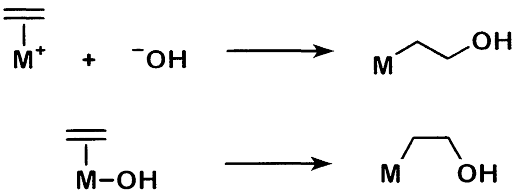
Synthesis and Structure Determination of an Oxygen-Functionalized Ruthenacycle: Intramolecular Attack of Coordinated Hydroxide on an Acetylenic Ligand

Masato Oshima, Minoru Kobayashi, Masako Tanaka,† and Hiroharu Suzuki*
Department of Chemical Engineering, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama , Meguro-ku, Tokyo 152
†*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226*

(Received July 21, 1995)

The reaction of a tetranuclegar hydroxoruthenium complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu_3\text{-}OH)]_4$ (**1**) with dimethyl acetylenedicarboxylate (DMAD) proceeded at 60 °C to generate a dinuclear oxygen-functionalized ruthenacycle $[(\eta^5\text{-}C_5Me_5)Ru]_2[\mu\text{-}\eta^5\text{-}OC_4(CO_2Me)_4]$ (**2**) via an intramolecular attack of hydroxo ligand on the coordinated C–C unsaturation. The molecular structure of **2** was determined by X-ray diffraction.

As well as intermolecular attack of hydroxide on an unsaturated hydrocarbon ligand, nucleophilic attack of the coordinated hydroxide on the coordinated substrate is one of the promising methods for the introduction of oxygen-functions into hydrocarbons.



Whereas considerable mechanistic studies including theoretical ones for the intermolecular attack of hydroxide or water on the olefinic ligand have been reported,[1,2] there have been a few examples of intramolecular oxymetallation of unsaturated hydrocarbons because of lack in structurally well established hydroxo complexes of transition metals.[3]

Recently, we have successfully been able to synthesize a novel cubane-type μ_3-hydroxo complex of ruthenium, $[(C_5Me_5)Ru(\mu_3\text{-}OH)]_4$ (**1**).[4] This complex would be a candidate for the key complex which accomplishes the intramolecular oxymetallation of unsaturated hydrocarbons. Here we report the formation of a novel oxygen-functionalized ruthenacycle via an intramolecular attack of the hydroxo ligand on the coordinated C–C unsaturated bond derived from DMAD.

The reaction of **1** with 6.2 equiv (1.54 equiv/Ru) of DMAD in toluene at 60°C for 6 h led to the formation of the dinuclear oxygen-functionalized ruthenacycle $(\eta^5\text{-}C_5Me_5)Ru[\mu\text{-}\eta^5\text{-}OC_4\text{-}(CO_2Me)_4]Ru(\eta^5\text{-}C_5Me_5)$ (**2**). Removal of the solvent under reduced pressure followed by chromatographic purification on neutral alumina (Merck Art. No. 1097) with toluene/THF afforded **2** in 87% yield as a green-brown crystalline solid.[5] Complex **2** is soluble in toluene and diethyl ether and very soluble in tetrahydrofuran and methanol while it is sparingly soluble in nonpolar solvent such as *n*-pentane. Single crystals of **2** suitable for X-ray diffraction study were obtained from toluene at -20°C.

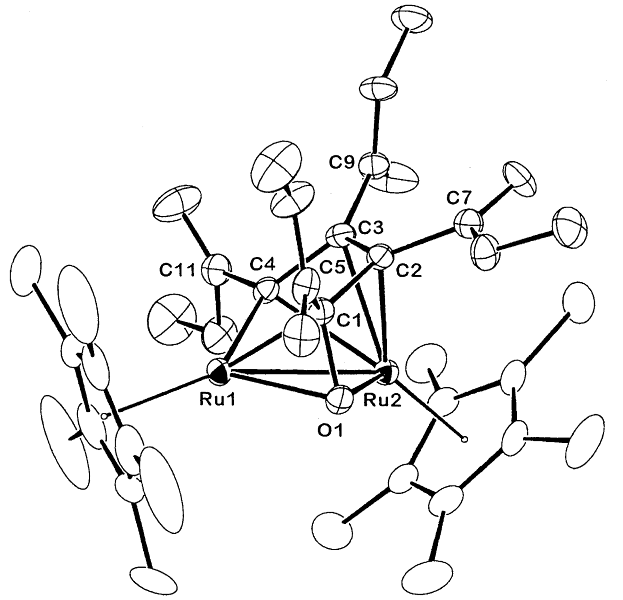
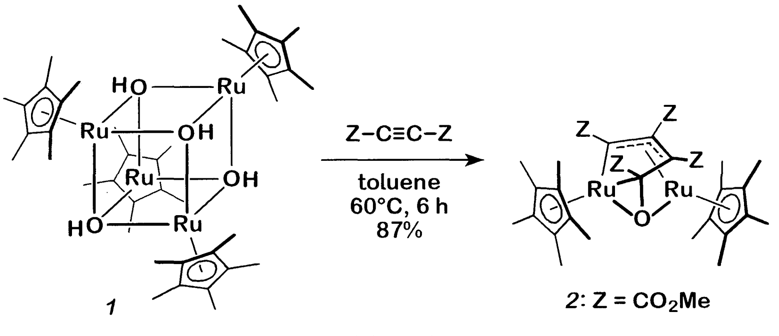
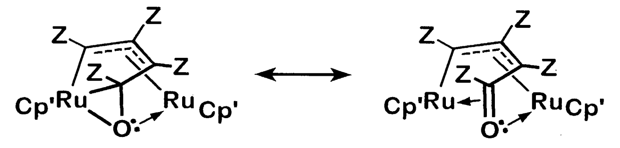


Figure 1. Ortep drawing of **2**.

The ^1H NMR spectrum exhibited four singlets for the methyl esters at δ 3.59, 3.52, 3.50, and 3.36, respectively, and a signal due to the inequivalent two C_5Me_5 ligands happened to be observed as a singlet at δ 1.62. In the ^{13}C NMR spectrum, the signals for these two C_5Me_5 groups separately appeared. Signals due to C(2) and C(3) were observed at δ 46.4 and 112.4. These



Scheme 1.



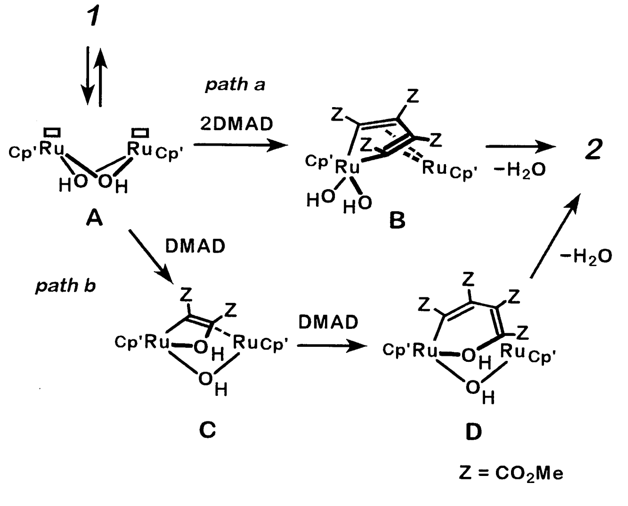
I Z = CO_2Me II

shifts are characteristic of those for terminal and central carbons, respectively, of a bridging η^3–allyl ligand. While five resonances for the carbonyl groups and C(1) appeared in a range from δ 160 to 180, signal for the quaternary carbon C(4) could not be observed in spite of measurement with changes in pulse intervals.

Table 1. Selected bond lengths (Å) and angles (°)

Bond Lengths (Å)		Bond Angles (°)	
Ru1-Ru2	2.7350(8)	Ru1-C1-C5	119.7(4)
Ru1-C1	2.069(6)	Ru1-C1-C2	111.6(5)
Ru1-C4	2.034(6)	C5-C1-C2	120.9(6)
Ru1-O1	2.026(4)	Ru1-C4-C11	123.1(5)
C1-O1	1.398(7)	Ru1-C4-C3	117.5(4)
Ru2-C2	2.176(6)	C11-C4-C3	117.8(6)
Ru2-C3	2.199(6)	C5-C1-O1	115.9(6)
Ru2-C4	2.203(6)	C2-C1-O1	108.4(5)
Ru2-O1	2.109(4)	C5-C1-C2	120.9(6)
C1-C2	1.514(8)	Ru1-C1-O1	68.4(3)
C2-C3	1.415(8)	C1-O1-Ru1	71.7(3)
C3-C4	1.431(8)	C1-O1-Ru2	82.8(1)
		C1-Ru1-O1	39.9(2)

Definitive proof of the structure of **2** was provided by crystallography.[6] The structure of **2** shown in Figure 1 clearly depicts the formation of the oxygen-fuctionalized five-membered ruthenacycle. The two ruthenium atoms are bridged by an η^3:η^4–$C_4(O)(CO_2Me)_4$ fragment. The values of 2.069(6) and 2.034(6) Å for the Ru(1)–C(1) and Ru(1)–C(4) distances, respectively, indicate that the ends of the bridging $C_4(O)$–$(CO_2Me)_4$ fragment, C(1) and C(4), are σ bonded to Ru(1). The long Ru(2)–C(1) distance (2.561(6) Å) indicates the absence of the bonding interaction between these atoms. The Ru(2)–C(2), Ru(2)–C(3), and Ru(2)–C(4) distances of 2.176(6), 2.199(6), and 2.203(6) Å, respectively, are significantly longer than those for a Ru–C σ bond and consistent with the Ru–C π–bonds. This result is compatible with the η^3–allyl coordination of C(2)–C(3)–C(4) moiety to Ru(2) suggested by the ^{13}C NMR chemical shifts. The C(1)–O(1) distance of 1.398(7) Å is slightly shorter than that for a C–O single bond (1.42–1.44 Å) but much longer than the carbon–oxygen double bond (1.18–1.25 Å). This may be explicable in terms of the contribution of a metallaoxirane-like hybrid **I**.



Scheme 2.

Plausible reaction paths are shown in Scheme 2, one of which involves the intramolecular nucleophilic attack of the coordinated hydroxide at the α–carbon of an intermediary ruthenacyclopentadiene (path **a**). $[(\eta^5\text{–}C_5Me_5)Ru(\mu\text{–}OH)]_4$ (**1**) would be in equilibrium in solution with the dinuclear di–μ–hydroxo complex **A**. Coordination of two molecules of DMAD followed by cyclometallation to form a ruthenacyclopentadiene **B** would be expected on the basis of a precedent.[7] Nucleophilic attack of the coordinated hydroxide on the ruthenacycle and subsequent liberation of water can yield **2**. Another possible route to **2** (path **b**) would involve a nucleophilic attack of hydroxide on the coordinated DMAD to yield an oxaruthenacyclobutene **C**, which would undergo acetylene–insertion and elimination of water to form **2**. The formation of the intermediate **C** also is supported on the basis of the precedent result for thiometallation.[8] Despite many efforts to detect the intermediates of this reaction spectroscopically, definitive evidence for the formation of **B** or **C** was not obtained.

This research was supported by Kawakami Memorial Foundation and Grant–in–Aid for Scientific Research on Priority Area of Reactive Organometallics (No. 05236104) from the Ministry of Education, Science and Culture. The authors also are grateful to Kanto Chemical Co., Inc., for the generous gift of pentamethylcyclopentadiene.

References

1 J.–E. Bäckvall, B. Åkermark, and S. O. Ljunggren, *J. Am. Chem. Soc.*, **101**, 2411 (1979) and references cited therein.

2 (a) J.–E. Bäckvall, E. E. Björkman, L. Pettersson, and P. Siegbahn, *J. Am. Chem. Soc.*, **106**, 4369 (1984). (b) O. Eisenstein and R. Hoffmann, *J. Am. Chem. Soc.*, **103**, 4303 (1981).

3 H. E. Bryndza, *Organometallics*, **4**, 406 (1985).

4 H. Suzuki, T. Kakigano, M. Igarashi, A. Usui, K. Noda, M. Oshima, M. Tanaka, and Y. Moro–oka, *Chem. Lett.*, **1993**, 1707.

5 Spectral data of **2**: ^1H NMR (500 MHz, C_6D_6) δ 3.59 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.50 (s, 3 H, OMe), 3.36 (s, 3 H, OMe), 1.62 (s, 30 H, C_5Me_5). ^{13}C NMR (125 MHz, C_6D_6) δ 175.4 (s), 171.2 (s), 170.2 (s), 168.6 (s), 166.0 (s), 116.8 (s, C4), 98.4 (s, C_5Me_5), 97.8 (s, C_5Me_5), 96.0 (s, C3), 51.9 (q, J = 146 Hz, CO_2Me), 51.0 (q, J = 145 Hz, CO_2Me), 50.7 (q, J = 145 Hz, CO_2Me), 50.0 (q, J = 145 Hz, CO_2Me), 45.4 (s, C2), 9.8 (q, J = 126 Hz, C_5Me_5), 9.3 (q, J = 127 Hz, C_5Me_5). IR (KBr) 2954 (s), 2912 (s), 1727 (s), 1707 (s), 1688 (s), 1448 (s), 1433 (s, sh), 1381 (m), 1342 (m), 1292 (s), 1265 (s), 1199 (s), 1154 (s), 1108 (s), 1967 (s), 1021 (s), 982 (m), 948 (m), 833 (w), 774 (s), 758 (m), 704 (s) cm^{-1}. Elemental analysis for $C_{22}H_{27}O_9Ru_2$, found (calcd): C, 49.21 (49.68); H, 5.45 (5.43).

6 Complex **2** crystallized from toluene in the monoclinic system, space group $P2_1/c$ (#14), with a = 17.690(2) Å, b = 8.920(3) Å, c = 20.650(2) Å, β = 95.781(9)°, V = 3241(1) Å^3, Z = 4, and D_c = 1.583 (g/cm^3). Intensity data were collected at 23 °C on a Rigaku AFC5R diffractometer with graphite-monochromated Mo–$K\alpha$ radiation in the $5° < 2\theta < 50°$ range. The final R and Rw values are 0.040 and 0.030 for 3449 reflections with $F_o > 3\sigma(F_o)$. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.

7 B. K. Campion, R. H. Heyn, and T. D. Tilley, *Organometallics*, **9**, 1106 (1990).

8 U. Koelle, C. Rietmann, J. T. Wagner, and U. Englert, *Organometallics*, **14**, 703 (1995).