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Synthesis of and catalytic nitrile hydration by a cationic tris(µ-

hydroxo)diruthenium(II) complex having PMe₃ ligands

Sayori Kiyota, Takako Kobori, Hirofumi Soeta, You-ichi Ichikawa, Nobuyuki Komine, Sanshiro Komiya[§] and Masafumi Hirano*

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-26 Nakacho, Koganei, Tokyo 184-8588, Japan

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CORRESPONDING AUTHOR FOOTNOTE: Phone and facsimile: +81 423 887 044. email: hrc@cc.tuat.ac.jp (MH). [§]Current address: Gakushuin University. Abbreviation used in this text: $COD = cyclooctadiene (C_8H_{12}), COT = cyclooctatriene (C_8H_{12}), Cp^* = pentamethylcyclopentadienyl$ $(C_5Me_5⁻). DMPE = 1,2-bis(dimethylphosphino)ethane (Me_2PC_2H_4PMe_2), DEPE = 1,2$ $bis(diethylphosphino)ethane (Et_2PC_2H_4PEt_2).$

KEYWORDS. C-O Bond activation, Tris(hydroxo)diruthenium(II), Hydration of nitriles

DEDICATION. This article celebrates Martin A. Bennett's 80th birthday and numerous path breaking contributions to organometallic chemistry.

ABSTRACT

While phenyl vinyl ether does not react with $[Ru(\eta^4-1,5-COD)(\eta^6-1,3,5-COT)]$ (1)/PMe₃, the C–O bond cleavage of phenyl vinyl ether occurs by 1/PMe₃ in the presence of water to give a tris(µhydroxo)diruthenium(II) complex $[(Me_3P)_3Ru(\mu-OH)_3Ru(PMe_3)_3]^+[OPh]^-HOPh$ (3·HOPh) with evolution of ethylene. The molecular structure of 3·HOPh is unequivocally determined by X-ray analysis. The most likely mechanism for the formation of 3·HOPh is protonation of $[Ru(\eta^4-1,5-COD)(PMe_3)_3]$ (2c) by water and subsequent insertion of phenyl vinyl ether into the resulting Ru–H bond followed by the β -phenoxide elimination and hydrolysis and dimerization of the phenoxoruthenium(II) species. Complex 3 acts as a catalyst for nitrile hydration. As a typical example, the hydration of benzonitrile was achieved by 3 (1.0 mol%) in 1,4-dioxane at 120 °C for 6 h to give benzamide quantitatively.

1. Introduction

C–O bond cleavage reactions by transition-metal complexes are attractive in relation to development of environmentally benign halogen-free process [1]. In fact, these reactions are widely used as an inlet for the molecular transformation in modern organic synthesis, but the C–O bond cleavage of ethers still remains difficult. The limited examples involve the Ar–OMe bond cleavage using a directing group [2], synthesis of biphenyl from anisol [3], the Ar–OMe cleavage in a pincer ligand [4], and the C–O bond cleavage in dialkyl ethers by Lewis acidic compounds [5]. The C–O bond cleavage in alkenyl ethers is also very difficult but the stoichiometric bimolecular C–O bond oxidative addition by a Lewis acidic Sm(II) complex [6] (Scheme 1, (A)), and β -siloxide elimination [7] from a putative β -siloxyethyl intermediate giving a siloxocobalt(I) are documented (Scheme 1, (B)) [8]. The definitive C–O bond oxidative addition of alkenyl ethers to a mono-nuclear complex has not yet been reported to our best knowledge.

Scheme 1. C-O Bond cleavage reactions of alkenyl ethers.



We have reported allylic C–O bond oxidative additions of carboxylates [9] and ethers [10] to $[Ru(\eta^4-1,5-COD)(\eta^6-1,3,5-COT)]$ (1) in the presence of tertiary phosphine [11] (Scheme 2). While similar vinylic C–O oxidative addition of carboxylates took place to give a

(carboxylato)(vinyl)ruthenium(II) [12], no C-O bond oxidative addition occurred when vinyl ether

was used for the reaction [13].

Scheme 2. Reactions of $[Ru(\eta^4-1,5-COD)(\eta^6-1,3,5-COT)]$ (1) with allyl and vinyl carboxylates and ethers.



However, we accidentally found that water promoted the C–O bond cleavage reaction of phenyl vinyl ether by $1/PMe_3$ to give a cationic tris(μ -hydroxo)diruthenium(II) [(Me₃P)₃Ru(μ -OH)₃Ru(PMe₃)₃]⁺[OPh]⁻ (**3**) with evolution of ethylene. In this paper, we disclose the reaction of phenyl vinyl ether with $1/PMe_3$ in the presence of water, and hydration of nitriles catalyzed by **3**.

2. Experimental Section

2.1. General

All procedures described in this paper were carried out under a nitrogen or argon atmosphere by use of Schlenk and screw-cap tubes and vacuum line techniques. Acetone was dried over Drierite and distilled under nitrogen. Benzene, toluene, hexane, THF, 1,4-dioxane and Et₂O were distilled over sodium benzophenone ketyl. These solvents were stored under a nitrogen atmosphere. Acetone- d_6 was dried over Drierite and was distilled under reduced pressure, and stored under vacuum. Benzene- d_6 was dried over sodium wire and stored under vacuum, and it was used by the vacuum distillation prior to use. Chloroform- d_1 was dried over calcium chloride and stored under vacuum. [Ru(η^4 -1,5-COD)(η^6 -1,3,5-COT)] (1) was prepared according to the literature method except for using magnetic stirring instead of ultrasonic irradiation [14]. Preparations of cis- $[\operatorname{Ru}(\operatorname{CH=CH}_2)(\operatorname{OAc-}\kappa^1 O)(\operatorname{dmpe})_2]$ (5a), cis- $[\operatorname{Ru}(\operatorname{CH=CH}_2)(\operatorname{OAc-}\kappa^1 O)(\operatorname{PMe}_3)_4]$ (5b) and trans- $[Ru(CH=CH_2)(OAc-\kappa^1 O)(depe)_2]$ (5c) were reported previously [9b]. Nitriles were used after degassed by freeze-pump-thaw cycles or purified by distillation under reduced pressure. NMR spectra were recorded on a JEOL LA-300 or a JEOL ECX-400P spectrometer (300 MHz and 400 MHz for ¹H, respectively) with chemical shifts reported in ppm downfield from TMS (the solvent peak as an internal standard) for ¹H. IR spectra were recorded on a JASCO FT/IR-410 or JASCO FT/IR4100 spectrometer using KBr disks. GLC analysis was performed on a Shimadzu GC-14B with FID detector equipped with a capillary column (TC-1, 0.25 mm \$\phi\$ x 30 m) for catalytic reactions. GC-8A with TCD detector equipped with a Porapak-Q column (5 mm \$\phi x 2 m) for the qualitative and quantitative analyses of ethylene. GC-MS spectra were performed on a Shimadzu QP2000 equipped with a capillary column (TC-wax and TC-1, 0.25 mm \$\phi\$ x 30 m). Elemental analysis was performed with a Perkin-Elmer 2400 series II CHN analyzer.

2.2. $[(Me_3P)_3Ru(\mu - OH)_3Ru(PMe_3)_3]^+[OPh] \cdot (HOPh)_n (3 \cdot (HOPh)_n).$

(A): Into a toluene solution (8 ml) of $[Ru(\eta^{4}-1,5-COD)(\eta^{6}-1,3,5-COT)]$ (1) (1.0382 g, 3.29

mmol), PMe₃ (2.4 ml, 23 mmol), phenyl vinyl ether (1.7 ml, 14 mmol) and H₂O (600 μ l, 33.3 mmol) were added in a Schlenk tube. The mixture was stirred at 50 °C for 1 day. The solution was added hexane to give complex **3**·1/3 HOPh as white powder in 62% yield (851.8 mg, 1.021 mmol).

(B): Into a toluene (2 ml) solution of **1** (231.1 mg, 0.734mmol), PMe₃ (381 µl, 3.67 mmol), phenyl vinyl ether (360.0 µl, 2.93 mmol) and H₂O (132.0 µl, 7.33 mmol) were added in a Schlenk tube. The mixture was stirred at 50 °C for 2 days to give **3**·HOPh as white powder in 43% yield (143 mg, 0.160 mmol). ³¹P{¹H} NMR (121.5 MHz, acetone- d_6 , 298 K): δ 24.4 (s). ¹H NMR (300 MHz, acetone- d_6 , 298 K): δ 1.41 (m, 54H, PMe₃), 6.24 (t, $J_{\text{H-H}}$ = 6.9 Hz, 2H, OPh(-p)), 6.69 (d, $J_{\text{H-H}}$ = 8.1 Hz, 4H, OPh(-o)), 6.88 ($J_{\text{H-H}}$ = 8.1, 6.9 Hz, 4H, OPh(-m)). IR (KBr, cm⁻¹): 3652(m), 3436(br), 3054(m), 2965(m), 2904(m), 1637(br), 1590(m), 1475(m), 1433(m), 1300(m), 1280(s), 1146(w), 1067(w), 1021(w), 936(vs), 822(w), 753(s), 716(s), 695(s), 667(s), 409(vs). Anal. Found: C. 40.18; H, 7.36. Calcd for C₃₀H₆₈O₅P₆Ru₂: C, 40.18; H, 7.64.

(C): A mixture of **1** (20.2 mg, 0.0641 mmol), PMe₃ (33.0 µl, 0.321 mmol), phenyl vinyl ether (31.0 µl, 0.252 mmol) and H₂O (11.5 µl, 0.638 mmol) in benzene- d_6 (500 µl) was heated for 2 days at 50 °C in an NMR tube. During the reaction, [Ru(η^4 -1,5-COD)(η^4 -1,3,5-COT)(PMe₃)] (**2b**) was initially formed but it gradually decreased with increase of [Ru(η^1 : η^3 -C₈H₁₀)(PMe₃)₃] (**2a**) and [Ru(η^4 -1,5-COD)(PMe₃)₃] (**2c**). The final distributions of the ruthenium species were as follows: **2a** (46%), **2b** (~0%), and **2c** (45%). Right after addition of water into the mixture of **2a-c** with phenyl vinyl ether in benzene- d_6 , white precipitate deposited (Note that tris(hydroxo)diruthenium complex **3** is almost insoluble to benzene). After removal of volatile matters, acetone- d_6 was introduced to make a homogeneous solution. The NMR experiment suggested formation of **3** in 36%/Ru (0.0233 mmol) with complete conversion of **2c** and recovery of **2a** in 40%/**1** (0.0254 mmol).

2.3. Analysis of evolved ethylene

(A): **1** (28.3 mg, 0.0898 mmol) was placed in a Schlenk tube to which dry toluene (2.00 ml) was added by a volumetric pipette and the solution was frozen using liquid nitrogen. On to the frozen solution, PMe₃ (46.5 μ l, 0.449 mmol), H₂O (16.2 μ l, 0.898 mmol) and phenyl vinyl ether (44.1 μ l, 0.359 mmol) were added and these reagents were also frozen by liquid nitrogen. After evacuation of gases, the closed system was heated at 50 °C for 2 days. After addition of methane as an internal standard, the generated gas was analyzed by GLC. Ethylene was generated in 20%/Ru.

(B): **1** (210.9 mg, 0.6695 mmol) was placed in a Schlenk tube to which dry toluene (2.00 ml) was added by a volumetric pipette and the solution was frozen using liquid nitrogen. On to the frozen solution, PMe₃ (348 μ l, 3.35 mmol), D₂O (184 μ l, 10.2 mmol) and phenyl vinyl ether (329 μ l, 2.68 mmol) were added and these reagents were also frozen by liquid nitrogen. After evacuation of gases, the closed system was heated at 50 °C for 2 days. The evolved gases were collected by Toepler pump and the gas was transferred to a gas cell for **IR**. The IR bands clearly suggested formation of ethylene-*d*₁. IR (gas cell, cm⁻¹): 3053(m), 3420(m), 3053(m), 2965(m), 2904(m), 1911(w), 1887(w), 1867(w), 1463(w), 1444 (m), 1419(br), 1005(m), 948(vs), 808(m). The solution involving **3** was evaporated to dryness and the IR spectrum of the residue was measured. IR (KBr, cm⁻¹): 3653(w), 3420(br), 3053(w), 2965(s), 2904(s), 2810(w), 2694(m), 2539(br), 1595(s), 1468(s), 1429(s), 1299(s), 1280(s), 936(vs), 852(m), 821(m), 754(s), 718(s), 694(s), 666(s), 610(s), 570(w), 514(s).

2.4. Reaction of 1 with 3 equiv of PMe₃ without addition of phenyl vinyl ether

Into an NMR tube containing **1** (23.3 mg, 0.0739 mmol), CHPh₃ as an internal standard for the ¹H NMR, and a sealed capillary containing P(OPh)₃ in benzene- d_6 as an internal standard for the ³¹P{¹H} NMR were added. Then benzene- d_6 (600 µl) was introduced into the NMR tube. After the first measurement of the NMR, PMe₃ (23.0 µl, 0.222 mmol) was added. The NMR tube was warmed at 50 °C and the NMR was measured periodically. After 32 h, the yield of **2a**, **2b**, and **2c** were estimated as 66%, 8%, and 20%, respectively.

2.5. $[(Me_3P)_3Ru(\mu-OH)_3Ru(PMe_3)_3]^+[O_2CMe]^-(HO_2CMe)$ (4·HO₂CMe).

A toluene solution (2.00 ml) of **1** (29.2 mg, 0.0927 mmol) with PMe₃ (53.5 µl, 0.556 mmol), H₂O (16.7 µl, 0.927 mmol), and allyl acetate (37.0 µl, 0.371 mmol) was heated at 50 °C for 2 days. Propylene was generated in 38%/Ru. **4**·HO₂CMe was produced in 37%/Ru yield with concomitant formation of **2a** in 58%/Ru yield. **4**·HO₂CMe was characterized by spectroscopies: ³¹P{¹H} NMR (121.5 MHz, acetone- d_6): δ 24.5 (s). ¹H NMR (300 MHz, acetone- d_6): δ 1.41 (br. s, 54H, PMe₃), 1.77 (s, 6H, O₂CMe). IR (KBr, cm⁻¹): 3651(sh), 3412(br), 2970(m), 2908(m), 1573(vs), 1408(vs), 1302(m), 1282(s), 1018(w), 943(vs), 853(m), 721(s), 667(s), 462(w).

2.6. Reaction of vinylruthenium(II) complexes with water

To a benzene- d_6 solution (600 µl) of *cis*-[Ru(CH=CH₂)(OAc- $\kappa^1 O$)(dmpe)₂] (**5a**: 13.55 mg, 0.02780 mmol), water (5.0 µl, 0.27 mmol) was added by a hypodermic syringe. After heating the reaction mixture at 50 °C for 1 day, unidentified deposition was observed with *trans*-[Ru(CH=CH₂)(OAc- $\kappa^1 O$)(dmpe)₂] in 37%. After injection of pure methane as an internal standard (98.5 µl, 0.00439 mmol), the GLC analysis showed evolution of ethylene (17%, 0.00484 mmol) and ethane (0.5%, 0.000152 mmol). A similar reaction using *cis*-[Ru(CH=CH₂)(OAc- $\kappa^1 O$)(PMe₃)₄] (**5b**) was also performed but **5b** did not react with water at all under these conditions.

2.7. Reaction of vinylruthenium(II) complexes with hydrochloric acid

trans-[Ru(CH=CH₂)(OAc- $\kappa^1 O$)(depe)₂] (**5c**: 9.0 mg, 0.015 mmol) was placed in an NMR tube and excess amount of hydrochloric acid (12 µl, 0.16 mmol) was added into the benzene- d_6 . **5c** was quantitatively converted to trans-[Ru(=CHMe)(OAc- $\kappa^1 O$)(depe)₂]⁺Cl⁻ or trans-

 $[Ru(=CHMe)Cl(depe)_2]^+[OAc]^-$. ¹H NMR (300 MHz, benzene-*d*₆): δ 0.8 (m, 12H, PCH₂*Me*), 1.0 (m,

12H, PCH₂*Me*), 1.24 (m, 4H, PCH₂Me), 1.56 (s, 3H, OA*c*), 1.5-1.8 (m, 12H, PCH₂Me), 1.9-2.0 (br, 4H, PCH₂CH₂P), 2.2-2.3 (m, 4H, PCH₂CH₂P), 2.59 (d, $J_{\text{H-H}} = 7$ Hz, 3H, Ru=CH*Me*), 16.7 (oct, $J_{\text{H-H}} = J_{\text{H-P}} = 7$ Hz, 1H, Ru=CHMe). ³¹P{¹H} NMR (122 MHz, benzene-*d*₆): δ 46.7 (s).

2.8. General procedure for the catalytic hydration of nitriles

(A): Complex **3** (21.2 mg, 0.0237 mmol) was placed in a Schlenk tube and acetone- d_6 (2.00 ml) was added by a volumetric pipette. A portion of the solution (500 µl) was moved to an NMR tube by a hypodermic syringe, and benzonitrile (30.3 µl, 0.296 mmol), water (18.0 µl, 1.0 mmol) and 1,4-dioxane (5.9 µl, 1.0 mmol) as an internal standard were added. The reaction mixture was warmed at 50 °C for 88 h.

(B): Complex **3** (18.3 mg, 0.0204 mmol), 1,4-dioxane (1.0 ml), benzonitrile (103.7 mg, 1.18 mmol), water (100 μ l, 5.53 mmol) were added in a screw-cap tube. The reaction mixture was heated at 100 °C for 12 h. After cooling the reaction mixture to room temperature, dibenzyl and methanol (1 ml) were added to give a homogeneous solution and the products were analyzed by GLC.

2.9. X-ray analysis of $[(Me_3P)_3Ru(\mu-OH)_3Ru(PMe_3)_3]^+[OPh]^-(HOPh)(3\cdot HOPh).$

Rigaku AFC-7R-Mercury II diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) were used for data collection at 200.0 K. A selected single crystal of **3**·HOPh was mounted on the top of glass capillary by use of Paraton N oil. The collected data were solved by direct methods (SIR92), and refined by a full-matrix least square procedure using SHELXL in the CrystalStructure (ver.4.2) package program [15,16]. All non-hydrogen atoms were refined with anisotropic displacement parameters. A hydrogen atom attached to O(1) was found from the differential Fourier map and it was solved isotropically. The other O-H protons were not found and were excluded from the calculations. The other hydrogen atoms were placed in calculated positions

and were not refined. The molecular structure was depicted with POV-Ray [17]. The

crystallographic data of 3. HOPh were deposited and available as CCDC1449576.

3. Results and Discussion

3.1. Synthesis of Cationic Tris(μ -hydroxo)diruthenium(II) Complex.

When phenyl vinyl ether was treated with $[Ru(\eta^4-1,5-COD)(\eta^6-1,3,5-COT)]$ (1)/PMe₃ in benzene at 50 °C, a mixture of *fac*- $[Ru(\eta^1:\eta^3-C_8H_{10})(PMe_3)_3]$ (**2a**) [18], $[Ru(\eta^4-1,5-COD)(\eta^4-1,3,5-COT)(PMe_3)]$ (**2b**) [18, 19] and $[Ru(\eta^4-1,5-COD)(PMe_3)_3]$ (**2c**) [20] was obtained in 46%, ~0% and 45% yields, respectively, and the added phenyl vinyl ether remained unreacted [21]. Because such a bunch of these phosphine complexes **2a-c** was formed from **1**/PMe₃ without addition of phenyl vinyl ether under the similar conditions (**2a**: 66%, **2b**: 8%, **2c**: 20%) [18, 22], phenyl vinyl ether did not engage with the formation of **2a-c** at all. However, we accidentally found that addition of water into the mixture involving **2a-c** and phenyl vinyl ether caused complete conversion of **2c** into white precipitates of $[(Me_3P)_3Ru(\mu-OH)_3Ru(PMe_3)_3]^+[OPh]^-HOPh ($ **3**-HOPh) in 36% yield based on**1** (81% yield based on**2c**), while**2a**remained intact. Because neither phenyl vinyl ether nor waterapparently reacts with**2c**individually, both of them must engage with this reaction. Thus, weintentionally added water into the starting solution involving**1**/PMe₃ phenyl vinyl ether, and thereaction at 50 °C for 2 days afforded**3**-HOPh in 43-62% yields, which was isolated as analyticallypure white powder (Scheme 3).

SCRI

Scheme 3. Reactions of $[Ru(\eta^4-1,5-COD)(\eta^6-1,3,5-COT)]$ (1)/PMe₃ with phenyl vinyl ether in the

presence of water.



Complex **3** was characterized by NMR, IR and elemental analysis but most unambiguously by X-ray analysis (*vide infra*). ³¹P{¹H} NMR spectrum of **3** in acetone- d_6 showed a singlet at δ 24.4, suggesting all PMe₃ to be equivalent. The ¹H NMR suggested that **3** had 1 equiv of associated phenol, which was indistinguishable from the phenoxide anion. By the subsequent experiments, **3** was found to have arbitrary amount of phenol by hydrogen bonding. The ¹H NMR showed a multiplet resonance of PMe₃ at δ 1.41 (54H) probably due to the A₃XX'₂ spin system, and phenoxide/phenol resonances at δ 6.24 (t, 2H), 6.68 (d, 4H), and 6.88 (t, 4H) in acebtone- d_6 . All hydroxo resonances have not been clearly observed in our complex in the ¹H NMR, but the IR spectrum suggests the presence of the hydroxo groups. Nakamoto reported compounds containing the hydroxo groups to exhibit the v(OH), δ (MOH) and v(MO) at 3760-3000, 1200-700, and 900-300 cm⁻¹, respectively [23]. In fact, **3**-HOPh showed characteristic bands at 3652 and 3436 cm⁻¹, which were assignable to the v(OH) bands.

3.2. Molecular structure of 3

Single crystals of **3** were obtained by the fractional crystallization from cold THF as analytically pure colorless needles. The molecular structure by the X-ray crystallographic analysis clearly indicated formation of **3**·HOPh, though the two of three hydroxo protons and a phenol proton could not be observed from the differential Fourier map (Fig. 1).



Fig. 1. Molecular structure of $[(Me_3P)_3Ru(\mu-OH)_3Ru(PMe_3)_3]^+[OPh]^- HOPh ($ **3**HOPh) with selected numbering schemes. All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability (R = 0.0475, wR = 0.1077).

Fig. 1 shows **3** being a cationic tris(μ -hydroxo)diruthenium(II) complex having six PMe₃ ligands. The Ru–O bond lengths are in the range 2.138-2.162 Å and the Ru(1)–O–Ru(2) angles are in 89.18-89.98°. The short bond length between O(4) and O(5) in phenol-phenoxide (2.39 Å) suggests an interaction through the hydrogen bond. Reetz and coworkers also reported the short O…O length in [NBu₄]⁺[PhO·HOPh]⁻ to be 2.471(5) Å [24]. The Ru(1)–Ru(2) is 3.0306(16) Å, and this issue is discussed later.

A handful of cationic tris(μ -hydroxo)diruthenium(II) complexes have been known. The first example was prepared as the arene complex $[(\eta^6-C_6H_6)Ru(\mu-OH)_3Ru(\eta^6-C_6H_6)]^+Cl^-[25,26]$ by the reaction of $[RuCl_2(\eta^6-C_6H_6)]_2$ with aqueous NaOH, and the X-ray structure of the mesitylene analogue was also reported [27]. The Cp* analogue $[Cp*Ru(\mu-OH)_3RuCp*]^+[NO_3]^-$ was prepared from $[RuCp*Cl_2]_2$ in refluxing water and AgNO₃ [28], and the triazacyclononane analogue $[LRu(\mu OH_{3}RuL_{1}^{2+}[PF_{6}]_{2}^{-}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) was prepared by treatment of $[LRu(\mu-O)(\mu-OAc)_2RuL]^+[PF_6]_2^-$ with H₂SO₄ in water and zinc amalgam, and subsequent oxidation of the mixed valence complex with $Na_2S_2O_8$ followed by the anion exchange produced corresponding Ru(III) analogues $[LRu(\mu-OH)_3RuL]^{3+}[PF_6]_3^{-1}$ and the perchlorate analogue [29]. The corresponding tertiary phosphine complexes have also been documented. Singleton and coworkers prepared the PMe₂Ph complex, $[(Me_2PhP)_3Ru(\mu-OH)_3Ru(PMe_2Ph)_3]^+[BPh_4]^-$ by hydrolysis of $[RuH(n^4-1,5-COD)(PMe_2Ph)_3]^+[BPh_4]^-$ in refluxing acetone-methanol [30]. The striking resemble example $[(Me_3P)_3Ru(\mu-OH)_3Ru(PMe_3)_3]^+[BF_4]^-$ was reported by treatment of a trivalent diruthenium complex $[(Me_3P)_3Ru(\mu-CH_2)_3Ru(PMe_3)_3]$ with Ph₃CBF₄ in THF [31], although the formation mechanism was not discussed in this paper. Bergman and coworkers briefly commented that treatment $[Ru(C_2H_4)(PMe_3)_4]$ with excess water may give a compound formulated as $[(Me_3P)_3Ru(\mu OH_{3}Ru(PMe_{3})_{3}^{+}[OH]^{-}$ as a side product [32].

Table 1 shows selected distances and angles for **3**·HOPh and reported tris(μ -hydroxo)diruthenium(II) complexes. Wilkinson and coworkers pointed relation between the Ru–Ru lengths in tris(μ -bridged)diruthenium complexes and the formal oxidation state [33]. In fact, the Ru^{IV}–Ru^{IV} in [(Me₃P)₃Ru(μ -CH₂)₃Ru(PMe₃)₃]²⁺[BF₄]₂⁻ and the Ru^{III}–Ru^{III} bond length in [(Me₃P)₃Ru(μ -CH₂)₃Ru(PMe₃)₃] fall in 2.641(1) Å and 2.650(1) Å, respectively, while the Ru–Ru bond length in [(Me₃P)₃Ru(μ -OH)₃Ru(PMe₃)₃]⁺[BF₄]⁻ [3.004(1) Å] was a good evidence for the Ru^{III}–Ru^{III} [31]. Wieghhardt and coworkers also documented the shorter Ru^{II}–Ru^{III} lengths in [LRu(μ -OH)₃RuL]²⁺[PF₆]₂⁻ [2.401(2) Å] and the Ru^{III}–Ru^{III} length in [LRu(μ -OH)₃RuL]³⁺[ClO₄]₃⁻ [2.505(3) Å] (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) [29]. The present Ru(1)–Ru(2) length is

3.0306(16) Å and is consistent with a Ru^{II} - Ru^{II} complex. These features are explained that the formal Ru–Ru bond order increases on going from Ru^{II} - Ru^{II} , Ru^{II} - Ru^{III} , Ru^{III} - Ru^{III} and Ru^{IV} - Ru^{IV} , because electrons from the anti-bonding orbitals are stepwise removed (Fig. 2) [29]. These complexes shown in Table 1 roughly reflect this feature.

Table 1. Selected bond and angles (deg) and distances (Å) for some tris(μ-hydroxo)diruthenium(II) complexes [25-31, 33].

Complex	Ru(1)-O-Ru(2)	Ru-O	Ru(1)-Ru(2)
$[(Me_{3}P)_{3}Ru(\mu-OH)_{3}Ru(PMe_{3})_{3}]^{*}[OPh]^{-}(HOPh) (3 \cdot HOPh)$	89.18-89.98	2.138-2.162	3.0306(16)
$[(Me_{3}P)_{3}Ru(\mu-OH)_{3}Ru(PMe_{3})_{3}]^{+}[BF_{4}]^{-}$	89.0-89.5	2.134-2.144	3.004(1)
$[(PhMe_2P)_3Ru(\mu-OH)_3Ru(PMe_2Ph)_3]^+[BF_4]^-$	90	2.15-2.21	3.08
$[(\eta^{6}\text{-}C_{6}H_{6})Ru(\mu\text{-}OH)_{3}Ru(\eta^{6}\text{-}C_{6}H_{6})]^{+}Cl^{-}3H_{2}O$	90.6-92.1	2.071-2.092	2.9812(7)
$[(\eta^{6}-C_{6}H_{3}Me_{3})Ru(\mu-OH)_{3}Ru(\eta^{6}-C_{6}H_{3}Me_{3})]^{+}CI^{-}\cdot 3H_{2}O$	90.9	2.087-2.109	2.989(3)
$[LRu(\mu\text{-}OH)_3RuL]^{2+}[PF_6]_2 \cdot H_2O^{a)}$	90.9(4)	1.955(10)	2.401(2)
$[LRu(\mu-OH)_{3}RuL]^{3+}[ClO_{4}]_{3}^{-a}$	75.0	2.06	2.505(3)

^{a)}L = 1,4,7-trimethyl-1,4,7-triazacyclononane



Fig. 2. Orbital diagrams for diruthenium complexes having D_{3h} symmetry.

In order to understand the mechanism, we performed this reaction in a closed system. The reaction produced **3**·HOPh in 25% yield with evolution of ethylene (20%) and concomitant formation of **2a** (74%) [Eq. (1)] [34].

1 $\xrightarrow{\text{PMe}_{3}, \text{H}_{2}\text{OPh}}$ 1 $\xrightarrow{\text{PMe}_{3}, \text{H}_{2}\text{O}}$ 1 $\xrightarrow{\text{toluene}}$ $3 \cdot \text{HOPh} + C_{2}\text{H}_{4} + 2a$ (1) 50 °C, 2 d 25%/Ru 20%/Ru 74%/Ru in closed system

We also used D_2O for this reaction and the evolved gas was collected in a gas cell for the IR spectrum. The IR spectrum of the collected gas involved characteristic bands at 1419(br), 1005(m), 948(vs), and 808(m) cm⁻¹ in the fingerprint region. The vibration modes for ethylene and a series of deuterated ethylenes are shown in Table 2 [35]. The most consistent understanding of this data is that the collected gas involves ethylene- d_1 . With agreement, a proton is coming from water to give ethylene- d_1 . Because phenyl vinyl ether is not hydrolyzed by water under these conditions, a ruthenium species must concern with the formation of ethylene.

Table 2. Vibration modes for ethylene and deuterated ethylenes.

mode	H H H H		D H D H					this work
 v_4	1027	1000			988	764	726	1005
ν_7		809	752	843	727	727	720	808
v ₈	943	943	944				780	948
v_{12}	1443	1404	1384	1344	1300	1300	1078	1419

The IR spectrum of deuterated analogue $[(Me_3P)_3Ru(\mu-OD)_3Ru(PMe_3)_3]^+[OPh]^-(DOPh)$ (3d₃·DOPh) suggests that the absorption bands at 3652 and 3463 cm⁻¹ in 3·HOPh shift to 2694 and 2539 cm⁻¹, respectively. This is consistent with replacement of O–H with O–D.

Similar treatment of 1/PMe₃ with allyl acetate was performed. As we have reported previously, the C–O bond oxidative addition of allyl acetate to 1/PMe₃ gives a η^3 -allylruthenium(II) complex, [Ru(OAc)(η^3 -C₃H₅)(PMe₃)₃] under the water-free conditions [9]. However, treatment of 1/PMe₃ with allyl acetate in the presence of water produced the corresponding cationic tris(μ hydroxo)diruthenium complex [(Me₃P)₃Ru(μ -OH)₃Ru(PMe₃)₃]⁺[O₂CMe]⁻·HO₂CMe (4·HO₂CMe) in 37% yield along with evolution of propylene (38%).

Scheme 4. Possible mechanism for the formation of 3·HOPh. $\begin{bmatrix} L_n Ru - H \end{bmatrix}^+ OH^+ \stackrel{\checkmark}{\longleftarrow} \begin{bmatrix} PhO_{\downarrow} \end{bmatrix}^+_{-}$ C



Possible formation mechanism of **3** is shown in Scheme 4. The initial reaction of **1** with PMe₃ gives an active zero-valent Ru species [Ru(η^4 -1,5-COD)(PMe₃)₃] (**2c**) with concomitant formation of the other Ru species **2a** and **2b**. A simple pathway is the C–O bond oxidative addition of phenyl vinyl ether to **2c** giving (phenoxo)(vinyl)ruthenium(II) **A**, and subsequent hydrolysis of **A** to give **B** with evolution of ethylene followed by hydrolysis and dimerization of **B** to give **3**·HOPh. However, because **2c** does react with phenyl vinyl ether, it is not clear about why water promotes the C–O oxidative addition to **2c** in this mechanism. We performed the model reactions of *cis*-

[Ru(CH=CH₂)(OAc- $\kappa^1 O$)(dmpe)₂] (**5a**) with water at 50 °C for 1 day but evolution of ethylene and ethane was observed in only 17% and 0.5% yields, respectively. Moreover, *cis*-[Ru(CH=CH₂)(OAc- $\kappa^1 O$)(PMe₃)₄] (**5b**) did not react with water at all under these conditions. When a much stronger acid, hydrochloric acid was added to *trans*-[Ru(CH=CH₂)(OAc- $\kappa^1 O$)(depe)₂] (**5c**) in benzene-*d*₆, **5c** was quantitatively converted into a new species having characteristic ¹H NMR resonances at δ 2.59 (d, *J* = 7 Hz, 3H) and 16.7 (oct, *J* = 7 Hz, 1H) assignable to the methyl and methine protons in Ru=CHMe, respectively. This fact suggests the proton has attacked the β-carbon in the vinyl group to give a carbene complex *trans*-[Ru(=CHMe)(OAc- $\kappa^1 O$)(depe)₂]⁺Cl⁻ or *trans*-

[Ru(=CHMe)Cl(depe)₂]⁺[OAc]⁻ [36]. These results suggest acidity of water being not enough for protonation the vinylruthenium(II) species under these conditions, and a proton favors to attack the β -carbon in the vinylruthenium(II) species rather than evolution of ethylene [37].

The second scenario is the protonation of **2c** by water to give **C** (Scheme 4), insertion of phenyl vinyl ether into the resulting Ru–H bond to give **D**, and subsequent β -phenoxide elimination with evolution of ethylene followed by the hydrolysis and dimerization [38]. Komiya and Shindo reported the β -phenoxide elimination from 2-phenoxyethyl group in *trans*-[PtBr(C₂H₄OPh)(PPh₃)₂] (6) to give ethylene [39]. Komiya and Yamamoto also documented the related β -acetate elimination to give ethylene by the reaction of *cis*-[RuH₂(PPh₃)₄] with vinyl acetate [40]. One of the concerns about this mechanism is that the β -phenoxide elimination from **D** may compete with the β -hydride elimination to reproduce **C**. The β -hydride elimination from **C** establishes reversibility between **C** and **D**, and this reversibility enables introduction of more than one deuterium atom in ethylene, which is inconsistent with the observed result. In fact, thermolysis of **6** at 100 °C is reported to liberate ethylene and phenyl vinyl ether in 1:2 ratio [39], suggesting the β -hydride elimination to proceed at the double rate for the β -phenoxide elimination. Caulton and coworkers also documented rapid and exclusive β -hydride elimination from β -ethoxyethylruthenium(II) [41]. However, the cationic ruthenium(II) center in **C** would have high electrophilicity and it therefore favors the β -phenoxide elimination. We favor this scenario, although we

could not get any mechanistic evidence by stoichiometric reaction of **2c** with water/phenyl vinyl ether by NMR.

3.4. Catalytic hydration of nitriles catalyzed by cationic tris(μ -hydroxo)diruthenium(II) Complex 3

Hydroxo complexes of late transition-metals have been postulated as critical intermediates for the Wacker type oxidation reaction [42] and hydration reaction [43]. Ruthenium complexes are particularly attractive for potential catalysts for hydration [44]. Although tris(μ hydroxo)diruthenium(II) is a common structural motif of hydroxoruthenium species as described above, their catalytic activities are unprecedented so far. We commenced our catalytic study by subjecting benzonitrile and water to catalytic amounts of **3**. By the preliminary studies, we found the optimized conditions to be the reaction in 1,4-dioxane at 120 °C for 6 h with 1.0 mol% of catalyst. With the optimized conditions, we have screened several Ru complexes as shown in Table

Table 3. Hydration of benzonitrile catalyzed by some Ru complexes and related compounds



entry	Cat	time/h	yield/%
1	3	6	100
2	1	18	7
3	$[Ru(acac)_2(\eta^4-1,5-COD)]$	6	0
4	$[RuCl_2(\eta^4\text{-}1,5\text{-}COD)]_n$	6	0
5	$RuCl_3 \cdot 3 H_2O$	6	1
6 ^a	3	88	100
7^{a}	PMe ₃	88	0
8^{a}	KOPh	88	0

^{*a*} acetone- d_6 as solvent at 50 °C.

ber Tris(µ-hydroxo)diruthenium(II) complex 3 catalyzed hydration of benzonitrile in 1,4-dioxane at 120 °C to give benzamide quantitatively. Among these Ru catalysts screened, 3 was the most active catalyst for the hydration. PMe₃ and KOPh do not catalyze the hydration, that excludes the catalysis performed by a liberated base such as PMe₃ or OPh⁻.

With the optimized conditions in hand, we examined the tolerance and electronic effect of functional groups (Table 4). Functional groups including *p*-nitro ($\sigma = 0.78$), *p*-chloro ($\sigma = 0.23$), *p*methyl ($\sigma = -0.17$), *p*-methoxy ($\sigma = -0.27$) and *p*-amino ($\sigma = -0.66$) groups were tolerated, and the reaction seems to be accelerated by an electron-withdrawing group. This result supports that an electrophilic attack of nitrile concerns with the rate-determining step. The *p*-hydroxo and *p*-formyl groups discouraged the hydration. The substituents at the ortho position also discouraged the reaction.

Table 4. Hydration of substituted benzonitrile catalyzed by 3.



Then we turned our attention to hydrolysis of alkyl and alkenyl nitriles (Table 5). Benzyl nitrile and butyronitile also produced corresponding amides in high yield, and acetonitrile was also converted into acetamide in a moderate yield. When acrylonitrile was used for this hydration, a mixture of 3-(2-cyanoethoxy)propanenitrile and acrylamide was produced. 3-(2-

Cyanoethoxy)propanenitrile is probably formed via β -cyanohydrine. One of the features of this catalysis is that the low catalyst loading provides high turnover numbers (TONs). For examples, the acetonitrile hydration proceeds with 2 mol% of **3** in 56% yield, whose TON is 28. With 0.04 mol% of **3**, the TONs reached to 200. In hydration reaction of acrylonitrile, although the TONs for 3-(2-cyanoethoxy)propanenitrile and acrylamide fall in only 0 and 3.5, respectively, with 2.00 mol% of **3**, their TONs (and also their yields) dramatically increased to 1020 and 600, respectively, with 0.03 mol% catalyst loading.

Table 5. Hydration of alkyl and alkenyl nitriles catalyzed by 3.



^{*a*}**3** (2.00 mol%) without solvent. ^{*b*}**3** (0.04 mol%) without solvent. ^{*c*}**3** (2.00 mol%) at 80 °C without solvent. ^{*d*}**3** (0.03 mol%) at 80 °C without solvent.

3.5. Mechanism for catalytic hydration

A simple mechanism for the present hydration catalyzed by **3** is that a nitrile coordinates to one of the Ru centers in diruthenium species and a hydroxo group comes to the coordinated nitrile from another Ru center [45]. However, because TON of the present hydration reaction dramatically increases in low catalyst loading conditions, a rational hypothesis is that a mono-nuclear hydroxoruthenium species is an active catalyst, which constitutes an equilibrium with **3** under the catalytic conditions [46]. In the catalytic benzonitrile hydration, electron-deficient nitriles encouraged the catalytic hydration and the *ortho* substituents discouraged the reaction. These features are consistent with the mechanism involving the prior coordination of nitrile to the resulting coordinatively unsaturated Ru species and nucleophilic attack of the hydroxo group to the coordinated nitrile.

In relation to the Ru-catalyzed nitrile hydrations, Murahashi and coworkers reported a wide range of nitrile hydrations catalyzed by *cis*-[RuH₂(PPh₃)₄] and they proposed an imino intermediate [RuH(N=C(OH)R)L_n] [47]. Sola, Joó and coworkers documented an interesting stoichiometric reaction of *trans*-[Ru(OH)(NCMe)₄(PⁱPr₃)]⁺[BF₄]⁻ to give the amidate complex *fac*-[Ru(NHCOMe-

 $\kappa^2 N, O$)(NCMe)₃]⁺[BF₄]⁻ [48]. In the case of hydroxoplatinum(II), Bennett and coworkers documented nucleophilic *syn* addition of the hydroxo group in [PtMe(OH)(PR₃)₂] to an electron-deficient alkene [49].

The consistent catalytic cycle starting from **3** is depicted in Scheme 5. Complex **3** is converted into a coordinatively unsaturated hydroxo species **E** to which a nitrile coordinates to give **F**. The hydroxo group is nucleophilic and the internal reaction gives **G**, which isomerizes to the more stable **H**. Finally, the hydrolysis of **H** produces amide with reproduction of the hydroxo complex **E**.

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Scheme 5. A possible catalytic cycle for the hydration of nitrile.



4. Conclusions

In summary, the C–O bond cleavage of phenyl vinyl ether occurred by $1/PMe_3$ in the presence of water to give a tris(hydroxo)diruthenium(II) complex $[(Me_3P)_3Ru(\mu-OH)_3Ru(PMe_3)_3]^+[OPh]^-HOPh$ (3-HOPh) in moderate yield. The actual precursor in the formation of 3-HOPh is $[Ru(\eta^4-1,5-COD)(PMe_3)_3]$ (2c) but water is indispensable for the C–O bond cleavage of phenyl vinyl ether. A possible mechanism for the formation of 3-HOPh is protonation of 2c with water, insertion of phenyl vinyl ether into the resulting Ru–H bond, β -phenoxide elimination with evolution of ethylene, and

subsequent hydrolysis and dimerization. Although such tris(hydroxo)diruthenium frameworks have been prepared by different routes, we establish a new direct access to **3** from a Ru(0) complex. We also found **3** to show high catalytic performance for the nitrile hydration reaction for the first time. This finding opens a new horizone for the catalytic applications of hydroxoruthenium complexes.

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References and notes

- (a) A. Yamamoto, Adv. Organomet. Chem. 34 (1992) 111. (b) Y.-S. Lin, A. Yamamoto, in S. Murai, Ed., Topics in Organometallic Chemistry, vol. 3, Springer-Verlag, Berlin, (1999) pp.162. (c) S. Komiya, M. Hirano, in H. Kurosawa, A. Yamamoto Eds., Current Methods in Inorganic Chemistry, vol. 3, Fundamentals of Molecular Catalysis, Elsevier, Amsterdam (2003) pp.115. (d) T. Yamamoto, J. Ishizu, A. Yamamoto, J. Am. Chem. Soc. 103 (1981) 6863.
- [2] F. Kakiuchi, M. Usui, S. Ueno, N. Chatani, S. Murai, J. Am. Chem. Soc. 126 (2004) 2706.
- [3] K. Nakamura, M. Tobisu, N. Chatani, Org. Lett. 17 (2015) 6142.
- [4] M.E. van der Boom, S. Liou, Y. Ben-David, L.J.W. Shimon, D. Milstein, J. Am. Chem. Soc. 120 (1998) 6531.
- [5] (a) P.L. Watson, J. Chem. Soc. Chem. Commun. (1983) 276. (b) Y.K. Gun'ko, P.B.
 Hitchcock, M.F. Lappert, J. Organomet. Chem. 499 (1995) 213.
- [6] K. Takaki, M. Maruo, T. Kamata, Y. Makioka, Y. Fujiwara, J. Org. Chem. 61 (1996) 8332.
- [7] S. Komiya, R.S. Srivastava, A. Yamamoto, T. Yamamoto, Organometallics 4 (1985) 1504.
- [8] The related C–S bond oxidative addition of alkenyl aryl sulfide is also rare but the detailed mechanistic study using Pt(0) is reported: H. Kuniyasu, A. Ohtaka, T. Nakazono, M. Kinomoto, H. Kurosawa, J. Am. Chem. Soc. 122 (2000) 2375.
- [9] (a) S. Komiya, T. Kabasawa, K. Yamashita, M. Hirano, A. Fukuoka, J. Organomet. Chem. 471 (1994) C6. (b) J.G. Planas, T. Marumo, Y. Ichikawa, M. Hirano, S. Komiya, J. Mol. Cat. A: Chem. 147 (1999) 137.
- [10] M. Hirano, N. Kurata, T. Marumo, S. Komiya, Organometallics 17 (1998) 501.
- [11] S. Komiya, M. Hirano, Dalton Trans. (2003) 1439.
- [12] (a) S. Komiya, J. Suzuki, K. Miki, N. Kasai, Chem. Lett. (1987) 1287. (b) J.G. Planas, T. Marumo, Y. Ichikawa, M. Hirano, S. Komiya, J. Chem. Soc., Dalton Trans. (2000) 2613.
- [13] J.G. Planas, M. Hirano, S. Komiya, Chem. Lett. (1999) 953.
- [14] K. Itoh, H. Nagashima, T. Ohshima, N. Oshima, H. Nishiyama, J. Organomet. Chem. 272 (1984) 179.
- [15] G.M. Sheldrick, SHELXL-97; University of Göttingen, Göttingen, Germany, 1997.
- [16] Rigaku crystal structure analysis program, Rigaku Co., Tokyo Japan
- [17] Persistence of vision raytracer Pty. Ltd 2003-2008.
- [18] M. Hirano, T. Marumo, T. Miyasaka, A. Fukuoka, T. Komiya, Chem. Lett. (1997) 297.
- [19] B. Chaudret, G. Commenges, R. Poilblanc, J. Chem. Soc., Chem. Commun. (1982) 1388.
- [20] **2c** was originally reported by Bennett and coworkers by the treatment of $[Ru(\eta^{6} naphthalene)(\eta^{4}-1,5-COD)]$ with PMe₃: M.A. Bennett, Z. Lu, X.-Q. Wang, M. Bown, D.C.R. Hockless, J. Am. Chem. Soc. 120 (1998) 10409. We confirmed the formation of **2c** by the reaction of **1** with PMe₃ under these conditions.

- [21] At the initial stage, **1** was converted into **2b** almost quantitatively.
- [22] S. Komiya, J.G. Planas, K. Onuki, Z. Lu, M. Hirano, Organometallics 19 (2000) 4051.
- [23] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th Ed., Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry, Wiley, New York, 1997, pp274.
- [24] R. Goddard, H.M. Herzog, M.T. Reetz, Tetrahedron 58 (2002) 7847.
- [25] D.R. Robertson, T.A. Stephenson, J. Organomet. Chem. 116 (1976) C29.
- [26] T.D. Kim, T.J. McNeesem A.L. Rheingold, Inorg. Chem. 27 (1988) 2554.
- [27] R.O. Gould, C.L. Jones, T.A. Stephenson, D.A. Tocher, J. Organomet. Chem. 264 (1984) 365.
- [28] R.O. Gould, C.L. Jones, D.R. Robertson, D.A. Tocher, T.A. Stephenson, J. Organomet. Chem. 226 (1982) 199.
- [29] P. Neubold, B.S.P.C. Della Vedova, K. Wieghardt, B. Nuber, J. Weiss, Inorg. Chem. 29 (1990) 3355.
- [30] T.V. Ashworth, M.J. Nolte, E. Singleton, J. Chem. Soc., Chem. Commun. (1977) 936.
- [31] R.A. Jones, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse, K.M. Abudul Malik, J. Chem. Soc., Dalton Trans. (1980) 1771.
- [32] M.J. Burn, M.G. Fickes, J.F. Hartwig, F.J. Hollander, R.G. Bergman, J. Am. Chem. Soc. 115 (1993) 5875.
- [33] M.B. Hursthouse, R.A. Jones, K.M. Adbul Malik, G. Wilkinson, J. Am. Chem. Soc. 101 (1979) 4128.
- [34] Although 3. HOPh is considered to be produced from 2c, it is not clear about why formation of 2a was promoted in this reaction. A significant difference in these conditions from the typical conditions is that this reaction was operated under reduced pressure for qualitative and quantitative analysis of ethylene.
- [35] B.L. Crawford, J.E. Lancaster, R.G. Inskeep, J. Chem. Phys. 21 (1953) 678.
- [36] Similar protonation of [FeCp(CH=CH₂)(CO)₂] with HBF₄ giving
 [FeCp(=CHMe)(CO)₂]⁺[BF₄]⁻ has been reported: K.A.M. Kremer, G.-H. Kuo, E.J. O'Connor, P. Helquist, R.C. Kerber, J. Am. Chem. Soc. 194 (1982) 6119.
- [37] Contrary to vinyl ether, allyl acetate readily reacts with 1/PMe₃ and protonation of [Ru(η^3 -C₃H₅)(OAc)(PMe₃)₃] is easily protonated by HCl to evolve propylene (91%). We cannot rule out the formation mechanism of 4 through the protonation of (acetate)(η^3 -allyl)ruthenium(II) intermediate in the case of allyl acetate.
- [38] However, the ¹H and ³¹P{¹H} NMR resonances of 2c remained unchanged in the presence of water without addition of phenyl vinyl ether. Probably, the equilibrium between 2c and C greatly lies to 2c side.
- [39] S. Komiya, T. Shindo, J. Chem. Soc., Chem. Commun. (1984) 1672.
- [40] S. Komiya, A. Yamamoto, J. Organomet. Chem. 87 (1975) 333.

- [41] J.N. Coalter III, G.J. Spivak, H. Gérard, E. Clot, E.R. Davidson, O. Eisenstein, K.G. Caulton, J. Am. Chem. Soc. 120 (1998) 9388.
- [42] J.W. Gilje, H.W. Roesky, Chem. Rev. 94 (1994) 895.
- [43] T.J. Ahmed, S.M.M. Knapp, D.R. Tyler, Coord. Chem. Rev. 255 (2011) 949.
- [44] R. García-Álvarez, J. Francos, E. Tomás-Mendivil, P. Crochet, V. Cadiermo, J. Organomet. Chem. 771 (2014) 93.
- [45] V.Y. Kukushkin, A.J.L. Pombeiro, Inorg. Chim. Acta, 358 (2005) 1.
- [46] Mononuclear hydroxoruthenium(II) complexes: *trans*-[RuH(OH)(dmpe)₂] and *cis*-[RuH(OH)(PMe₃)₄]: ref. 32, *trans*-[Ru(OH)₂(dmpe)₂]: A.W. Kaplan, R.G. Bergman, Organometallics 17 (1998) 5072.
- [47] (a) S.-I. Murahashi, E. Sasao, E. Saito, T. Naota, J. Org. Chem. 57 (1992) 2521. (b) S.-I. Murahashi, H. Takaya, Acc. Chem. Res. 33 (2000) 225.
- [48] M. Martín, H. Horváth, E. Sola, Á. Kathó, F. Joó, Organometallics 28 (2009) 561.
- [49] M.A. Bennett, H. Jin, S. Li, L.M. Rendina, A.C. Willis, J. Am. Chem. Soc. 117 (1995) 8335.

Synopsis

Treatment of $[Ru(\eta^4-1,5-COD)(\eta^6-1,3,5-COT)]$ (1)/PMe₃ with phenyl vinyl ether in the presence of water gives a tris(μ -hydroxo)diruthenium(II) complex $[(Me_3P)_3Ru(\mu-OH)_3Ru(PMe_3)_3]^+[OPh]^-$ HOPh (**3**·HOPh) with evolution of ethylene. The molecular structure of **3**·HOPh is unequivocally determined by X-ray analysis. Complex **3** acts as a catalyst for nitrile hydration. The hydration of benzonitrile was achieved by **3** (1.0 mol%) in 1,4-dioxane at 120 °C for 6 h to give benzamide quantitatively.

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