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Synthesis and Dehydrative Condensation of Monomeric Hydroxoruthenium Complexes with Hydrotris(3,5-diisopropylpyrazolyl)borate Ligand, $Tp^{iPr_2}Ru(L_2)-OH$ (L_2 = dppe, bipy)

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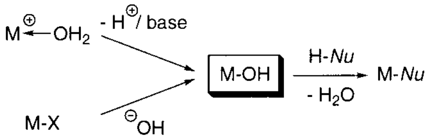
Introduction

Transition metal hydroxo complexes[1] are recognized as versatile precursors for coordination compounds because a variety of compounds are readily obtained via dehydrative condensation with acidic substrates (Scheme 1). One of advantages of dehydrative condensation is that separation of byproduct (water) is very facile compared to other condensation reactions accompanying, for example, salt elimination. Water may be separated from the organic phase, and addition of drying agent would make an equilibrated condensation reaction irreversible. Hydroxo complexes are usually prepared by deprotonation of an aquo complex or by metathesis with hydroxide anion.

We have been carrying out a synthetic study of transition metal complexes with hydrotris(3,5-diisopropylpyrazolyl)borate (Tp^{iPr_2}) related to dioxygen activation.[2,3] As a result, a series of peroxo, hydroperoxo, and alkylperoxo complexes are successfully prepared by dehydrative condensation of the corresponding hydroxo complexes with hydrogen peroxide and alkyl hydroperoxide. During the course of our study of the ruthenium complexes with the Tp^{iPr_2} ligand,[2e−g] we succeeded in the synthesis and characterization of rare examples of mononuclear neutral hydroxoruthenium complexes and the elucidation of the mechanism of their dehydrative condensation reactions.

Experimental Section

Scheme 1



General Methods. All manipulations were carried out under an inert atmosphere by using standard Schlenk tube technique. Aqueous KOH solution was degassed and kept under Ar. $[Tp^{iPr_2}Ru(OH_2)(L_2)]OTf$ [L_2 = dppe (**1a**), bipy (**1b**)] samples were prepared according to the reported method.[2e] Details of X-ray crystallography are included in Supporting Information.

Tp^{iPr_2}RuOH(dppe) (2a). To a THF solution (7 mL) of **1a**·THF (188 mg, 0.16 mmol) was added 1.0 M aqueous KOH (10 mL). The resultant yellow precipitate was collected and dried under reduced pressure. The residue was dissolved in 15 mL of ether and filtered through a Celite pad. Evaporation followed by crystallization from THF−hexane gave **2a** as orange crystals (141 mg, 0.14 mmol, 92% yield). Anal. Calcd for $C_{53}H_{71}BN_6OP_2Ru$ (**2a**): C, 64.82; H, 7.29; N, 8.56. Found: C, 64.67; H, 7.12; N, 8.47.

$Tp^{iPr_2}RuOH(H_2O)$(bipy) (2b). Complex **2b** was obtained from **1b** as a dark-green solid (49%) following the procedure described for **2a**. Anal. Calcd for $C_{37}H_{57}BN_8O_2Ru$ (**2b**): C, 58.64; H, 7.58; N, 14.79. Found: C, 58.43; H, 7.60; N, 15.01.

$Tp^{iPr_2}Ru(OCOCH_3)$(dppe) (3c). Acetic acid (20 μL, 0.35 mmol) was added to a toluene solution (10 mL) of **2a** (81 mg, 0.082 mmol), and the mixture was stirred for 5 h at room temperature. After removal of the volatiles under vacuum, the residue was dissolved in 10 mL of toluene. NaOMe (50 mg, 0.93 mmol) was added and filtered through a Celite pad. The filtrate was evaporated to dryness under reduced pressure. Recrystallization from THF−hexane at −30 °C gave **3c** (75 mg, 0.073 mmol, 89% yield) as a pale-yellow solid. Anal. Calcd for $C_{55}H_{73}BN_6O_2P_2Ru$ (**3c**): C, 64.51; H, 7.19; N, 8.21. Found: C, 64.66; H, 7.41; N, 7.95.

$Tp^{iPr_2}Ru(OCOC_6H_4Cl)$(dppe) (3d). Complex **3d** was obtained from **2a** and *m*-chlorobenzoic acid as a yellow solid (62%) following the procedure described for **3c**. Anal. Calcd for $C_{60}H_{74}BClN_6O_2P_2Ru$ (**3d**): C, 64.31; H, 6.66; N, 7.50. Found: C, 64.06; H, 7.01; N, 6.98.

$Tp^{iPr_2}Ru(OH_2)(dppe)\cdot(OCOCH_3)$ (4a). To a toluene solution (5 mL) of **2a** (75 mg, 0.076 mmol) was added acetic acid (4.5 μL, 0.079 mmol). Removal of the solvent under reduced pressure followed by washing of the residue with a minimum amount of cold hexane gave **4a** (51 mg, 0.049 mmol, 64% yield) as a yellow solid. Anal. Calcd for $C_{55}H_{75}BN_6O_3P_2Ru$ (**4a**): C, 63.39; H, 7.25; N, 8.06. Found: C, 63.55; H, 7.14; N, 7.84.

$Tp^{iPr_2}Ru(OH_2)(dppe)\cdot(OCOC_6H_4Cl)$ (4b). To a toluene solution (10 mL) of **2a** (126 mg, 0.13 mmol) was added *m*-chlorobenzoic acid (20 mg, 0.13 mmol). After the solution was stirred for 5 min at room temperature, the volatiles were removed under reduced pressure. Crystallization of the resultant yellow solid from THF−hexane gave yellow crystals of **4b**·2THF. Drying the crystals under reduced pressure afforded the yellow solid of **4b** (121 mg, 0.11 mmol, 83% yield). Anal. Calcd for $C_{60}H_{76}BClN_6O_3P_2Ru$ (**4b**): C, 63.29; H, 6.73; N, 7.38. Found: C, 62.95; H, 7.11; N, 7.17.

$Tp^{iPr_2}Ru[(CH_3CO_2)_2H]$(dppe) (5). A mixture of **2a** (122 mg, 0.12 mmol) and acetic acid (20 μL, 0.35 mmol) dissolved in ether (10 mL) was stirred for 12 h at room temperature. After removal of the volatiles under reduced pressure, the residue was washed with a small amount of hexane and analytically pure **5** was obtained as a pale-yellow solid (109 mg, 0.10 mmol, 81% yield). Anal. Calcd for $C_{57}H_{77}BN_6O_4P_2Ru$ (**5**): C, 63.15; H, 7.16; N, 7.75. Found: C, 63.02; H, 7.44; N, 7.94.

Results and Discussion

Synthesis of Hydroxo Complexes, $Tp^{iPr_2}Ru(L_2)-OH$ (2). Treatment of a THF solution of aquo-dppe complex **1a** with an aqueous KOH solution afforded hydroxo complex **2a** as yellow powders (Scheme 2).[4] Attempted hydroxylation of the chloro complex $Tp^{iPr_2}Ru(dppe)-Cl^{2e}$ by an aqueous NaOH solution

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[2] Our recent studies of Tp^{R_x} second-row metal complexes. Rh: (a) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121. (b) Ohta, K.; Hashimoto, M.; Takahashi, Y.; Hikichi, S.; Akita, M.; Moro-oka, Y. *Organometallics* **1999**, *18*, 3234. (c) Takahashi, Y.; Hashimoto, M.; Hikichi, S.; Akita, M.; Moro-oka, Y. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3074. (d) Akita, M.; Hashimoto, M.; Hikichi, S.; Moro-oka, Y. *Organometallics,* in press. Ru: (e) Takahashi, Y.; Akita, M.; Hikichi, S.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 3186. (f) Takahashi, Y.; Hikichi, S.; Akita, M.; Moro-oka, Y. *Organometallics* **1999**, *18*, 2571. (g) Takahashi, Y.; Hikichi, S.; Akita, M.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1999**, 1491. Pd: (h) Akita, M.; Miyaji, T.; Hikichi, S.; Moro-oka, Y. *Chem. Lett.* **1999**, 813. (i) Akita, M.; Miyaji, T.; Muroga, N.; Mock-Knoblauch, C.; Adam, W.; Hikichi, S.; Moro-oka, Y. *Inorg. Chem.* **2000**, *39*, 2096. Review (in Japanese): (j) Akita, M.; Hikichi, S.; Moro-oka, Y. *J. Synth. Org. Chem.* **1999**, *57*, 619. (j) See also references cited in refs 2b and 2i.

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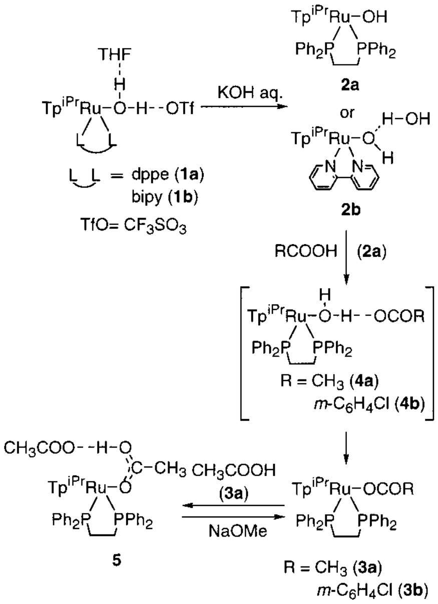
Table 1. Spectroscopic Data for **2**−**5**[a]

	$^1H/\delta_H$/ppm[b]			IR/cm^{-1} [d]		
complex	OH_x, OR	4-pz^{iPr_2}−H[c]	$^{31}P/\delta_P$/ppm	ν(O−H)	ν(C=O)	ν(B−H)
$Tp^{iPr_2}RuOH(dppe)$ (**2a**)	−5.07 (Ru−OH)	5.37, 6.02	79.0	3675 (w)		2539 (m)
$Tp^{iPr_2}RuOH(H_2O)(bipy)$ (**2b**)	−4.1 (Ru−OH), 1.48 (H_2O)	5.81, 6.34		3448 (br)		2532 (w)
$Tp^{iPr_2}Ru(OCOCH_3)(dppe)$ (**3a**)	1.92 (CH_3CO)	5.31, 6.08	75.0		1635 (vs)	2541 (w)
$Tp^{iPr_2}Ru(OCOC_6H_4Cl)(dppe)$ (**3b**)		5.33, 6.06	76.3		1646 (s)	2546 (w)
$Tp^{iPr_2}Ru(OH_2)(dppe)\cdot(OCOCH_3)$ (**4a**)	1.94 (CH_3CO)	5.30, 6.02	78.4	3411 (br)	1712 (w)	2541 (w)
$Tp^{iPr_2}Ru(OH_2)(dppe)\cdot(OCOC_6H_4Cl)$ (**4b**)	*e*	5.28, 6.02	75.5	3423 (br)	1732 (m)	2542 (w)
$Tp^{iPr_2}Ru[(CH_3CO_2)_2H](dppe)$ (**5**)	2.01, 1.76 (CH_3CO)	5.29, 6.05	73.8	3405 (br)	1741 (m), 1584 (s)	2547 (w)

[a] NMR spectra were observed in C_6D_6 at 200 MHz (^1H) and 81 MHz (^{31}P). [b] All listed signals are singlet signals. Other signals appeared in the following ranges: CH in iPr (δ 2.5−4.0), CH_3 in iPr (δ −0.5−1.5), PPh_2 (δ 6.5−8.5). Signals for the CH_2CH_2 parts in dppe overlap with the iPr signals, and signals of bipy and C_6H_4Cl moieties overlap with the PPh_2 signals. [c] The 4-pyrazolyl proton signals. Intensity ratio is $\delta_H:\delta_H \approx 5.8:6.0 = 1H/2H$. [d] IR spectra were recorded as KBr pellets. [e] H_2O signal was not observed.

Scheme 2



resulted in recovery of the starting material. A ^1H NMR spectrum of **2a** (Table 1) contains a sharp signal at δ_H −5.07 (1H), which is assigned to the OH proton, and the chemical shift value is comparable to those of previously reported neutral mononuclear hydroxoruthenium complexes: δ_H −5.57 for $Cp^*RuOH(PMe_3)_2$;[5] −5.41 for *trans*-$(dmpe)_2RuOH(H)$.[6] This signal disappeared upon addition of D_2O, indicating rapid proton exchange with external water. The weak ν_{OH} absorption observed at 3675 cm^{-1} is in contrast to the intense broad band for **1a** around 3400 cm^{-1}. These spectral features supported formation of a mononuclear hydroxoruthenium complex **2a**, and its molecular structure was determined by X-ray crystallography. An ORTEP view is shown in Figure 1a, and selected bond lengths and angles are listed in Table 2. Complex **2a** is a hexacoordinate complex with Tp^{iPr_2}, dppe, and η^1-hydroxo ligands. According to the CSDS database, while structurally characterized examples of many polynuclear ruthenium complexes with a bridging hydroxo ligand and several cationic monomeric hydroxo ruthenium complexes have been reported so far, complex **2a** belongs to a rare class of structurally characterized monomeric neutral hydroxoruthenium complexes.

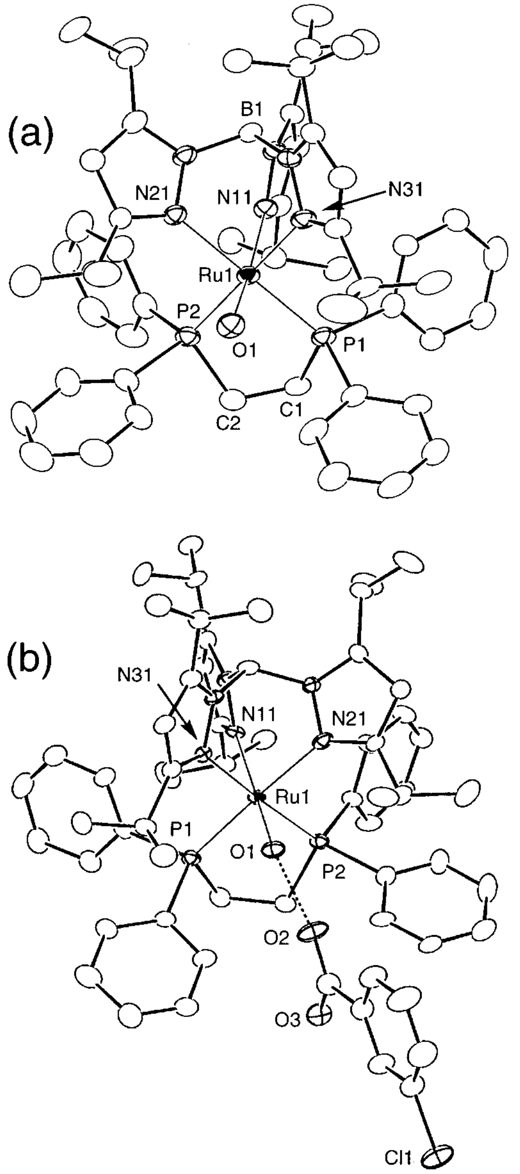


Figure 1. Molecular structures of **2a** (a) and **4b** (b) drawn at the 30% probability level.

The Ru1−O1 length (2.067(4) Å) is significantly shorter than those for the cationic Ru(II)-aquo complexes **1a** [2.148(8) Å][2e] and $[Tp^{iPr_2}Ru(III)(dppe)-OH]PF_6$ [2.158(5) Å],[2g] suggesting increased covalent character of the Ru−O bond in **2a**. The Ru−O length is comparable to those reported for mononuclear hydroxoruthenium complexes, $RuOH(NO_2)_2(NH_3)_2(NO)$ [1.945-

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Table 2. Selected Bond Lengths (in Å) and Angles (in deg) for **2a**, **4b**, and **1a**

	2a	**4b**[a]	**1a**[b]
Ru1−O1	2.067(4)	2.136(8)	2.148(8)
Ru1−P1	2.276(2)	2.273(3)	2.311(4)
Ru1−P2	2.268(2)	2.294(2)	2.287(5)
Ru1−N11	2.232(5)	2.182(7)	2.19(1)
Ru1−N21	2.236(6)	2.237(9)	2.21(1)
Ru1−N31	2.214(5)	2.175(6)	2.20(1)
O1···O2		2.50(1)	2.69(2)
O1−Ru1−P1	92.0(2)	92.7(2)	98.5(3)
O1−Ru1−P2	89.4(1)	96.1(2)	95.5(3)
O1−Ru1−N11	171.3(2)	168.9(2)	165.1(4)
O1−Ru1−N21	87.1(2)	84.2(3)	80.1(4)
O1−Ru1−N31	85.6(2)	81.1(3)	83.8(4)
P1−Ru1−P2	84.82(7)	84.93(8)	84.4(2)

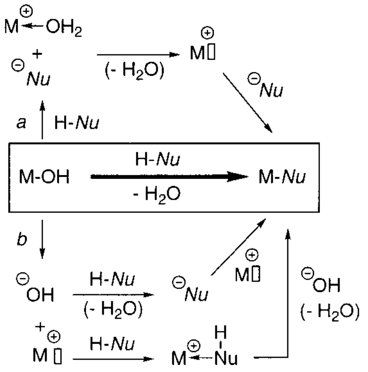
[a] C3−O2: 1.29(1). C3−O3: 1.22(2). O2−C3−O3: 126(1). O2−C3−C2: 115(1). O3−C3−C2: 119.4(8). [b] Reference 2e.

(10) Å][7] and [(η^6-$C_5Me_4CH_2$)RuOH($Me_2NCH_2CH_2NMe_2$)]$^+$ [1.990(3) Å].[8] Although four THF molecules are involved as crystallization solvates in **2a**, no hydrogen-bonding interaction with them is observed. The distance from the hydroxo oxygen atom (O1) to the closest THF molecule [3.83(3) Å] is much longer than the hydrogen-bonded O···O distances found for **1a**, **4b** (vide infra), and related compounds (2.6−2.8 Å).[9]

Deprotonation of aquo-bipy complex **1b** also afforded hydroxo complex **2b** as a dark-green solid in 49% yield. The strong, broad ν_{OH} absorption band around 3448 cm^{-1} and the sharp ^{1}H NMR signal at δ 1.48 (2H) in addition to the broad OH signal at δ −4.1 (1H), however, suggest the presence of an additional water molecule hydrogen-bonded to the hydroxo ligand. The more electron-donating bipyridine ligand [oxidation potentials: −0.244 V (**2a**) vs −0.628 V (**2b**) in THF vs Ag/Ag$^+$] would increase the basicity of the oxygen atom in **2b** to lead to hydration.

Condensation with Protic Substrates. Hydroxo complex **2a** was found to be basic enough to be condensed with acidic substrates such as carboxylic acid.[10] Addition of 1 equiv of acetic acid to **2a** at room temperature produced acetato complex **3a** after stirring for several hours at ambient temperature. Complex **3a** was readily assigned to an octahedral structure on the basis of its spectroscopic features indicating the presence of κ^1-acetato, κ^3-Tp^{iPr_2},[2a] and κ^2-dppe ligands (Table 1). Monitoring the reaction in C_6D_6 by ^{1}H NMR revealed that the condensation consisted of two steps. Addition of the acid caused formation of intermediate **4a**, which showed a distinctive acetate methyl signal at δ_H 1.94 (cf. δ_H 1.92 for **3a**), and continued reaction at room temperature resulted in a gradual conversion to acetato complex **3a**. Intermediate **4a** could be isolated by removal of the volatiles immediately after addition of the acid, and an isolated sample of **4a** was gradually converted to **3a** upon dissolution in C_6D_6. In contrast to **3a**, **4a** showed a broad ν_{OH} vibration, suggesting the presence of hydrogen-bonding interaction similar to those of **1a** and **2b**. Although single crystals of **4a** could not be obtained, *m*-chlorobenzoate derivative **4b**, which showed IR features similar to those of **4a**, was unequivocally characterized by X-ray crystallography as a cationic aquo complex with hydrogen-bonding interaction (Figure 1b). Selected structural parameters of **4b** are given in Table 2. The Ru1−O1 length of 2.136(8) Å is similar to that in **1a** [2.148(8) Å][2e] and longer than that in hydroxo complex **2a**. The *m*-chlorobenzoate anion interacts with the resultant aquo ligand through hydrogen-bonding interaction. Although the overall interaction mode of **4b** and **1a** is essentially the same, the basic carboxylate anion makes the hydrogen-bonding interaction in **4b** considerably stronger than that in **1a** as judged by the O1···O2 separation [2.50(1) Å; 2.69(2) Å in **1a**].[2e] This hydrogen-bonding interaction reveals that the hydroxo oxygen atom in **2a** is basic enough to be protonated by carboxylic acid. Similar behavior was observed for **2b**. Action of an excess amount of acetic acid to **3a** or **1a**, however, gave **5** showing two sets of AcO signals (Table 1), which was assigned as an adduct of acetic acid to acetato complex **3a**. Of the two C═O vibrations, the higher-energy band (1741 cm^{-1}) is comparable to the $\nu_{C=O}$ values for the aquo complexes **4** and the other absorption appears in an energy region lower than that of the carboxylato complexes **3**. Treatment of adduct **5** with NaOMe regenerated acetato complex **3a**.

Scheme 3



These results lead to the conclusion that the dehydrative condensation of the hydroxo complex **2** proceeds by way of the protonated intermediate **4** (Scheme 3). In principle, a couple of mechanisms are possible for dehydrative condensation of coordinatively saturated hydroxometal species. A plausible mechanism involves protonation of the coordinated hydroxo ligand to give the cationic aquo intermediate (route a). Because the water molecule is a good leaving group as usually observed for S_N1 reactions of alcohols in acidic media, a reactive, coordinatively unsaturated cationic species may be formed via elimination of water. The dehydrated species [κ^4-Tp^{iPr_2}Ru(dppe)]$^+$ with an agostic interaction with an iPr methyl proton was actually isolated and fully characterized as recently reported in a communication.[2f] Subsequent coupling with the deprotonated form of the nucleophile affords the substituted product. In another mechanism, spontaneous dissociation of the hydroxide anion followed by a combination of addition of nucleophile and elimination of proton furnishes the condensate (route b). This type of reaction is feasible only when the metal species bears electron-donating ligands that can stabilize the cationic metal residue. In addition, it is well-known that the hydroxide anion is a poor leaving group, and therefore, nucleophilic substitution of an OH group is usually an ineffective method in organic synthesis. Bergman et al. reported functionalization of the hydroxo−hydrido ruthenium complex with two highly electron-donating 1,2-bis(dimethylphosphino)ethane (dmpe)

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(10) Attempted reaction of **1** with ROOH resulted in oxidation of the Ru(II) center to give [Tp^{iPr_2}Ru^{III}(L_2)−OH]$^+$.[2g]

ligands, Ru(H)(OH)$(dmpe)_2$, which was converted to a variety of derivatives by way of oxidative addition or dehydrative condensation.[6] For the reaction with aprotic substrates (H_2 and $HSnPh_3$), they proposed a mechanism related to route b, which involved the ion pair intermediate $[Ru(H)(dmpe)_2]^+(^-OH)$. The ion pair would undergo oxidative addition and could be actually trapped by CO as an ionic adduct, $[Ru(H)(dmpe)_2(CO)]^+(^-OH)$. Although the mechanism for the condensation with protic substrates (phenol, thiophenol, acetone, and 1-alkyne) was not discussed therein, it may proceed via route a. While the mechanism following route a is very simple, the present study verified such a mechanism for the first time by isolation and unequivocal characterization of the intermediates and products.

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Supporting Information Available: Experimental details from X-ray crystallography, tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles, and atomic numbering schemes. This material is available free of charge via the Internet at http://pubs.acs.org.

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