Isolation of (η^5-Cyclopentadienyl)(1,2,3,4,5-η^6-*exo*-methoxy-7-oxo-2,4-cycloheptadienyl)ruthenium(II) as a Key Intermediate for the Selective H/D Exchange on Its Coordinated Tropone Moiety by KOH/CD_3OD

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Synopsis. (η^5-Cyclopentadienyl)(η^5-ligand)ruthenium(II) (ligand=1,2,3,4,5-η^6-*exo*-methoxy-d_3-7-oxo-2,4-cycloheptadienyl-2*d* **3a**, 1,2,3,4,5-η^6-*exo*-methoxy-7-oxo-2,4-cycloheptadienyl-2*d*, 1,2,3,4,5-η^6-*exo*-methoxy-7-oxo-2,4-cycloheptadienyl, and 1,2,3,4,5-η^6-*exo*-ethoxy-7-oxo-2,4-cycloheptadienyl) was isolated in fairly good yields by treatment of (η^5-C_5H_5)(η^6-tropone)ruthenium(II)BF_4 with KOH in CD_3OD, CH_3OD, CH_3OH, and ethanol, respectively. The selectively deuterated tropone-2*d* was readily removed by photolysis of **3a** accompanied by demethoxylation with visible light in the presence of large excess of $P(OCH_3)_3$.

During the course of the development of nonlinear response of sandwich type ruthenium complexes,[1] Kimura et al. found that [Ru(η^5-C_5H_5)(η^5-anisole)]BF_4 **1** was susceptible to H/D exchange, and converted to pure (η^5-C_5H_5)(1,2,3,4,5-η^6-oxo-2,4-cyclohexadienyl-1*d*)ruthenium(II)BF_4 quantitatively in the presence of excess KOH in CD_3OD.[2a] Similar H/D exchange reaction was observed for [Ru(η^5-C_5H_5)(η^5-thiophene)]BF_4 by Spies and Angelici.[2b] They pointed out the fact that thiophene moiety in the π thiophene Ru complex undergoes H/D exchange with basic CD_3OD by a mechanism involving direct proton abstraction from the thiophene moiety by OH^- or CD_3O^-.[2c] When tropone was tested as a typical nonbenzenoid ligand in stead of thiophene and anisole,[3,4] we found another role of CD_3O^- for H/D exchange of a tropone moiety in (η^5-C_5H_5)(η^6-tropone)ruthenium(II)BF_4 (**2**). Treatment of **2** with KOH in CD_3OD gave (η^5-cyclopentadienyl)(1,2,3,4,5-η^6-*exo*-methoxy-d_3-7-oxo-2,4-cycloheptadienyl-2*d*)ruthenium(II) **3a** as an intermediate for selective H/D exchange of the tropone moiety. We would like to report the details of the H/D exchange and characterization of the intermediate.

We prepared **2** by our method for **1**. The structure of **2** was assigned by its ^1H NMR, IR, UV, and Mass spectra, and CH analysis. The selective H/D exchange of the tropone moiety was observed as follows. After a CD_3OD (3 dm^3) solution of **1** (1.0 mmol) was stirred for 4 h in the presence of KOH (1.0 mmol) at room temperature, **3a** was obtained by usual work up in 67% yield. The selectively deuterated tropone-2*d* (Fig. 1) was readily removed by photolysis of **3a** accompanied by unprecedented demethoxylation with visible light in the presence of large excess of $P(OCH_3)_3$.[5,6] (η^5-Cyclopentadienyl)(1,2,3,4,5-η^6-*exo*-methoxy-7-oxo-2,4-cycloheptadienyl-2*d*)ruthenium(II) (**3b**), (η^5-cyclopentadienyl)(1,2,3,4,5-η^6-*exo*-methoxy-7-oxo-2,4-cycloheptadienyl)ruthenium(II) (**3c**), and (η^5-cyclopentadienyl)(1,2,3,4,5-η^6-*exo*-methoxy-7-oxo-2,4-cycloheptadienyl)ruthenium(II) (**3d**) were isolated quantitatively in CH_3OD, CH_3OH, and ethanol solutions respectively. The mother structure **3c** of a series **3** was assigned by its ^1H NMR, 2D-HETCOR (Fig. 2), nondecoupling ^{13}C NMR, IR, UV, and Mass spectra and CH analysis. The spectroscopic characteristics of **3** establish that the alkoxyl groups are *exo*, suggesting the nucleophilic *exo*-attack. Thus, the ^1H NMR spectra of **3c** and **3d** contain δ=3.59 and 3.69 resonance with the 7.5 and 8.0 Hz coupling constants to their vicinal protons, respectively, and they are characteristic to an *endo* cycloheptadienyl-1-one protons.[4] Coupling constants of a carbon and an adjacent hydrogen in the seven membered ring also constitute a characteristic feature of **3**. As $J_{C2,H2}$, $J_{C3,H3}$, $J_{C4,H4}$, $J_{C5,H5}$, $J_{C6,H6}$, and $J_{C7,H7}$ are 119, 160, 154, 166, 167, and 154 Hz, respectively, the hybridization of C2 is assigned to sp^3 and that of

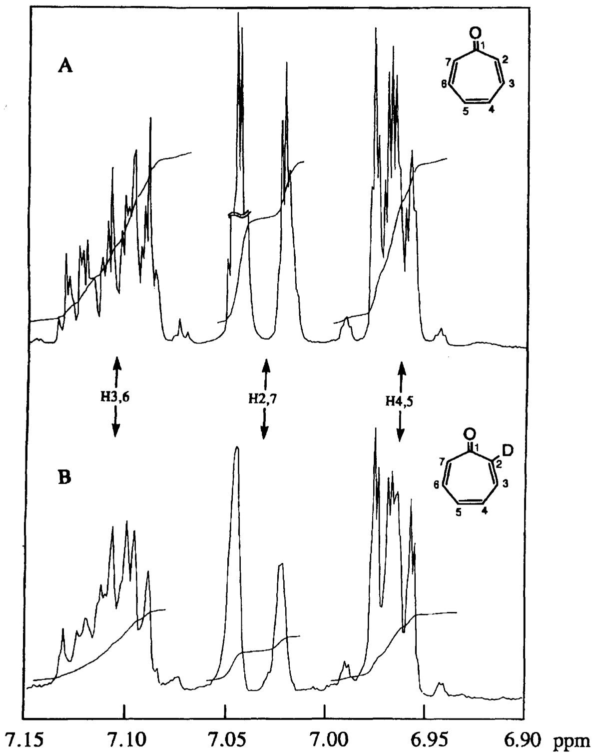


Fig. 1. A: ^1H NMR spectrum of tropone in $CDCl_3$. B: ^1H NMR spectrum of tropone-2*d* isolated from the photolysis of **3a** in $CDCl_3$.

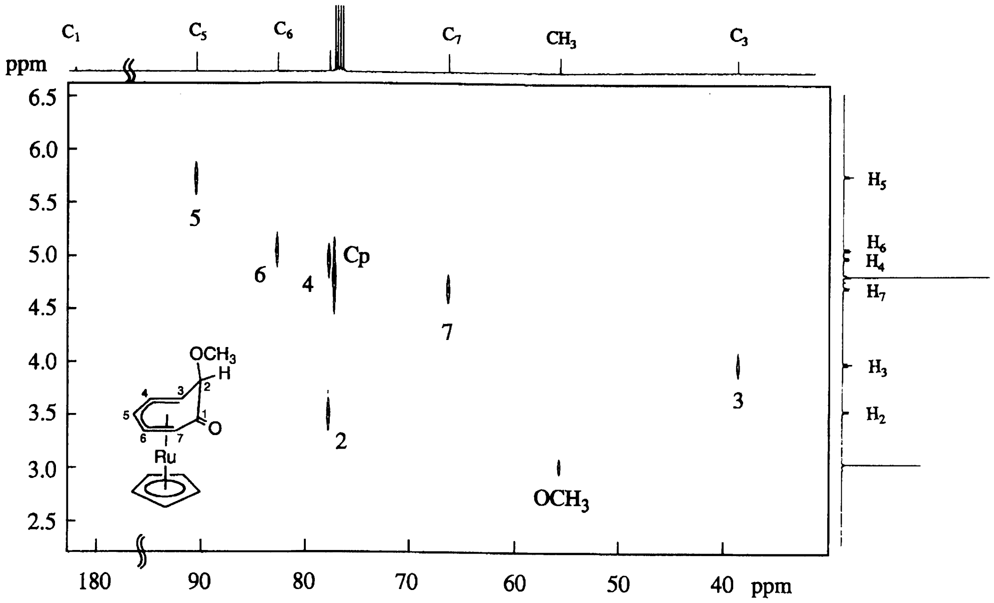


Fig. 2. 2D-HETCOR contour plot for the compound **3a**.

other carbons to sp^2. Because the hybridization (sp^n) may be estimated according to the equation J (a coupling constant)$=500/(n+1)$.[7] The H2 should be susceptible to a base, because the H2 is acidic due to a keto–enol tautomerization between the α-proton H2 to the adjacent carbonyl group. Therefore, compound **3c** may undergo selective H/D exchange by action of OH^- in CD_3OD or CH_3OD. Actually the hydrogen adjacent to the carbonyl group in **3c** was selectively deuterated in CH_3OD in the presence of KOH at room temperature within 4 h to give only **3b** as shown in Fig. 3, but tropone itself was not deuterated under the same conditions. We rationalized the selective H/D exchange observed in the tropone through three successive steps as shown in Scheme 1.

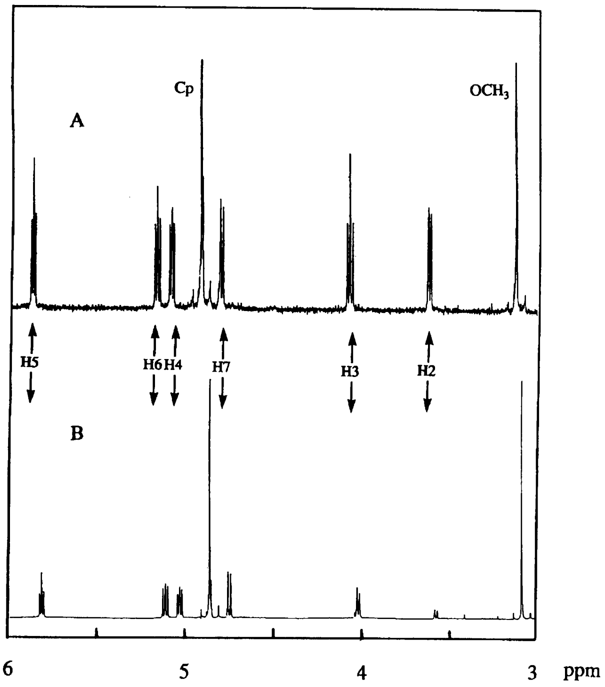
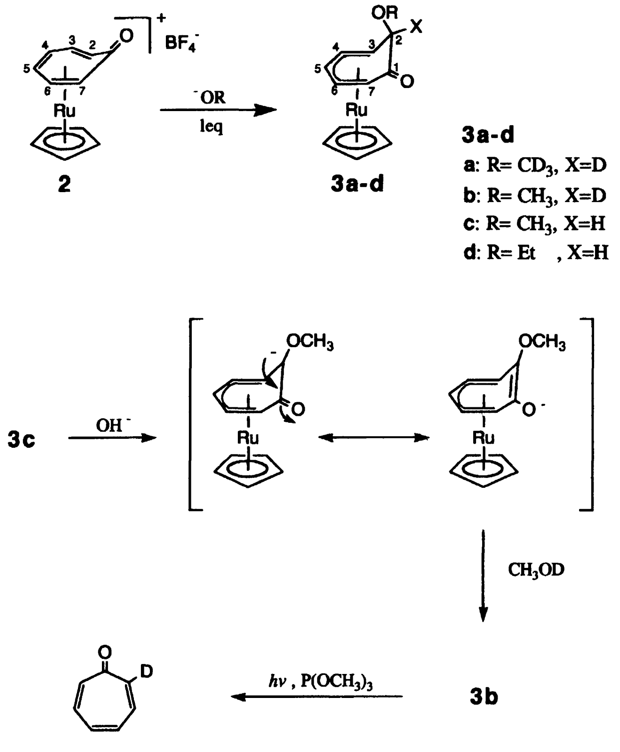


Fig. 3. A: ^{1}H NMR spectrum of **3c** in $CDCl_3$ before the treatment with CD_3OD/KOH in $CDCl_3$. B: That of **3c** after the treatment with CD_3OD/KOH in $CDCl_3$.

Experimental

All melting points are uncorrected. Infrared spectra were obtained on a JASCO FT/IR 5000 spectrometer. Ultraviolet spectra were measured with a Hitachi UV-200 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-500 spectrometer (500 and 125 MHz, respectively) with tetramethylsilane as an internal standard. Mass spectra were obtained with a JEOL-JMS-D300 mass spectrometer of VG Instruments 70-S GAS Chromatograph/Mass spectrometer.

(η^5-C_5H_5)(η^6-tropone)ruthenium(II)BF_4 (2). A solution of $RuCl(\eta^5\text{-}C_5H_5)\text{-}(PPh_3)_2$ (330 mg, 0.46 mmol) and tropone (500 mg, 4.7 mmol) in dichloromethane (10 dm^3) was added to a solution of $AgBF_4$ (140 mg, 0.72 mmol) in methanol (0.5 dm^3). The mixture was stirred at room temperature under an atmosphere of nitrogen for 24 h. The mixture was filtered to remove AgCl. A pale yellow compound precipitated upon addition of diethyl ether to the filtrate. Compound **2** was recovered in a 73% yield. Recrystallization from a mixed solvent (dichloromethane/ether=5:1) gave pale yellow needles; mp 254—255 °C; ^{1}H NMR (CD_3CN) $\delta=6.21$ (s, 5H, C_5H_5), 6.27 (dd, 2H, $J_{23}=10$ Hz, $J_{24}=1.5$ Hz, H2, H7), 6.91 (m, 2H, H3, H6), and 7.43 (m, 2H, H4, H5); ^{13}C NMR (DMSO-d_6) $\delta=78.56$ (C2, C7), 84.96 (C_5H_5), 92.25 (C3, C6), 97.11 (C4, C5), and 174.89 (C1); IR (KBr) ν_{max} 3060, 1640, 1499, 1419, 1085, 1036, 861, 632, 499 cm^{-1}; UV (CH_3CN) λ_{max} 206 ($\log\varepsilon=4.5$), 278 (sh, 3.4), and 328 nm (sh, 3.2); MS m/z 273 $(M-BF_4)^+$; Anal. Calcd for $C_{12}H_{11}BF_4ORu$: C, 40.14; H, 3.09%. Found: C, 40.08;



Scheme 1.

H, 3.08%.

(η^5-Cyclopentadienyl)(1,2,3,4,5-η^6-*exo*-methoxy-d_3-7-oxo-2,4-cycloheptadienyl-2*d*)ruthenium(II) 3a. This was prepared by the above method in methanol-d_4 instead of methanol in a 67% yield: pale yellow needles; mp 121—123 °C; ^{1}H NMR (CDCl$_3$) δ=4.03 (d, 1H, J_{34}, J=7.0 Hz, H3), 4.75 (d, 1H, J_{67}=8.0 Hz, H7), 4.87 (s, 5H, C$_5$H$_5$), 5.04 (dd, 1H, J_{45}=5.5 Hz, H4), 5.12 (dd, 1H, J_{56}=6.5 Hz, H6), 5.82 (dd, 1H, H5); ^{13}C NMR (CDCl$_3$) δ=38.65 (C3), 55.83 (-OCD$_3$), 66.58 (C7), 77.49 (C$_5$H$_5$), 77.87 (C2), 78.03 (C4), 82.95 (C6), 90.81 (C5), and 184.21 (C1); IR (KBr) $\nu_{\max}$ 3084, 3018, 2924, 2240, 2060, 1636, 1412, 1386, 1305, 1209, 1116, 1100, 978, 835, 789, 545, and 426 cm^{-1}; UV (CH$_3$OH) $\lambda_{\max}$ 206 (log ε=4.3), 244 (3.8), and 356 nm (3.2); MS (FAB) m/z 309 (M+1)$^+$; Anal. Calcd for $C_{13}H_{10.8}D_{3.2}O_2Ru$: C, 50.92; H, 5.64%. Found: C, 50.73; H, 5.44%.

(η^5-Cyclopentadienyl)(1,2,3,4,5-η^6-*exo*-methoxy-7-oxo-2,4-cycloheptadienyl-2*d*)ruthenium(II) (3b). This was prepared by the above method in CH$_3$OD instead of methanol in a 89% yield: pale yellow needles; mp 124—126 °C; ^{1}H NMR (CDCl$_3$) δ=3.06 (s, 3H, OCH$_3$), 4.00 (d, 1H, J_{34}, J=7.5 Hz, H3), 4.73 (d, 1H, J_{67}=8.5 Hz, H7), 4.84 (s, 5H, C$_5$H$_5$), 5.02 (dd, 1H, J_{45}=5.5 Hz, H4), 5.10 (t, 1H, J_{56}=6.0 Hz, H6), 5.80 (q, 1H, J_{45}=5.5 Hz, J_{56}=6.0 Hz, H5); ^{13}C NMR (CDCl$_3$) δ=38.61 (C3), 55.81 (-OCH$_3$), 66.57 (C7), 77.48 (C$_5$H$_5$), 77.86 (C2), 78.01 (C4), 82.94 (C6), 90.80 (C5), and 184.02 (C1); IR (KBr) $\nu_{\max}$ 3084, 3018, 2982, 2928, 2820, 1636, 1412, 1386, 1305, 1201, 1100, 992, 835, 789, 549, and 427 cm^{-1}; UV (EtOH) $\lambda_{\max}$ 204 (log ε=4.4), 243 (3.9), and 354 nm (3.3); MS (FAB) m/z 306 (M+1)$^+$; Anal. Calcd for $C_{13}H_{13.2}D_{0.8}O_2Ru$: C, 51.31; H, 4.90%. Found: C, 51.01; H, 4.54%.

(η^5-Cyclopentadienyl)(1,2,3,4,5-η^6-*exo*-methoxy-7-oxo-2,4-cycloheptadienyl)ruthenium(II) (3c). A solution of KOH (17 mg, 0.3 mmol) in methanol (2 dm^3) was added to a suspension of **1** (67 mg, 0.19 mmol) in methanol (20 dm^3). It was stirred at room temperature under an atmosphere of nitrogen for 3.5 h. The reaction mixture was concentrated under reduced pressure to give brown residue, which was extracted with small amounts of dichloromethane. The extract was chromatographed on silica gel eluting with a mixed solvent (ethyl acetate/ethanol=4 : 1). Concentration of collected yellow fractions under reduced pressure gave yellow compound in a 89% yield. Recrystallization from a mixed solvent (carbon tetrachloride/hexane=5 : 1) gave pale yellow needles; mp 123—125 °C; ^{1}H NMR (CDCl$_3$) δ=3.09 (s, 3H, -OCH$_3$), 3.59 (d, 1H, J_{23}=7.5 Hz, H2), 4.04 (t, 1H, J_{34}, J=8.0 Hz, H3), 4.77 (dd, 1H, J_{67}=7.5 Hz, J_{57}=1.0 Hz, H7), 4.88 (s, 5H, C$_5$H$_5$), 5.05 (t, 1H, J_{45}=6.5 Hz, H4), 5.13 (t, 1H, J_{56}=7.0 Hz, H6), 5.83 (t, 1H, H5); ^{13}C NMR (CDCl$_3$) δ=38.62 (C3), 55.83 (-OCH$_3$), 65.54 (C7), 77.50 (C$_5$H$_5$), 78.00 (C2), 78.02 (C4), 82.95 (C6), 90.82 (C5), and 183.94 (C1); IR (KBr) $\nu_{\max}$ 3082, 3018, 2982, 2928, 2820, 1638, 1412, 1388, 1303, 1201, 1100, 1083, 992, 866, 835, 700, 557, 431, and 417 cm^{-1}; UV (CH$_3$CN) $\lambda_{\max}$ 207 (log ε=4.4), 244 (3.9), and 356 nm (3.3); MS (FAB) m/z 304 (M)$^+$; Anal. Calcd for $C_{13}H_{14}O_2Ru$: C, 51.48; H, 4.65%. Found: C, 51.31; H, 4.46%.

(η^5-Cyclopentadienyl)(1,2,3,4,5-η^6-*exo*-ethoxy-7-oxo-2,4-cycloheptadienyl)Ru(II) (3d). Treatment of **1** with KOH (1 equiv) in ethanol affords the corresponding ethoxy derivative in a 36% yield; mp 79—80.5 °C; ^{1}H NMR (CDCl$_3$) δ=0.99 (t, 3H, J=7 Hz, -OCH$_2$CH$_3$), 3.27—3.33 (q, 2H, J=7 Hz, -OCH$_2$CH$_3$), 3.69 (dd, 1H, J_{23}=8.0 Hz, J_{24}=2.0 Hz, H2), 4.02 (t, 1H, J_{23}=7.5 Hz, H3), 4.74 (d, 1H, J_{67}=8.0 Hz, H7), 4.85 (s, 5H, C$_5$H$_5$), 5.02 (t, 1H, H4), 5.10 (dd, 1H, J_{56}=6.5 Hz, H6), 5.80 (t, 1H, J_{45}=6.0 Hz, H5); ^{13}C NMR (CDCl$_3$) δ=15.07 (-CH$_3$), 39.05 (C3), 63.15 (-OCH$_2$-), 66.56 (C7), 77.42 (C$_5$H$_5$), 77.47 (C2), 78.02 (C4), 82.97 (C6), 90.90 (C5), and 184.18 (C1); IR (KBr) $\nu_{\max}$ 2976, 2912, 2878, 1636, 1102, 1097, 1023 cm^{-1}; UV (EtOH) $\lambda_{\max}$ 206 (log ε=4.4), 243 (sh, 3.9), and 357 nm (3.2); MS (EI) m/z 318 (M)$^+$, 289 (M−CO)$^+$, and 245 (M−CO−OCH$_2$CH$_3$)$^+$; Anal. Calcd for $C_{14}H_{16}O_2Ru$: C, 52.97; H, 5.08%. Found: C, 52.67; H, 4.93%.

Tropone-2*d*. A nitrogen saturated solution of **3a** (24 mg, 0.08 mmol) and P(OCH$_3$)$_3$ (400 mg, 3.2 mmol) in CH$_2$Cl$_2$ (6 dm^3) was irradiated with sunlight for 2.5 h in a sealed Pyrex tube (10 dm^3). The reaction mixture was concentrated under reduced pressure to give dark residue, and was chromatographed on silica gel eluting with a mixed solvent (ethyl acetate/hexane=1 : 1). Evaporation of the collected fraction containing tropone-2*d* gave tropone-2*d* (65% H/D exchange) in a 75% yield (3.5 mg, 0.03 mmol). ^{1}H NMR (CDCl$_3$, 500 MHz) δ=6.77 (m, 2H, H4,5), 7.03 (d, 1.3H, H2,7), and 7.11 (m, 2H, H3,6); IR (KBr) $\nu_{\max}$ 1632, 1578, and 1466 cm^{-1}; MS (EI) m/z 107 (M)$^+$, and 79 (M−CO)$^+$; Anal. Calcd for $C_7H_{5.2}D_{0.8}O$: C, 78.62; H, 6.43%. Found: C, 78.76; H, 6.31%.

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