC(Me)=C*H*), 3.36 (dd, J = 4.3 and 3.0 Hz, 1H, RuCH=C*H*), 6.85 (m, J = 4.3, 1.9, and 1.2 Hz, 1H, RuC*H*=CH); ^{13}C NMR (THF-d_8, 100 MHz) δ 11.5 (q, J_{CH} = 126.3 Hz, C_5Me_5), 11.7 (q, J_{CH} = 126.1 Hz, C_5Me_5), 11.8 (q, J_{CH} = 126.0 Hz, C_5Me_5), 34.8 (q, J_{CH} = 123.9 Hz, RuC(*Me*)=CH), 61.6 (d, J_{CH} = 152.6 Hz, RuCH=*C*H), 64.7 (d, J_{CH} = 150.8 Hz, RuC(Me)=*C*H), 90.3 (s, C_5Me_5), 90.7 (s, C_5Me_5), 95.8 (s, C_5Me_5), 166.4 (d, J_{CH} = 154.3 Hz, RuCH=CH), 170.5 (s, RuC(Me)=CH). Anal. Calcd for $C_{35}H_{54}Ru_3$: C, 54.03; H, 7.00. Found: C, 54.10; H, 7.89.

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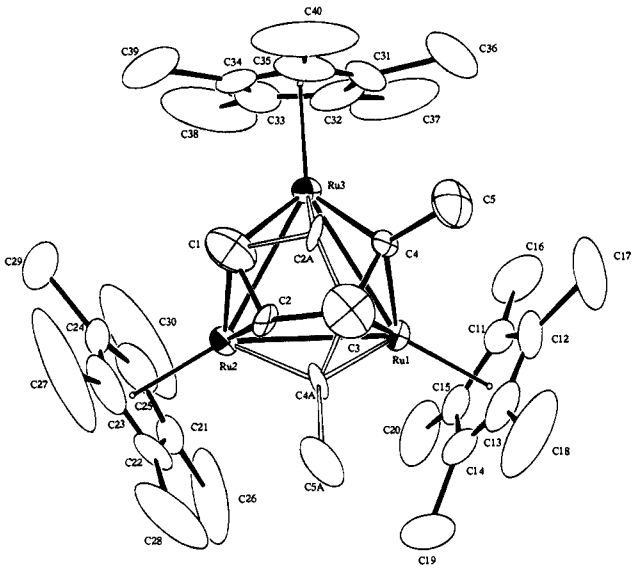

Figure 1. Molecular structure of $[(C_5Me_5)Ru(\mu\text{-}H)]_3[\mu_3\text{-}\eta^4\text{-}C(Me)=CHCH=CH]$ (**3**). The thermal ellipsoids correspond to 30% probability. C2A, C4A, and C5A show the disorder in the crystal. Selected bond lengths (Å) and angles (deg) are as follows: Ru1–Ru2 2.916(2), Ru1–Ru3 2.860(2), Ru2–Ru3 2.866(2), Ru3–C1 2.13(2), Ru3–C4 2.11(2), C1–C2 1.45(2), C2–C3 1.41(3), C3–C4 1.42(3), C4–C5 1.52(3), Ru2–C1 2.08(2), Ru2–C2 2.20(2), Ru1–C3 2.28(2), Ru1–C4 2.14(2); Ru2–Ru1–Ru3 59.48(4), Ru1–Ru2–Ru3 59.29(4), Ru1–Ru3–Ru2 61.23(4), C1–Ru3–C4 75.4(7), Ru3–C1–C2 115(1), C1–C2–C3 108(2), C2–C3–C4 121(2), Ru3–C4–C3 111(1), C3–C4–C5 116(2), Ru3–C4–C5 128(1).

Monitoring the reaction of **1** with 5 equiv of cyclopentadiene in THF-d_8 at room temperature by ^{1}H NMR spectrometry showed the initial formation of an intermediary ruthenacyclohexadiene, **2**, as a result of the oxidative addition of C(sp^2)–C(sp^3) to one of the ruthenium centers. After 90 min, the yield of **2** reached 53%. With the reaction time, a progressive increase in the intensities of the signals for **3** and a significant decrease in those for **2** were observed. After 6 h, the signals attributed to **1** disappeared and the yields of **3** and **2** reached 85% and 15%, respectively. The time-conversion curves are shown in Figure 2. These results clearly indicate that ruthenacyclopentadiene **3** is formed by way of **2**.

Although **2** could not be isolated, it was characterized on the basis of the ^{1}H and ^{13}C NMR, ^{1}H–^{1}H COSY, and ^{1}H–^{13}C HSC spectra.[9] Notable features of the ^{13}C NMR spectrum are the resonance signals appearing at δ −1.45 (t, J_{CH} = 133.7 Hz) and 153.4 ppm (d, J_{CH} = 148.9 Hz). They are attributed to methylene (C5) and methine (C1) carbons σ-bonded to the ruthenium atom. The signals for C2, C3, and C4 appeared at δ 57.6 (d, J_{CH} = 153.4 Hz), 48.6 (d, J_{CH} = 159.8 Hz), and 39.1 ppm (d, J_{CH} = 154.7 Hz), respectively. A downfield shift of the signal for C1 and an upfield shift of those for C2, C3, and C4 confirmed the coordination of the diene moiety to Ru2 and Ru1 in a μ-η^2:η^2 fashion similar to the coordination mode observed in complex **3**. Although the ^{1}H NMR signals for protons attached to C3 and C4 were obscured by those of the cyclopentadienyl ligands, they were assigned by virtue of the ^{1}H–^{1}H COSY and ^{1}H–^{13}C HSC spectra.

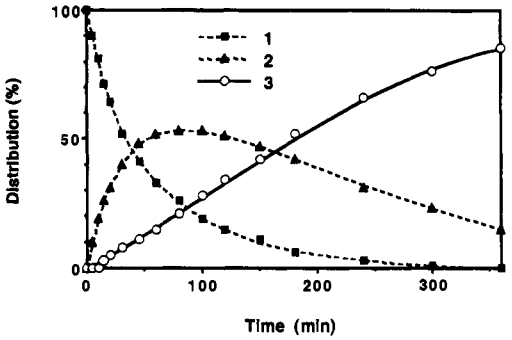

Figure 2. Distribution of **1**, **2**, and **3** vs time from integrated ^{1}H NMR spectra.

The formation of **2** strongly suggests that two of three ruthenium centers in **1** act as coordination sites and the third metal takes the role of an activation site in the initial stage of the reaction with cyclopentadiene. To our knowledge, this is the first example of the selective activation of an unactivated carbon–carbon bond in cooperation with three metal centers. Further reactivity studies of **1** with substituted cyclopentadienes and studies pertaining to the mechanism behind the formation of **3** will be reported in due course.

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Supplementary Material Available: The ^{1}H–^{1}H COSY and ^{1}H–^{13}C HSC spectra of **2** and **3**, text providing details of the data collection and of structure solutions and refinements, and tables of the crystal data, data collection, refinement parameters, positional parameters, anisotropic thermal parameters, and bond lengths and angles (26 pages), listing of observed and calculated structure factors (20 pages) for compound **3**. This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(8) Complex **3** crystallized from THF/MeOH in the triclinic system, space group $P\bar{1}$, with a = 11.132(2) Å, b = 18.278(4) Å, c = 8.500(2) Å, α = 93.97(2)°, β = 105.00(2)°, γ = 89.34(2)°, V = 1666.5(5) Å^3, Z = 2, and D_{calc} = 1.550 g cm^{-3}. Intensity data were collected at 23 °C on a Rigaku AFC-5R four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) in the 2° < 2θ < 50° range. The data were processed using the TEXSAN crystal solution package operated on a micro VAX computer. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2883 observed reflections ($I > 3.00\sigma(I)$) and 370 variable parameters and converged with agreement factors of R = 0.054 and R_w = 0.056.

(9) **2**: ^{1}H NMR (THF-d_8, 400 MHz) δ −23.22 (d, J = 5.9 Hz, 1H, Ru*H*Ru), −18.95 (d, J = 2.6 Hz, 1H, Ru*H*Ru), −18.39 (t, J = 4.7 Hz, 1H, Ru*H*Ru), −0.15 (dd, J = 6.2 and 6.1 Hz, 1H, RuC*H*H'), 1.17 (d, J = 6.2 Hz, 1H, RuCH*H'*), 1.56 (s, 15H, C_5Me_5), 1.68 (s, 15H, C_5Me_5), 1.78 (s, 15H, C_5Me_5), 3.97 (dd, J = 5.5 and 4.9 Hz, 1H, RuCH=C*H*), 6.72 (d, J = 5.5, 1H, RuC*H*=CH); the signals for protons attached to C3 and C4 are obscured by those of the cyclopentadienyl ligands; ^{13}C NMR (THF-d_8, 100 MHz) δ −1.5 (t, J_{CH} = 133.7 Hz, Ru*C*H$_2$), 10.3 (q, J_{CH} = 126.8 Hz, C_5Me_5), 11.1 (q, J_{CH} = 126.1 Hz, C_5Me_5), 11.6 (q, J_{CH} = 126.2 Hz, C_5Me_5), 39.1 (d, J_{CH} = 154.7 Hz, RuCH$_2$=*C*H), 48.6 (d, J_{CH} = 159.8 Hz, RuCH$_2$-CH=*C*H), 57.6 (d, J_{CH} = 153.4 Hz, RuCH=*C*H), 88.7 (s, C_5Me$_5$), 89.9 (s, C_5Me$_5$), 95.0 (s, C_5Me$_5$), 153.4 (d, J_{CH} = 148.9 Hz, Ru*C*H=CH).