The Base-Catalyzed H/D-Exchange of Anisole Moiety of Ruthenium Complex in Cooperation with Demethylation by Hydroxide Anion in Methanol-d_4

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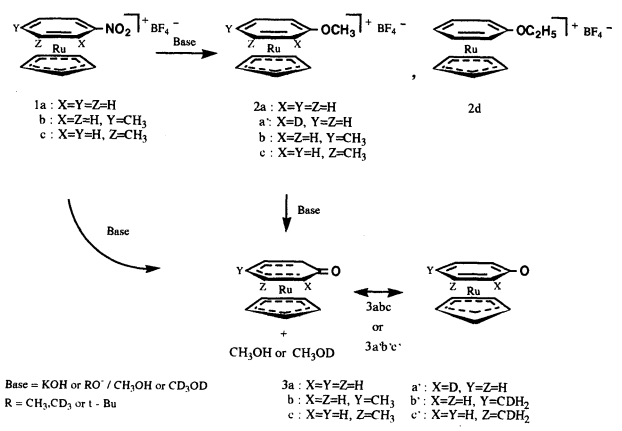
Synopsis. [Ru(η^5-C_5H_5)(η^6-arene A)]BF_4 (arene A=nitrobenzene, *m*- or *p*-nitrotoluene, anisole, phenetole, *m*- or *p*-methylanisole) were quantitatively converted to pure [Ru(η^5-C_5H_5)(η^6-arene B)]BF_4 (arene B=phenoxido-2*d*, *m*- or *p*-monodeuterated methylphenoxido) in the presence of excess KOH in CD_3OD, whereas [Ru(η^5-C_5H_5)(η^6-anisole)] BF_4 was quantitatively obtained by treatment [Ru(η^5-C_5H_5)(η^6-nitrobenzene)] BF_4 with 1 equivalent KOH or CH_3OK.

Since Wilkinson opened a new chemistry of sandwich-type complexes of transition metals, several interesting synthetic methods for the development of the complexes and applications for catalytic hydrogenation with Ru complexes have been discovered.[1] In particular, we have been interested in roles of a combination of OH^- and alcohols in hydrogenation with Ru complexes. Recently, Jia and Morris reported synthesis of some η^2-dihydrogen and dihydride Ru complexes using hydroxide ion and alcohols.[2] Further, Spies and Angelici reported a new deutration method using [Ru(η^5-C_5H_5)(η^5-thiophene)]BF_4 and KOH in methanol-d_4, however the utility of this method for other arenes has not been tested.[3,6] When we examined nitrobenzene as a typical electron deficient π-aromatic compound, a change of [Ru(η^5-C_5H_5)(η^6-nitrobenzene)]BF_4 **1a** to [Ru(η^5-C_5H_5)(η^6-phenoxide)] **3a** and Ru(η^5-C_5H_5)(η^6-OC_6H_5-2-*d*) **3a′** was observed in the presence of base catalyst in both methanol and methanol-d_4, respectively. The treatment of a CD_3OD solution of **1a** with KOH (1 equiv) at room temperature curiously gave [Ru(η^5-C_5H_5)(η^6-anisole)]BF_4 **2a** without affording deuterated products **1a′** and **2a′**. **2a** changed to **3a** or **3a′** accompanied by the formation of CH_3OH or CD_3OD in the presence of base catalysis in methanol or methanol-d_4. Herein, we report an interesting regioselective H/D exchange reaction of phenoxo moiety derived from **1**.

We prepared [Ru(η^5-C_5H_5)(η^6-*p*-methylnitrobenzene)] BF_4 **1b**, [Ru(η^5-C_5H_5)(η^6-*o*-methylnitrobenzene)] BF_4 **1c**, [Ru(η^5-C_5H_5)(η^6-anisole)] BF_4 **2a**, and [Ru(η^5-C_5H_5)(η^6-phenetole)]BF_4 **2d** by our method for the preparation of **1a**.[4] General procedure for the H/D exchange: a dry CD_3OD (1 ml, 24 mmol) solution of **1a–1c** or **2a–2d** (0.05 mmol) was stirred for 4 h in the presence of KOH (0.14 mmol) at room temperature. After usual workup, **3a′–3c′** were isolated in quantitative total yields. The structure of **3a′–3c′** were assigned by their ^1H NMR, IR, UV, MS, and CH analysis. Nondeuterated **3a–3c** were isolated, when the reaction was performed in methanol. A possibility of deuteride contribution to the H/D exchange is neglected, because even CH_3OD works for the H/D exchange. It should be notable that despite of the synthesis of [Ru(η^5-C_5H_5)(η^6-OC_6H_5)] 2PhOH **4** reported by Chandreds, mother structure **3a** has not been known.[5] The compound **4** shows the ^1H NMR resonances for the ortho, meta, and para hydrogens at δ=4.96, 5.46, and 5.27, whereas **3a′** does the corresponding resonances at δ=5.46, 5.75, and 5.56, respectively. Carbon signals in ^{13}C NMR for **3a′** appear at δ=83.95 ($C_5H_5^-$), 75.47, 74.73, 76.09 (phenolato), and 114.97 (C=O). The larger chemical shift difference in the ortho hydrogens probably relates to the degree of double bond character of the CO bonds in **3a′** and **4**. This reaction can be applied to the preparation of free phenoxido–ruthenium complexes **3**. Although the integration value of the absorption peak of the corresponding 2,6-protons of **3a′** is 60% of that of 3,5-protons (Fig. 1), the value decreases up to 50% as the concentration of KOH increases.

A quite efficient and regioselective H/D exchange was accomplished in the reaction. When just 1 equivalent amount of CH_3OK was added into the solution of **1a–1c** in methanol, corresponding anisole products, **2a–2c**, were isolated quantitatively. Even in methanol-d_4, only **2a–2c** were obtained without H/D exchange. In the first step in the scheme, there are two possible substitution manners, an ipso substitution and a cine substitution. For the distinction, para- and meta-nitrotoluene complexes **1b** and **1c** were used for the reaction, and the corresponding **2b** and **2c** were isolated as a sole product of the ipso substitution. On the otherhand, treatment of **2b** and **2c** with KOH/CD_3OD gives rise to selective H/D exchange of methyl group in phenolato moiety of **3b′** and **3c′**. As a slow exchange of protons is known in the reaction of related methylthiophene Ru complex, this selective H/D-exchange on the methyl substituents are remarkable.[6] The presence of KOH is not definite,



Scheme 1.

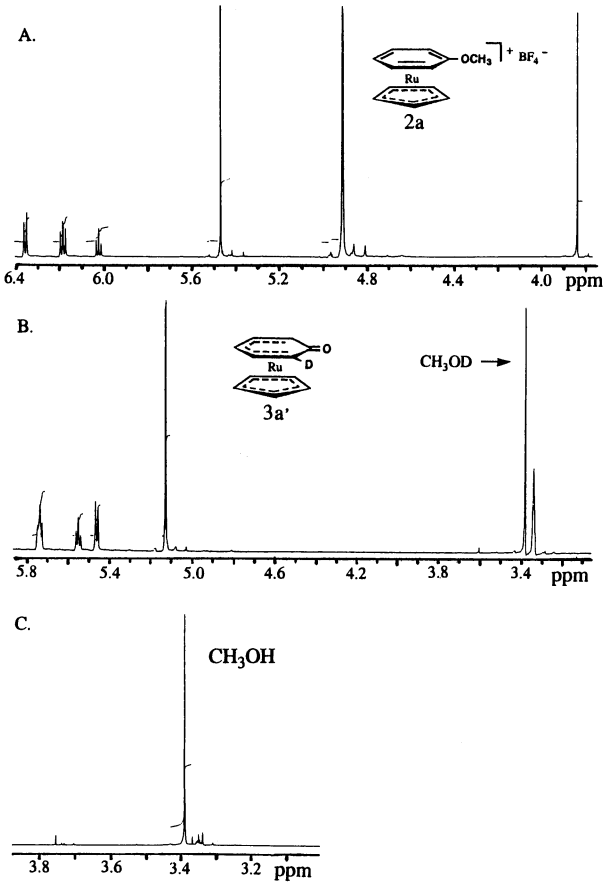


Fig. 1. A=^{1}H NMR spectrum of **2a** before the treatment with CD_3OD/KOH; at room temperature. ^{1}H NMR: 500 MHz/Varian VX-500; Solvent: CD_3OD; Internal standard: TMS; B=^{1}H NMR spectrum of a reaction mixture of **2a** afforded by the treatment with CD_3OD/KOH; C=^{1}H NMR spectrum of methanol in CD_3OD.

because the treatment of **1** with excess CD_3ONa or *t*-BuOK in abs methanol-d_4 or abs *t*-butanol afforded **3a'** or **3a** quantitatively. From these findings, we considered a possibility that a base catalyzed solvolysis of **2a** took place prior to the H/D exchange, followed by the H/D exchange of **2a** giving **3a'** and the corresponding methanol. We confirmed the presence of CH_3OH in the mixture by 500 MHz NMR spectrum by comparison of the singlet resonance peak at 3.39 ppm and that of authentic methanol having the corresponding peak at 3.39 ppm. We recognized that the hydroxide anion attacks the methyl carbon on **2** followed by the H/D exchange to yield **3a'** and CH_3OH or CD_3OD. As the H/D exchange of **3a** and **3b** would not proceed under the reaction conditions, the reaction is characteristic to the base catalyzed H/D-exchange accompaning demethylation by nucleophilic at the methyl group by hydroxide anion. Therefore, phenetole complex **3d** also undergoes the base catalyzed H/D-exchange reaction to give the phenoxido complexes and the corresponding ethanol.

Now we have rationalized all the new reactions of **1** with KOH/CD_3OD in terms of ipso-substitution and the demethylation of anisole moiety in **2** accompanied by H/D exchange in π arene complexes of ruthenium. We are cotinuing both the synthesis and the H/D exchange study of other arene complexes.

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 NMR spectra were recorded on a Varian XL-500 spectrometer (500 MHz) or a JEOL-JNMPMX60 spectrometer (60 MHz) with tetramethylsilane as an internal standard. Mass spectra were obtained on a JEOL-JMS-D300 mass spectrometer of VG Instruments 70-S GAS Chromatograph/Mass Spectrometer.

[Ru(η^5-C_5H_5)(η^6-Nitrobenzene)] BF_4 1a was prepared by the method of Kimura et al.[4]

1a: Yield=73% (lit, 47%); mp 256—259 °C (decomp); ^{1}H NMR (CD_3CN, 60 MHz) δ=5.50 (lit, 5.50) (s, 5H, C_5H_5), 6.46 (6.45) (m, 3H), 7.17 (7.15) (m, 2H).

[Ru(η^5-C_5H_5)(η^6-*p*-Methylnitrobenzene)]BF_4 1b and [Ru-(η^5-C_5H_5)(η^6-*o*-Methylnitrobenzene)]BF_4 1c were prepared from *p*-nitrotoluene and *m*-nitrotoluene by the method as above.

1b: Yield=57%; yellow crystals, mp 288—290 °C; ^{1}H NMR (CD_3CN, 500 MHz) δ=2.37 (s, 3H, OCH_3), 5.46 (s, 5H, Cp), 6.43 (d, 2H, $J_{2,3}$=6.0 Hz), and 7.09 (d, 2H, $J_{3,2}$=6.0 Hz); IR (KBr) ν_{max} 3090, 3026, 1574, 1350, 1036, and 866 cm^{-1}; UV (CH_2Cl_2) λ_{max} 229 nm (log ε=3.8), 279 (sh), and 307 (sh).

1c: Yield=45%; yellow crystals, mp 292—294 °C; ^{1}H NMR (CD_3CN, 500 MHz) δ=2.45 (s, 3H, OCH_3), 5.45 (s, 5H, Cp), 6.35 (d, 1H, $J_{6,5}$=5.8 Hz), 6.37 (t, 1H, $J_{5,4}$=5.7 Hz), 7.06 (dt, 1H, $J_{4,5}$=5.7 Hz), and 7.19 (s, 1H); IR (KBr) ν_{max} 3108, 3028, 1570, 1352, 1036, and 862 cm^{-1}; UV (CH_2Cl_2) λ_{max} 230 nm (log ε=3.8), 255 (sh), and 305 (sh).

Ru(η^5-C_5H_5)(η^6-Phenoxido) 3a from 1a. The solution of KOH (11 mg, 0.19 mmol) in methanol (1 ml) was added to the suspension of **1a** (21 mg, 0.055 mmol) in methanol (1 ml). It was stirred at room temperature under an atmosphere of nitrogen. After stirring 5 min, 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 (300—400 mesh) with a modified syringe for chromatography, eluting with a mixed solvent (ethyl acetate/ethanol=4/1). Concentration of the collected yellow fraction under reduced pressure gave a yellow compound in 88% yield. Recrystallization of this compound from a mixed solvent (carbon tetrachloride/hexane=5/1) gave pale yellow needles; mp 237—239 °C (decomp); ^{1}H NMR ($CDCl_3$, 500 MHz) δ=4.93 (s, 5H, C_5H_5), 5.24 (t, 1H, $J_{4,3}$=5.5 Hz, H4), 5.29 (d, 2H, $J_{3,2}$=7.0 Hz, H2, H6), 5.42 (dd, 2H, $J_{3,4}$=$J_{4,3}$ and $J_{3,2}$=$J_{2,3}$); IR (KBr) ν_{max} 2924, 2856, 1638, 1531, 1468, and 1415 cm^{-1}; UV (EtOH) λ_{max} nm 211 nm (log ε=4.2), 3.10 (3.9); MS (FAB, (Gly)) m/z 261 $(M+1)^+$.

Ru(η^5-C_5H_5)(η^6-*p*-Methylphenoxido) 3b and **Ru(η^5-C_5H_5)-(η^6-*m*-Methylphenoxido) 3c** are prepared by the same method as above starting from **1b** and **1c**, respectively.

3b: Yield=99%; brownish oil; ^{1}H NMR (CD_3CN, 500 MHz) δ=2.19 (s, 3H), 5.10 (s, 5H), 5.47 (d, 2H, $J_{3,2}$=5.8 MHz), 5.77 (d, 2H, $J_{2,3}$=5.8 Hz); IR (KBr) ν_{max} 1541 cm^{-1}; UV (EtOH) λ_{max} 230 nm (log ε=3.8), 272 (sh, 3.4), and 313 (sh, 3.0); MS (FAB, (Gly)) m/z 275 $(M+1)^+$.

3c: Yield=92%; brownish oil; ^{1}H NMR (CD_3CN, 500 MHz) δ=2.24 (s, 3H), 5.09 (s, 5H), 5.40 (d, 1H, $J_{6,5}$=6.0 MHz), 5.58 (bs, 1H), 5.59 (d, 1H, $J_{4,5}$=6.0 MHz), 5.71 (t, 1H, $J_{5,4}$=6.0 Hz, $J_{5,6}$=6.0 Hz); IR (KBr) ν_{max} 2926, 1533 cm^{-1}; UV (EtOH) λ_{max} 230 nm (log ε=3.8), 272 (sh, 3.2), and 315 (sh, 3.0);

MS (FAB, (Gly)) m/z 275 $(M+1)^+$.

Ru(η^5-C_5H_5)(η^6-Phenoxido-2-*d*) 3a′ from 1a. The suspension of **1a** in methanol-d_4 was treated as described in the previous experiment. After the work up, the yellow product was obtained in 98% yield; mp 237—239°C (decomp); ^{1}H NMR ($CDCl_3$, 500 MHz) δ=4.93 (s, 5H, C_5H_5), 5.24 (t, 1H, $J_{4,3}$=4.5 Hz, H4), 5.30 (d, 1H, $J_{6,5}$=6.5 Hz, H6), 5.43 (m, 2H, H3, and H5). **3b′** and **3c′** were preapred by the method as above.

3b′: Yield=92%; brownish oil; ^{1}H NMR ($CDCl_3$) δ=2.182 (2H, m, $-CH_2D$), 5.105 (5H, s, C_5H_5), 5.440 (2H, d, J=5.6 Hz), and (2H, m); IR (KBr) ν_{max} 1535 cm^{-1}; MS (FAB, (Gly)) m/z 276 $(M+1)^+$.

3c′: Yield 76%; brownish oil; ^{1}H NMR ($CDCl_3$)=2.221 (2H, m, $-CH_2D$), 5.090 (5H, s, C_5H_5), 5.405 (1H, t, J=6 Hz), 5.705 (2H, s and d, ortho to C–O), and 5.705 (1H, t, J=6 Hz, metha to C–O); IR (KBr) ν_{max} 1528 cm^{-1}; MS (FAB, (Gly)) m/z 276 $(M+1)^+$. Phenetole, respectively, by the method for **1a**.

[Ru(η^5-C_5H_5)(η^5-Anisole)] BF_4 2a and **[Ru(η^5-C_5H_5)(η^6-Phenetole)] BF_4 2d** were prepared from anisole and phenetole, respectively, by the method for **1a**.

2a: Yield=51%: mp 128—129°C (decomp); ^{1}H NMR (CD_3CN, 500 MHz) δ=3.73 (s, 3H, OCH_3), 5.31 (s, 5H, C_5H_5), 5.85 (t, 1H, para), 6.01 (t, 2H, $J_{3,4}$=6.8 Hz, metha), and 6.12 (d, 2H, $J_{2,3}$=6.8 Hz, ortho); ^{13}C NMR (CD_3CN, 125 MHz) δ= 57.33, 74.75, 80.24, 83.34, 84.58, and 107.01; IR (KBr) ν_{max} 3064, 1531, 1261, and 1085 cm^{-1} (BF_4); MS (FAB, MNBA) m/z 275 (M^+-BF_4); Anal. Calcd for $C_{12}H_{13}BF_4ORu$: C, 39.91; H, 3.63%. Found: C, 39.73; H, 3.49%.

2d: Yield=54%: mp 111—112°C; ^{1}H NMR (CD_3CN, 60 MHz) δ=1.34 (t, 3H, J=6.9 Hz), 4.00 (q, 2H, J=6.9 Hz), 5.29 (s, 5H, C_5H_5), 5.76—6.23 (m, 5H); IR (KBr) ν 2290, 1216, 1033, 1085 cm^{-1} (BF_4); MS (FAB, MNBA) m/z 289 (M^+-BF_4): Anal. Calcd for $C_{13}H_{15}BF_4ORu$: C, 41.62; H, 4.03%. Found: C, 41.55; H, 4.05%.

Treatment of 2a with KOH in Methanol or 10% *t*-BuONa in *t*-Butanol. The solution of KOH (3.7 mg, 0.07 mmol) in methanol (2 ml) was added to the suspension of **2a** (19 mg, 0.05 mmol) in methanol (0.5 ml). The mixture was stirred at room temperature under an atmosphere of nitrogen for 5 min. After the work up as described in previous experiment, a yellow **3a** was obtainied in 29% yield: mp 237—239°C; ^{1}H NMR, IR, UV spectra are identical to the authentic sample. When the reaction was performed with CD_3OD in the presence of 3 equiv $KOCD_3$, the quantitative formation of the deuterated **3a′** and CH_3OD was observed by ^{1}H NMR spectroscopy.

Treatment of 2a with KOH in Ethanol. After work up as above, the quantitative formation of **3a** and ethanol were confirmed by a ^{1}H NMR measurement.

Treatment of 1a with 8% MeONa in Methanol or 10% *t*-BuONa in *t*-Butanol. The solution of 8% MeONa in dry methanol (2 ml) was added to the suspension of **1a** (0.05 mmol) in methanol (0.5 ml). The mixture was stirred at room temperature under an atmosphere of nitrogen for 5 min. After the work up as described in a previous experiment, yellow products **3a** and **3a′** were obtained in 41 and 65% yields, respectively: their ^{1}H NMR, IR, UV spectra are identical to the authentic samples. The treatment of **1a** with 10% *t*-BuONa in *t*-butanol gave **3a** in 50% yield.

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References

1) D. J. Cole- Hamilton, R. J. Young, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, **1976**, 1995; M. V. Baker, L. D. Field, and D. J. Young, *J. Chem. Soc., Chem. Commun.*, **1988**, 546; X. L. R. Fontain, E. H. Fowles, and B. L. Shaw, *ibid.*, **1988**, 482; S. Antoniutti, G. Albertin, P. Amendola, and E. Bordingnon, *ibid.*, **1989**, 229.

2) R. H. Morris, J. F. Sawyer, M. Shiralian, and J. Zubkowski, *J. Am. Chem. Soc.*, **107**, 5581 (1985).

3) a) G. H. Spies and R. J. Angelici, *J. Am. Chem. Soc.*, **107**, 5569 (1985); b) N. N. Sauer and R. J. Angelici, *Organometallics*, **6**, 1146 (1987).

4) M. Kimura, H. Abdel- Halim, D. W. Robinson, and D. O. Cowan, *Organomet. Chem.*, **403**, 365 (1991).

5) B. Chaudred, X. He, and Y. Huang, *J. Chem. Soc., Chem. Commun.*, **1989**, 1844.

6) N. N. Sauer and R. J. Angelic, *Organometallics*, **6**, 1146 (1987).