Synthesis of Various Cationic Ruthenium−Aqua Complexes with Hydrotris(3,5-diisopropylpyrazolyl)borate Ligand, $Tp^{iPr}Ru(OH_2)_n(L)_{3-n}\cdot(CF_3SO_3)(THF)_x$, and Their Structures Supported by Hydrogen-Bonding Networks[1]

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Received February 19, 1998

The labile cationic aqua complex, $Tp^{iPr}Ru(OH_2)_2(THF)\cdot(OTf)(THF)_2$, **2**, containing the hydrotris(3,5-diisopropylpyrazolyl)borate ligand (Tp^{iPr}), is prepared by protonolysis of the ruthenium pentahydride complex Tp^{iPr}-RuH_5, **1**, with trifluoromethanesulfonic acid (TfOH) in THF. Treatment of **2** with various 2e and 4e donors results in displacement of the THF and aqua ligands to give $Tp^{iPr}Ru(OH_2)_n(L)_{3-n}\cdot(OTf)(THF)_x$, **3**−**6** (L= py, bipy, phen, pz^{iPr}-H, PPh_3, dppe, MeCN, ^{t}BuCN, =C=C(H)Ph; $n = 0-2$), and thus, complex **2** serves as a versatile precursor for a variety of cationic ruthenium aqua complexes. X-ray crystallographic analysis of the di- (**2**, **3b**,**c**) and monoaqua complexes (**4c**, **5**) reveals ternary hydrogen-bonding networks among the aqua, OTf^-, and THF fragments.

Introduction

Transition metal aqua complexes are classical coordination compounds[2] and have been studied from different viewpoints. They have been recognized as versatile precursors for various coordination compounds, because the aqua ligand in the complexes is usually so labile as to be replaced by other donor ligands.[3] Another important synthetic aspect of aqua complexes is their interconversion with hydroxo[4] and oxo species[5] via deprotonation or oxidation. We have recently established that hydroxo complexes [$(Tp^RM-OH)_n$: $n = 1, 2$] with the hydrotris(pyrazolyl)borate ligand (Tp^R)[6,7] serve as versatile starting compounds for a variety of transition metal complexes (Tp^RM-A) through their condensation with protic substrates (A−H) accompanied by elimination of water. In particular, the reaction of the first row metal hydroxo complexes (Cu, Fe, and Mn) with R′OOH (R′ = H, alkyl) produced various peroxo and alkylperoxo complexes relevant to metalloproteins (O_2-transport proteins and oxygenases). Our research target has been extended to the dioxygen complexes of transition metals not involved in metalloproteins in the hope of achieving a comprehensive understanding of the transition metal dioxygen species.[8] At present, we are studying the synthesis and chemical properties of ruthenium−aqua complexes supported by the hydrotris(3,5-diisopropylpyrazolyl)borate ligand [Tp^{iPr} (Chart 1)],[1] since they are potential precursors for hydroxo complexes.

Usually, aqua complexes are prepared by hydrolysis of halide precursors (Scheme 1). When hydrolysis is carried out in organic solvents, a silver salt is frequently added to enforce the removal of halide ion from the coordination sphere. However, this method is useless for ruthenium complexes supported by the Tp^{iPr} ligand, because the $Tp^{iPr}RuX_n$- and $Tp^{iPr}Ru(L)_2X$-type starting halide complexes are not available.[9] Therefore we chose a hydride complex as an alternative precursor. If H_2 evolution can result from the protonation of a hydride complex, a vacant coordination site will be formed and subsequent trapping by a water molecule will give an aqua complex (Scheme 1). Protonation of hydride complexes has been studied extensively with a particular interest in the formation of molecular hydrogen (η^2-H_2) complexes.[10] It was reported that, in some cases, H_2 evolution followed by incorporation of an external 2e donor (including OH_2) actually afforded a coordination product.

(1) Abbreviations used in this paper. Tp^{iPr}= hydrotris(3,5-diisopropylpyrazolyl)borate; pz^{iPr}-H = 3,5-diisopropylpyrazole; pz = pyrazolyl ring; Tp^{Me} = hydrotris(3,5-dimethylpyrazolyl)borate.

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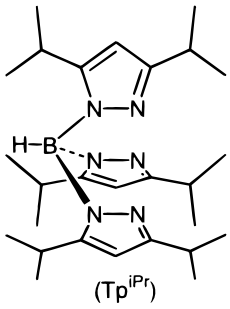
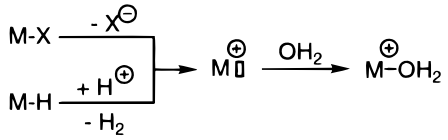
S0020-1669(98)00180-3 CCC: $15.00
Published on Web 06/05/1998

Chart 1



Scheme 1



Herein we disclose the synthesis and structure determination of ruthenium-aqua complexes derived from the protonation of the pentahydride complex $Tp^{iPr}RuH_5$, **1**, derivatives of which were already characterized as bis(dihydrogen) hydride species by Chaudret and co-workers.[11] They studied the protonation of pentahydride complex and adduct formation via a $[Tp^{R}Ru^{+}]$ species. X-ray crystallography of the $Tp^{iPr}Ru$−aqua complexes obtained in our present study reveals that they are incorporated in networks of hydrogen-bonded interactions with the OTf^{-} (counteranion) and THF (solvent). In addition to their unique structural aspects, ligand substitution reaction of the $Tp^{iPr}Ru$−aqua complexes provides an entry into unsymmetrically substituted $Tp^{iPr}Ru(L)_3$-type complexes, not readily accessible via other synthetic routes.[9] Furthermore labile organometallic complexes have potential utility as precursors for catalysts in organic transformation.[12]

Results and Discussion

Synthesis and Structure of the Cationic Diaqua−THF−ruthenium Complex $Tp^{iPr}Ru(THF)(OH_2)\cdot(OTf)(THF)_2$, 2. The transformations discussed in this paper are summarized in Scheme 2.

Treatment of a THF solution of the pentahydride complex **1**[13] with an equimolar amount of trifluoromethanesulfonic acid (TfOH) resulted in H_2 evolution, and orange crystals of **2** were obtained after concentration and cooling at −20 °C. Spectroscopic analysis of **2** revealed the presence of the OH_x, THF, and OTf^{-} components in addition to the κ^3-Tp^{iPr} ligand,[8a] but the featureless broad ^1H and ^{13}C NMR signals observed at room temperature suggested the occurrence of a dynamic process (see below). Then the crystallographic structure determination was performed at a low temperature (−60 °C). An overview is reproduced in Figure 1, and pertinent structural parameters are summarized in Table 1. The central ruthenium atom with octahedral geometry is coordinated by one THF molecule, two water molecules, and the Tp^{iPr} ligand. The Ru−O and Ru−N distances are within the accepted range. The aqua ligands are further hydrogen bonded with two THF molecules and one OTf^{-} counteranion in the second coordination sphere; two of the three oxygen atoms in the OTf^{-} anion interact with the two aqua ligands in a κ^2 mode. The O···O distances of ∼2.7 Å fall in the range of hydrogen-bonding interaction, and details will be discussed later. Although an additional THF solvate molecule is involved, no hydrogen-bonding interaction is found for it.

In order to get information on the dynamic behavior, variable-temperature NMR measurements were examined (Tables S1 and S2, Supporting Information). However, because attempted measurements in CD_2Cl_2 and toluene-d_8 did not give us any analyzable spectra, measurements were carried out in THF-d_8. A ^1H NMR spectrum recorded at −50 °C contained the singlet aqua signal at δ_H 5.06 in addition to the pz and THF signals. Although the three pyrazolyl ring proton signals were accidentally overlapped with each other (δ_H 6.08), the isopropylmethine proton signals appeared in a 1:2 ratio [δ_H 3.06 (2H), 3.29 (1H); the remaining methine proton signals were overlapped with the THF signals] The 1:2 pattern together with the observation of two kinds of ^{13}C NMR signals for the pyrazolyl rings [δ_C 100.5, 100.8 (4-pz), 157.58, 157.73 (5-pz), 167.2, 168.5 (3-pz)] is consistent with the apparent mirror-symmetrical structure determined by X-ray crystallography (Figure 1). As for the lability of the THF moieties, only one set of the THF signals close to free THF signals was observed. Therefore not only the coordinated THF ligand but also the hydrogen-bonded THF molecules were replaced by the solvent at a rate faster than the NMR line-broadening time scale. These observations revealed (1) the labile character of the THF ligand and (2) the dissociation of the hydrogen-bonded THF molecules in a solution.

It is rather difficult to determine the number of THF molecules included in the system by spectroscopic methods. According to the results of NMR and elemental analyses, the THF molecules coordinated to the Ru center and hydrogen bonded with the aqua ligands are not removed by drying under reduced pressure, but the THF solvates are partly or completely removed after drying.

The aqua−THF complex **2** should be formed via the following reaction sequence: (i) initial protonation giving the cationic tris(η^2-dihydrogen) intermediate, $[Tp^{iPr}Ru(\eta^2\text{-}H_2)_3]^{+}$,[11] (ii) replacement of the η^2-H_2 ligands by THF leading to the tris-THF species, $[Tp^{iPr}Ru(THF)_3]^{+}$, and (iii) final replacement of the THF ligands by OH_2. The aqua ligands should come from a trace amount of moisture in the solvent.[3,9i] Although we attempted drying solvents as rigorously as possible, we could not isolate the tris-THF adduct and no intermediate could be detected by ^1H NMR experiments. It is notable that the THF ligand attached to the Ru center in **2** was not replaced even in the presence of an excess amount of water.

(10) Recent papers on η^2-H_2 complexes (see also references therein): (a) Rocchini, E.; Mezzetti, A.; Rüegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Mertinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711. (b) Ayllón, J. A.; Gervaux, C.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1997**, *16*, 2000. (c) Galbert, R.; Moreno, M.; Llunch, J. M.; Lledós *Organometallics* **1997**, *16*, 3805. (d) Jia, G.; Lee, H. M.; Williams, I. D.; Lau, C. P.; Chen, Y. *Organometallics* **1997**, *16*, 3941. (e) Chan, W.-C.; Lau, C.-P.; Chen, Y.-Z.; Fang, Y.-Q.; Ng, S.-M.; Jia, G. *Organometallics* **1997**, *16*, 34. (f) Bohanna, C.; Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Martínez, M.-P. *Organometallics* **1997**, *16*, 4464.

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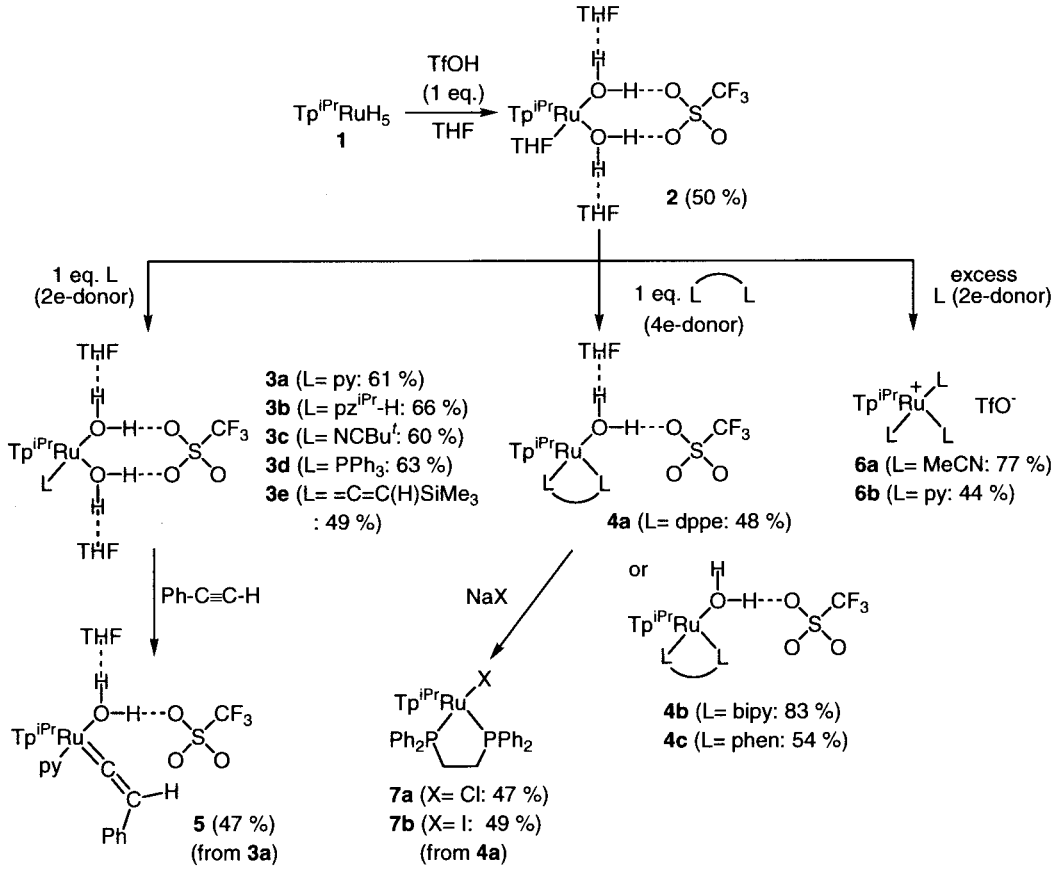
(12) See, for example, ROMP with aqua−ruthenium species: (a) McGrath, D. V.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 3611. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542. (c) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960. (d) Lynn, D. M.; Mohr, B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 1627. Catalytic transformation with ruthenium species: (e) Bruneau, C.; Dixneuf, P. *J. Chem. Soc., Chem. Commun.* **1997**, 507.

(13) The starting pentahydride complex **1** was prepared by hydrogenation of $Tp^{iPr}Ru(H)(cod)$ following the procedure reported for the Tp^{Me} derivative.[11b]

Scheme 2



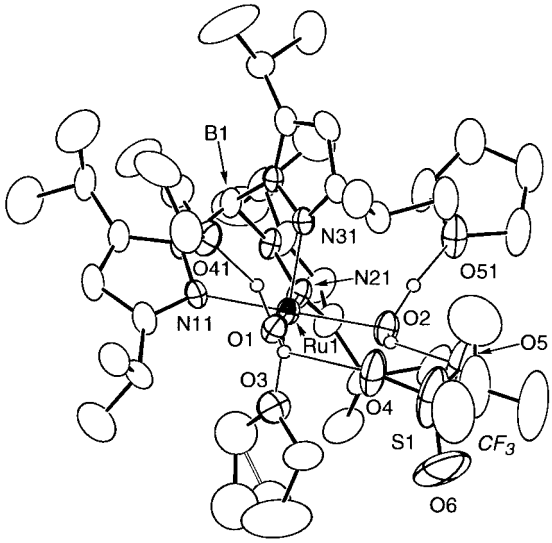


Figure 1. Molecular structure of **2** drawn at the 30% probability level.

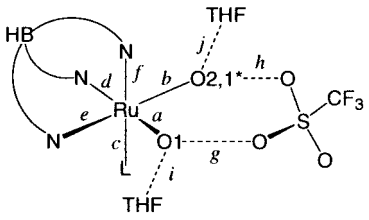
Ligand Substitution Reaction of 2. The aqua−THF complex **2** is expected to be labile as mentioned in the Introduction, and two reaction sites are feasible: one is the THF ligand directly attached to the Ru center, and the other is the aqua ligand incorporated in the hydrogen-bonding network. Both ligands are known to be replaced by 2e donors.

Addition of an equimolar amount of a 2e donor (py, pz^{iPr}-H, $NCBu^t$, PPh_3, $Me_3SiC{\equiv}CH$) to the THF complex **2** in THF afforded the substituted products, $Tp^{iPr}Ru(OH_2)_2(L)\cdot(OTf)\text{-}(THF)_2$ **3** (Scheme 2). The mirror-symmetrical structures resulting from the replacement of the THF ligand rather than the aqua ligand are characterized by NMR features (Tables S1 and S2) similar to those observed for **2** [(1) the ^1H NMR signals of the 4-pyrazolyl ring protons appearing in a 1:2 ratio (δ_H (CD_2Cl_2) 5.84 (2H), 6.09 (1H) (**3a**); 5.88 (2H), 6.04 (1H) (**3b**); 5.90 (2H), 6.05 (1H) (**3c**); 5.63 (2H), 6.08 (1H) (**3d**)); (2) two sets of ^{13}C NMR signals for the pyrazolyl rings]. The aqua proton signals are located in the region (δ_H 3.57−4.00) slightly higher than that of **2**. For the examination of hydrogen-bonding interaction as observed for **2**, molecular structures of **3b**,**c** are characterized by X-ray crystallography. As can be seen from their ORTEP views (Figures 2 and 3), not only the core structures but also the hydrogen-bonding interactions are quite similar to those observed for the starting THF complex **2**. The hydrogen-bonding interaction with the THF molecules is as weak as that observed for **2** (see above), because, for example, dissolution of **4a** (see below) in acetone followed by evaporation of the volatiles caused disappearance of the THF signals.

The vinylidene complex **3e** formed via a 1,2-H shift of (trimethylsilyl)acetylene was readily identified on the basis of the highly deshielded α-carbon signal located at δ_C 339.8.[14] The molecular structure of **3e** was confirmed by X-ray crystallography, but considerable disorder of the OTf^- part was found. [Crystallographic data: $C_{45}H_{84}BN_6O_8F_3SiSRu$, MW = 1066.2, monoclinic space group $P2_1/c$, a = 13.37(1) Å, b = 16.787(9) Å, c = 27.19(1) Å, β= 103.78(6)°, V = 5928(7) Å^3, Z = 4, d_{calcd} = 1.19, μ = 3.8 cm^{-1}, R (R_w) = 0.099 (0.114) for 4140 unique data with $I > 3\sigma(I)$ and 570 variables. Important structural parameters: Ru═C, 1.85(1) Å; C═CH, 1.22(2) Å; ∠Ru═C═C, 170(1)°; C═C−Si, 117(1)°.] Although, in the solid state, complex **3e** adopts an apparent symmetrical structure with the vinylidene mirror plane bisecting the structure, the three pyrazolyl groups are inequivalent (δ_H (THF-d_8) 5.19, 5.99, 6.01)

(14) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

Table 1. Pertinent Interatomic Distances (in Å) for the Ru−Aqua Complexes **2**, **3b**,**c**,**e**, **4a**, and **5**



complex	L	*a* *b*	*c*	*d* *e*	*f*	*g* *h*	*i* *j*
2	THF	2.155(5) (Ru1−O1) 2.151(5) (Ru1 − O2)	2.155(7) (Ru1−O3)	2.036(6) (Ru1−N21) 2.044(6) (Ru1−N11)	2.041(6) (Ru1−N31)	2.724(9) (O1−O4) 2.76(1) (O2−O5)	2.748(8) (O1−O41) 2.790(9) (O2−O51)
3b	pz^{iPr}-H	2.189(6) (Ru1−O1) 2.189(6) (Ru1−O1*)	2.060(8) (Ru1−N31)	2.060(7) (Ru1−N11) 2.060(7) (Ru1−N11*)	2.10(1) (Ru1−N21)	2.889(8) (O1−O2) 2.889(8) (O1*-O2*)	2.84(1) (O1−O41) 2.84(1) (O1*-O41*)
3c	^{t}BuCN	2.168(4) (Ru1−O1) 2.169(4) (Ru1−O2)	2.005(6) (Ru1−N41)	2.060(5) (Ru1−N21) 2.059(5) (Ru1−N31)	2.069(5) (Ru1−N11)	2.679(9) (O1−O3) 2.797(6) (O2−O4)	2.712(7) (O1−O51) 2.729(7) (O2−O61)
3e[a]	=C=C(H)$SiMe_3$	2.152(7) (Ru1−O1) 2.142(7) (Ru1−O2)	1.85(1)[b] (Ru1−C1)	2.02(1) (Ru1−N31) 2.08(1) (Ru1−N11)	2.214(9) (Ru1−N21)	2.72(1) (O1−O3) 2.80(1) (O2−O4)	2.75(1) (O2−O51) 2.77(1) (O1−O41)
4a[c]	dppe	2.148(8) (Ru1−O1) 2.287(5)[d] (Ru1−P2)	2.311(4)[d] (Ru1−P1)	2.19(1) (Ru1−N11) 2.20(1) (Ru1−N31)	2.21(1) (Ru1−N21)	2.69(2) (O1−O2)	2.74(2) (O1−O81)
5[e]	py C=C(H)Ph	2.106(3) (Ru1−O1) 1.802(4)[b] (Ru1−C1)	2.077(3) (Ru1−N41)	2.071(4) (Ru1−N21) 2.199(3) (Ru1−N31)	2.072(3) (Ru1−N21)	2.787(6) (O1−O4)	2.664(4) (O1−O5)

[a] Full details are not reported due to a disorder problem. See text. [b] Ru−C = distance. [c] L and O2 are assumed to be the dppe ligand. [d] Ru−P distances. [e] O2 and L are assumed to be the C=C(H)Ph and py ligands, respectively.

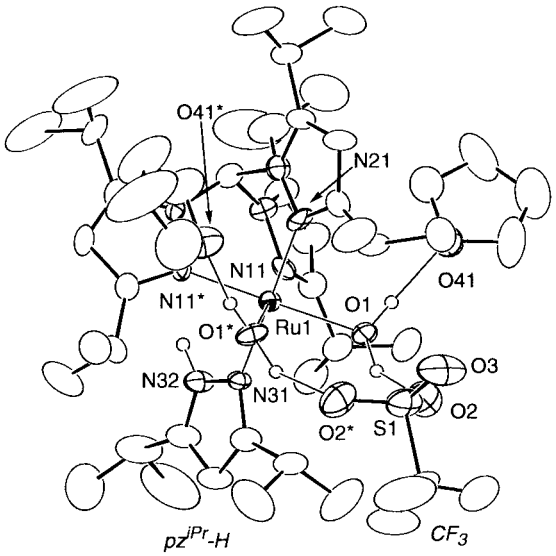


Figure 2. Molecular structure of **3b** drawn at the 30% probability level.

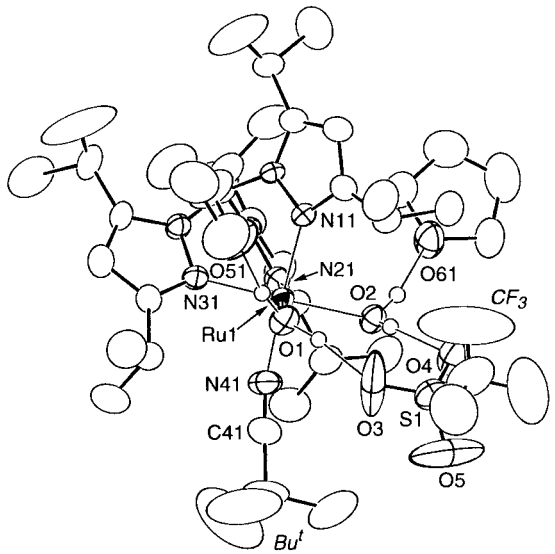


Figure 3. Molecular structure of **3c** drawn at the 30% probability level.

presumably due to hindered motion arising from steric repulsion among the bulky isopropyl and trimethylsilyl groups.

Addition of a 4e donor (L_2: dppe, bipy, phen) to **2** resulted in replacement of the THF ligand and one of the two aqua ligands to give the monoaqua complexes, $Tp^{iPr}Ru(OH_2)(L_2)$·-(OTf)$(THF)_x$, **4** (Scheme 2). The molecular structure of the dppe complex **4a** characterized crystallographically (Figure 4) contains hydrogen-bonding interactions among the aqua, THF, and OTf^- groups similar to those observed for the THF complex **2**. However, because the number of aqua ligands is decreased from two (**2**, **3**) to one (**4**), the OTf^- anion interacts with the aqua ligand in a κ^1 mode. The aqua proton signals are located at a still higher field (δ_H 1.74−3.89) compared to the diaqua complexes **3**. In contrast to the dppe complex **4a**, THF signals were not detected for the bipy (**4b**) and phen complexes (**4c**) by ^{1}H NMR. Therefore they were assigned to the structures

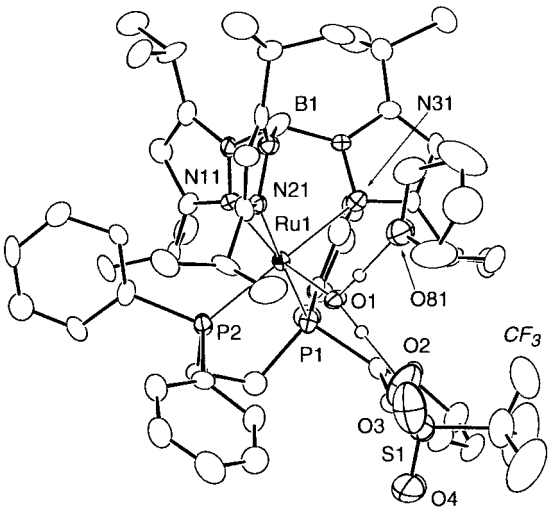


Figure 4. Molecular structure of **4a** drawn at the 30% probability level.

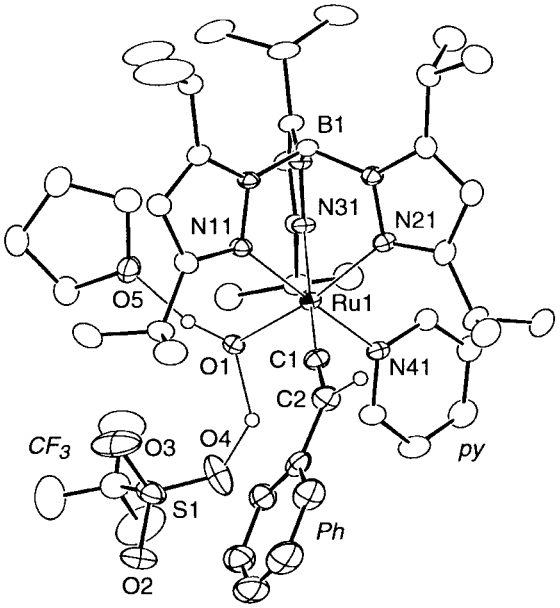
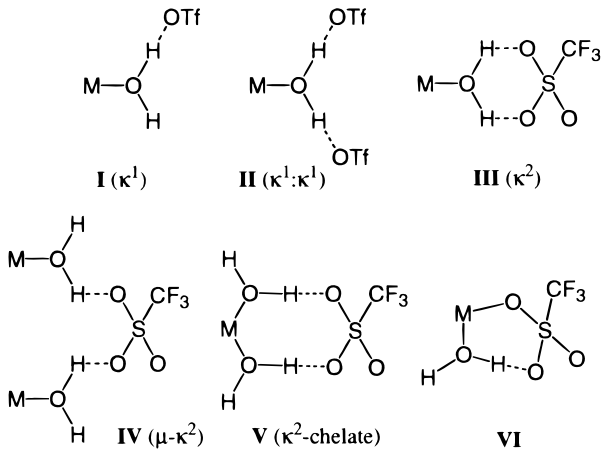


Figure 5. Molecular structure of **5** drawn at the 30% probability level.

depicted in Scheme 2, which lacked the hydrogen-bonding interaction with THF.[14] The more basic nitrogen donors such as bipy and phen would reduce the acidity of the aqua hydrogen atoms which may be hydrogen bonded with THF.

The labile ligands in **2** can be replaced by 2e donors in a stepwise manner. In particular, successive treatment of **2** with two different kinds of 2e donors provides an unsymmetrical, chiral complex. Addition of phenylacetylene to the pyridine adduct **3a** gave the vinylidene complex **5** (Scheme 2), which was characterized by spectroscopy as well as crystallography (Figure 5). The three pyrazolyl rings were inequivalent as observed by NMR (δ_H 5.81, 5.86, 6.07; see Tables S1 and S2). The vinylidene ligand was readily characterized on the basis of the ^{13}C NMR signal located at δ_C 369.2,[14] and the vinylidene β-hydrogen atom signal was observed at δ_H 5.26. As can be seen from the ORTEP view (Figure 5), the THF ligand and one of the two aqua ligands in **2** are substituted by the pyridine and vinylidene ligands, and the latter should be formed via a 1,2-H shift of a transient η^2-alkyne intermediate.[14] In accord with the NMR data, the three different ligands [OH_2, THF, and C═C(H)Ph] occupy the facial coordination sites to make the structure chiral with respect to the 3-fold B···Ru axis. The vinylidene plane is twisted from the in-plane arrangement with respect to the mirror plane of the $Tp^{iPr}Ru$ moiety.

Chart 2



Treatment of **2** with an excess amount of 2e donors such as acetonitrile and pyridine resulted in replacement of all three oxygen donors in **2** to give the tris-adduct, $Tp^{iPr}Ru(L)_3{\cdot}(OTf)$, **6** (Scheme 2). The Tp^{Me} analogue of the acetonitrile adduct **6a** was already prepared by protonolysis of $Tp^{Me}RuH_5$ in MeCN as reported by Chaudret et al.[11] In accord with the formulation, no evidence for a hydrogen-bonding interaction was obtained for **6**.

Finally, we also found that neutral complexes were prepared by treatment of the cationic Tp^{iPr}Ru-aqua complex with anionic species. For example, addition of halide anion to the dppe complex **4a** readily produced the halide complexes **7**, which were characterized by spectroscopic and crystallographic methods.[15] Their metathesis with Grignard and organolithium reagents [9n] would lead to a variety of organoruthenium compounds with the Tp^{iPr} auxiliary. Thus the labile THF complex **2** serves as a versatile precursor for cationic $[Tp^{iPr}Ru(L_1)(L_2)(L_3)]^+$- and neutral $Tp^{iPr}Ru(L_1)(L_2)(X)$-type complexes through successive treatment with 2e or 4e donors.

Molecular Structures of the Tp^{iPr}Ru-aqua Complexes. Trifluoromethanesulfonate (OTf^-) is frequently incorporated in a network of hydrogen-bonding interaction, in particular, when associated with aqua ligands or water solvates, as found for the Tp^{iPr}Ru−aqua complexes **2**−**5** obtained by our present study. Various modes including the typical examples shown in Chart 2 have been reported so far, though direct coordination of the oxygen atom of the OTf^- anion to the metal center is also established.[16] Interaction of one of the three oxygen atoms in

(15) (a) An ORTEP drawing of **7a** is included in the Supporting Information. Important bond lengths: Ru−Cl; 2.352(2) Å; Ru−P, 2.274(2), 2.287(3) Å; Ru−N, 2.220(7), 2.229(5), 2.259(5) Å. (b) Crystallographic data for **7b**: $C_{53}H_{70}BN_6P_2RuI$, MW = 1091.9, triclinic space group P1, a = 13.30(1) Å, b = 19.391(8) Å, c = 11.46(1) Å, α = 99.27(6)°, β = 114.09(5)°, γ = 85.52(5)°, V = 2662(3) Å^3, Z = 2, d_{calcd} = 1.36, μ = 9.7 cm^{-1}, R (R_w) = 0.081 (0.082) for 3282 unique data with $I > 3\sigma(I)$ and 389 variables. The phenyl groups were refined using rigid group models because of the limited number of diffraction data. Important bond lengths: Ru−I, 2.685(3) Å; Ru−P, 2.278(7), 2.312(7) Å; Ru−N, 2.21(2), 2.23(3), 2.33(2) Å.

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OTf^- with an aqua hydrogen atom gives structure **I**,[17] and both of the aqua hydrogen atoms can be involved in hydrogen-bonding interaction with two OTf^- anions as shown in **II**.[18] The type **I** structure is the most frequently encountered pattern of hydrogen-bonding interaction of the OTf^- anion. Two oxygen atoms in a OTf^- fragment can also take part in the hydrogen-bonding network (κ^2 interaction). The 1:1 and 1:2 adduct formation leads to the cyclic (**III**)[19]and bridging structures (**IV**),[20] respectively. When more than two aqua ligands are coordinated to the metal center, chelating structure **V**[21] is also possible. In the case of the Tp^{iPr}Ru-aqua complexes **2**−**5**, additional interactions with THF molecules are notable. Other examples including **VI**[22] (a combination of the direct coordination and **I**) are also reported.

The structural parameters of the aqua complexes pertinent to the core parts are summarized in Table 1. The structures of the diaqua complexes **2**, **3b**, and **3c** can be characterized as the κ^2-chelate structure **V** with additional symmetrical hydrogen-bonding interaction with two THF molecules. The ternary interaction among H_2O, OTf^-, and THF has a few precedents as reported for the zirconium complexes: $Cp_2Zr(OH_2)_3(OTf)_2(THF)$[19c] and $Cp_2Zr_2(\mu\text{-}OH)_2(OH_2)_6(OTf)_4(THF)_4$.[21a] The structures of the monoaqua complexes **4a** and **5** fall in category **I** with additional hydrogen-bonding interaction with the THF molecule.

The $Ru-OH_2$ distances in the narrow range 2.148−2.189 Å (with the exception of the vinylidene complex **5** [2.106(3) Å]) are comparable to those observed for related cationic ruthenium(II) aqua complexes [2.098−2.171 Å;[23] examples of sulfonate and alkane- and arenesulfonate complexes: $[Ru(OH_2)_6]OTs_2$, 2.107−2.139(2) Å; $[Ru(OH_2)_6](OTs)_2$ (OTs: *p*-toluenesulfonate), 2.107−2.139(2) Å;[23a] $[Ru(\eta^6\text{-}C_6H_6)(OH_2)_3](SO_4)$, 2.095(3), 2.095(2), 2.135(2) Å;[23b] $[Ru(cod)(OH_2)_4](OTs_2)$, 2.158(1), 2.095(2) Å;[23c] $[Ru(Me_4thiophene)(OH_2)_3](OTf)_2$, 2.16(1), 2.17(1) Å;[23d] $[Ru(trispyrazolylmethane)(OH_2)_3](OTs)_2$, 2.121(1), 2.134(1), 2.139(1) Å;[23e] $[RuCp^*(CO)_2(OH_2)]OTf$, 2.171(3) Å].[23f] A shorter bond length was reported for a Ru(IV) complex: $[L_{OEt}(H_2O)Ru(\mu\text{-}O)_2Ru(OH_2)L_{OEt}(OTf)_2]$ (L_{OEt} = $CpCo[P(=O)(OEt)_2]_3$): 2.050(4) Å].[17e] Dependence of the $Ru-OH_2$ distances on other supporting ligands is evident. In the case of **3e** and **5**, the π-accepting vinylidene ligand reduces the electron density at the metal center. The partial multiple bonding character arising from π donation of the aqua oxygen lone-pair electrons would cause the shortening of the $Ru-OH_2$ bond (*a*, *b*). The $Ru-OH_2$ distance of **3e** is in the shorter end of the above-mentioned range, and that of **5** is found to be as short as 2.106(3) Å. On the other hand, the electron-donating pz^{iPr}-H ligand in **3b** causes an increase of electron density at the aqua oxygen atom as well as the hydrogen atoms. As a result, the interaction of the less Lewis acidic aqua hydrogen atoms with the Lewis bases (OTf^- and THF) will be weakened. Judging from the values of *a*, *b*, and *d*−*f*, the electron-donating abilities of L can be estimated to be in the order of pz^{iPr}-H > *t*BuCN ∼ THF > ═C═C(H)R. The O···OTf (*g*, *h*) and O···O (THF) (*i*, *j*) distances fall in the ranges 2.69−2.89 and 2.66−2.84 Å, respectively. Again the O···O distances of the pz^{iPr}-H complex (**3b**) (averaged values: *g*, *h*, 2.89 Å; *i*, *j*, 2.84 Å) are the longest among the complexes examined in our present study, but the tendency for the other ligands is not so straightforward as observed for the $Ru-OH_2$ distances.

Conclusions

The chemistry of Tp^R complexes has been studied as a comparative system of the corresponding $\eta^5\text{-}C_5R_5$ complexes.[7] The electronic and steric environment of the metal center can be tuned by introduction of appropriate substituents to the pyrazolyl rings, and novel structures and reactivities not found for the $\eta^5\text{-}C_5R_5$ system are expected to be established on the basis of the Tp^R system. But as far as the substitution pattern of the $[Tp^{iPr}Ru(L)_3]^+$- and $Tp^{iPr}Ru(L)_2(X)$-type ruthenium complexes is concerned, it is not always easy to synthesize complexes with various combinations of the three ligands, L and X.[9] Symmetrically substituted complexes such as $[Tp^R\text{-}Ru(L)_2(L')]^+$ and $Tp^RRu(L)_2(X)$ may be accessible from the diene complexes $Tp^RRu(\eta^4\text{-diene})(X)$, but so far no general synthetic approach to unsymmetrical complexes with different ligands (L, X) has been reported. We have found that the labile THF complex **2** obtained by the protonolysis of pentahydride complex **1** is a versatile starting compound for a variety of ruthenium complexes **3**−**7** supported by the Tp^{iPr} ligand. Stepwise replacements of **2** with 2e donors lead to unsymmetrically substituted cationic, $[Tp^{iPr}Ru(L^1)(L^2)(L^3)]^+$, and neutral complexes, $Tp^{iPr}Ru(L^1)(L^2)X$.

The aqua complexes derived from **2** involve ternary hydrogen-bonding networks among the aqua, OTf, and THF fragments as was revealed by X-ray crystallographic analysis. Depending on the stoichiometry of the aqua ligand, the single **I**-type and

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double **V**-type structures are formed but such structures are broken in a solution.

Studies on the conversion of the aqua complexes to hydroxo and oxo complexes are now under way, and results will be reported in due course.

Experimental Section

General Methods. All manipulations were carried out under an inert atmosphere by using standard Schlenk tube techniques. THF, ether, hexanes (Na−K alloy), and CH_2Cl_2 (P_2O_5) were treated with appropriate drying agents, distilled, and stored under argon. KTp^{iPr} [24] and pz^{iPr}-H (3,5-diisopropylpyrazole)[24] were prepared according to reported methods, and other chemicals were purchased and used as received. ^1H and ^{13}C NMR spectra were recorded on JEOL GX-270 (^1H, 270 MHz; ^{13}C, 67 MHz), GX-500 (^1H, 500 MHz; ^{13}C, 125 MHz), EX-400 (^1H, 400 MHz; ^{13}C, 100 MHz), and Bruker AC-200 spectrometers (^1H, 200 MHz). Solvents for NMR measurements containing 0.5% TMS were dried over molecular sieves, degassed, distilled under reduced pressure, and stored under Ar. IR spectra (KBr pellets) were obtained on a JASCO FT/IR 5300 spectrometer.

Preparation of $Tp^{iPr}RuH_5$ (1). The pentahydride complex **1** was prepared following the procedures reported for the Tp^{Me} derivative.[11b]

An ethereal solution of $Tp^{iPr}Ru(H)(cod)$[25] (872 mg, 1.29 mmol) in a glass autoclave was pressurized at 5 atm (H_2) and was stirred for 9 h at room temperature. After removal of the volatiles under reduced pressure, the residue was washed with a small amount of pentane at −78 °C. Drying under reduced pressure gave **1** (310 mg, 0.54 mmol, 42% yield) as a colorless solid. **1**: δ_H (C_6D_6) 6.00 (3H, s, pz), 3.71, 3.63 (3H × 2, sept × 2, J = 7.0 Hz, C*H*Me$_2$), 1,27, 1.26 (18H × 2, d × 2, J = 7.0 Hz, CH*Me*$_2$), −11.16 (5H, s, RuH_5); δ_C (C_6D_6) 161.1 (s, 3-pz), 155.3 (s, 5-pz), 98.1 (d, J = 171 Hz, 4-pz), 30.1, 26.6 (d × 2, J = 129 Hz, *C*HMe$_2$), 23.7, 22.9 (qt × 2, J = 127 and 6 Hz, CH*Me*$_2$); IR 2965 (vs), 2930 (s), 2868 (m), 2540 (m, ν_{B-H}), 2388 (w br, ν_{H-H}), 1958 (s, ν_{Ru-H}), 1538 (s), 1462 (s), 1399 (m), 1382 (s), 1306 (s), 1178 (vs), 1054 (s), 821 (m), 788 (s), 765 (m). Anal. Calcd for $C_{27}H_{51}BN_6Ru$: C, 56.73; H, 8.99; N, 14.70. Found: C, 56.25; H, 8.43; N, 14.50.

Preparation of $Tp^{iPr}Ru(OH_2)_2(THF)\cdot(OTf)(THF)_2$ (2). When TfOH (7.5 μL, 0.85 mmol) was added to a THF solution (15 mL) of **1** (485 mg, 0.85 mmol) via a microsyringe, evolution of hydrogen gas was observed. After the resultant mixture was stirred for 12 h at room temperature, the mixture was filtered through a Celite pad. Concentration and cooling at −20 °C gave **2**·THF (443 mg, 0.43 mmol, 50% yield) as pale yellow crystals: IR 3640 (w, ν_{OH}), 3359 (m br, ν_{OH}), 2970 (vs), 2873 (s), 2547 (m, ν_{BH}), 2158 (m), 1538 (s), 1474 (s), 1429 (m), 1396 (s), 1366 (m), 1297 (vs), 1239 (vs), 1181 (vs), 1056 (vs), 1031 (vs), 892 (br w), 796 (m), 765 (w), 663 (m), 638 (s). Anal. Calcd for $C_{40}H_{74}N_6O_8BF_3SRu$ (**2**): C, 49.63; H, 7.71; N, 8.68. Found: C, 49.97; H, 7.78; N, 8.35.

Preparation of $Tp^{iPr}Ru(OH_2)_2(py)\cdot(OTf)(THF)_2$ (3a). Pyridine (18 μL, 0.22 mmol) was added to a THF solution (10 mL) of **2**·THF (228 mg, 0.22 mmol). After the resultant mixture was stirred for 20 min at room temperature, concentration and cooling at −20 °C gave **3a**·0.5THF (135 mg, 0.13 mmol, 61% yield) as yellow crystals: IR 3379 (br s, ν_{OH}), 2971 (vs), 2932 (s), 2871 (s), 2541 (m, ν_{BH}), 2151 (m), 1634 (br w), 1538 (s), 1472 (s), 1450 (m), 1428 (m), 1397 (s), 1382 (s), 1365 (m), 1297 (vs), 1241 (vs), 1177 (vs), 1055 (vs), 1031 (vs), 897 (m), 829 (w), 798 (m), 765 (s), 698 (m), 662 (m), 638 (s), 574 (m), 517 (m). Anal. Calcd for $C_{43}H_{75}BN_7O_{7.5}F_3SRu$ (**3a**·0.5THF): C, 51.08; H, 7.48; N, 9.70. Found: C, 51.29; H, 7.60; N, 9.93.

Preparation of $Tp^{iPr}Ru(OH_2)_2(pz^{iPr}\text{-}H)\cdot(OTf)(THF)_2$ (3b). To a THF solution (10 mL) of **2**·THF (119 mg, 0.11 mmol) was added 3,5-diisopropylpyrazole (18 mg, 0.12 mmol), and the resultant mixture was stirred for 12 h at room temperature. Concentration followed by cooling at −20 °C gave **3b**·THF (85 mg, 0.076 mmol, 66% yield) as yellow crystals: IR 3637 (w, ν_{OH}), 3460 (s br, ν_{OH}), 2968 (vs), 2872 (s), 2545 (w, ν_{BH}), 2155 (s), 1627 (w, 1570 (w), 1538 (s), 1472 (s), 1428 (m), 1397 (s), 1383 (s), 1365 (m), 1293 (vs), 1244 (vs), 1182 (vs), 1056 (vs), 1028 (vs), 899 (w), 795 (s), 767 (m), 663 (m), 639 (s), 574 (w), 518 (m). Anal. Calcd for $C_{49}H_{90}BN_8O_8F_3N_6SRu$ (**3b**·THF): C, 52.54; H, 8.10; N, 10.00. Found: C, 52.26; H, 8.19; N, 9.99.

Preparation of $Tp^{iPr}Ru(OH_2)_2(NCBu^t)\cdot(OTf)(THF)_2$ (3c). To a THF (5 mL) solution of **2**·THF (528 mg, 0.51 mmol) was added ^{t}-BuCN (50 μL, 0.45 mmol). After the resultant mixture was stirred for 1 h at ambient temperature, it was concentrated and cooled at −20 °C to give **3c**·THF as yellow crystals (322 mg, 0.31 mmol, 60% yield): IR 3370 (br s, ν_{OH}), 2968 (vs), 2870 (s), 2540 (m, ν_{BH}), 2241 (m, ν_{CN}), 1635 (br w), 1539 (s), 1471 (s), 1399 (s), 1383 (s), 1293 (vs), 1243 (vs), 1177 (vs), 1054 (s), 1031 (vs), 789 (m), 766 (m), 662 (m), 640 (s). Anal. Calcd for $C_{45}H_{83}BN_7O_8F_3SRu$ (**3c**·THF): C, 51.42; H, 7.96; N, 9.33. Found: C, 51.39; H, 7.96; N, 9.63.

Preparation of $Tp^{iPr}Ru(OH_2)_2(PPh_3)\cdot(OTf)(THF)_2$ (3d). PPh_3 (66 mg, 0.25 mmol) was added to a THF solution of **2**·THF (262 mg, 0.25 mmol), and the mixture was stirred for 1 h at room temperature. Then hexanes were added, and the mixture was concentrated under reduced pressure and cooled at −20 °C. **3d** (185 mg, 0.16 mmol, 63% yield) was isolated as pale yellow needles: IR 3373 (br s, ν_{OH}), 2968 (vs), 2932 (s), 2871 (s), 2541 (w, ν_{BH}), 2155 (w), 1538 (s), 1471 (s), 1433 (m), 1397 (s), 1382 (s), 1293 (vs), 1237 (vs), 1180 (vs), 1162 (vs), 1057 (s), 1028 (vs), 898 (w), 794 (m), 767 (m), 696 (m), 663 (m), 638 (s), 517 (m). Anal. Calcd for $C_{54}H_{81}BN_6O_7F_3PSRu$ (**3d**·2THF): C, 56.00; H, 7.05; N, 7.26. Found: C, 56.24; H, 7.16; N, 7.50.

Preparation of $Tp^{iPr}Ru(OH_2)_2(=C=CHSiMe_3)\cdot(OTf)(THF)_2$ (3e). $Me_3SiC{\equiv}CH$ (12 μL, 0.085 mmol) was added to a THF solution (10 mL) of **2**·THF (89 mg, 0.086 mmol). The mixture was stirred for 3 h at room temperature and then cooled at −20 °C to give yellow crystals. **3e** (36 mg, 0.034 mmol, 39% yield) was isolated as pale yellow needles: IR 3628 (w), 3193 (m br), 2970 (vs), 2933 (s), 2871 (s), 2549 (w, ν_{BH}), 1630 (s), 1538 (s), 1473 (s), 1429 (m), 1396 (s), 1365 (m), 1294 (s), 1249 (vs), 1179 (vs), 1055 (vs), 1032 (vs), 848 (m), 794 (m), 765 (m), 661 (m), 639 (s), 520 (w). Anal. Calcd for $C_{45}H_{84}BN_6O_8F_3SiSRu$ (**3e**·2THF): C, 50.69; H, 7.94; N, 7.88. Found: C, 50.88; H, 8.11; N, 8.36.

Preparation of $Tp^{iPr}Ru(OH_2)(dppe)\cdot(OTf)$ (4a). To **2**·THF (150 mg, 0.14 mmol) dissolved in 10 mL of THF was added dppe (57 mg, 0.14 mmol), and the resultant mixture was stirred for 4 h at ambient temperature. Filtration through a Celite pad, concentration, and addition of hexanes followed by cooling at −20 °C gave **4a** as pale yellow crystals (83 mg, 0.085 mmol, 59% yield): δ_P 81.2 (s); IR 3617 (m, ν_{OH}), 3385 (m br, ν_{OH}), 3059 (m), 2967 (vs), 2932 (s, 2870 (s), 2548 (m, ν_{BH}), 1624 (m), 1539 (s), 1461 (s), 1453 (s), 1383 (s), 1365 (s), 1292 (vs), 1250 (vs), 1224 (s), 1178 (vs), 1159 (vs), 1099 (m), 1052 (s), 1031 (vs), 795 (s), 748 (m), 698 (s), 662 (m), 638 (s), 528 (s), 492 (m). Anal. Calcd for $C_{46}H_{70}BN_6O_5F_3SP_2Ru$ (**4a**·THF): C, 57.85; H, 6.70; N, 6.98. Found: C, 57.70; H, 6.80; N, 7.32.

Preparation of $Tp^{iPr}Ru(OH_2)(bipy)\cdot(OTf)$ (4b). Upon addition of bipy (10 mg, 0.064 mmol) to a THF (5 mL) solution of **2**·THF (63 mg, 0.061 mmol) the solution color changed into purple. After the mixture was stirred for 10 min at room temperature, the volatiles were removed under reduced pressure. Recrystallization from acetone−hexanes gave **4b** as purple needles (45 mg, 0.051 mmol, 83% yield): IR 3651 (br, ν_{O-H}), 2968 (vs), 2933 (s), 2870 (m), 2543 (w, ν_{B-H}), 1538 (m), 1461 (s), 1396 (s), 1364 (m), 1262 (vs), 1176 (vs), 1031 (vs), 789 (m), 767 (s), 665 (m), 639 (s). Anal. Calcd for $C_{38}H_{56}N_6O_4BF_3SRu$ (**4b**·THF): C, 51.29; H, 6.34; N, 12.59. Found: C, 51.29; H, 6.36; N, 13.00.

Preparation of $Tp^{iPr}Ru(OH_2)(phen)\cdot(OTf)$ (4c). Upon addition of phen·H_2O (9 mg, 0.045 mmol) to a THF solution (5 mL) of **2**·THF (43 mg, 0.041 mmol) the solution color changed from yellow to red-purple. After the mixture was stirred for 30 min at room temperature, volatiles were removed under reduced pressure. Recrystallization from THF−hexanes gave **4c**·THF (22 mg, 0.022 mmol, 54% yield) as purple needles: IR 3449 (br, ν_{O-H}), 2968 (vs), 2932 (s), 2869 (m), 2540 (w, ν_{B-H}), 1539 (m), 1469 (s), 1428 (s), 1395 (s), 1263 (vs), 1177 (vs), 1052 (s), 1032 (vs), 846 (m), 791 (m), 720 (m), 639 (vs). Anal. Calcd

(24) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277.

(25) Details will be reported elsewhere. Akita, M.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. Manuscript in preparation.

Table 2. Crystallographic Data

complex	**2**	**3b**	**3c**	**4a**	**5**	**7a**
formula	$C_{44}H_{81}N_6O_9BRuSF_3$ (**2**·THF)	$C_{49}H_{90}N_8O_8BRuSF_3$ (**3b**·THF)	$C_{45}H_{83}N_7O_8BRuSF_3$ (**3c**·THF)	$C_{78}H_{120}N_6O_{10}BRuSPF_3$ (**4a**·5THF)	$C_{53}H_{83}N_7O_7BRuSF_3$ (**5**·2THF)	$C_{61}H_{90}N_6O_2BP_2ClRu$ (**7a**·2Et_2O)
fw	1039.1	1120.2	1051.3	1564.7	1131.2	1148.7
space group	*Pbca*	*Cmc*2_1	*P*2_1/*c*	*P*2_1/*n*	$P\bar{1}$	*P*2_1/a
a/Å	33.33(3)	16.121(5)	13.287(3)	18.18(1)	13.35(2)	17.985(2)
b/Å	19.440(3)	21.492(5)	16.412(4)	19.685(4)	23.699(8)	19.453(5)
c/Å	16.698(3)	17.156(4)	26.64(2)	24.253(7)	10.158(3)	20.194(3)
α/deg					96.46(2)	
β/deg			102.66(4)	108.77(4)	112.60(5)	115.19(1)
γ/deg					80.97(5)	
V/Å^3	10819(6)	5943(2)	5668(4)	8217(6)	2925(3)	6393(1)
Z	8	4	4	4	2	4
T/°C	−60	−60	−60	−60	−60	25
λ/Å	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
d_{calcd}/g·cm^{-3}	1.28	1.25	1.23	1.27	1.28	1.19
μ/cm^{-1}	3.9	3.6	3.7	3.2	3.7	3.8
$R(F_o)^a$	0.085	0.052	0.071	0.107	0.053	0.064
$R_w(F_o)^b$	0.103	0.034	0.081	0.114	0.057	0.108

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$.

for $C_{40}H_{56}N_8O_4BF_3SRu$ (**4c**): C, 52.90; H, 6.29; N, 11.98. Found: C, 52.58; H, 5.94; N, 11.56.

Preparation of Tp^{iPr}Ru(OH$_2$)(py)[=C=C(H)Ph)]·(OTf)(THF) (5). To a THF solution of **3a** (211 mg, 0.25 mmol) was added PhC≡CH (28 *μ*L, 0.25 mmol), and the mixture was stirred at room temperature for 2 h. After the volatiles were removed under reduced pressure, crystallization from THF−hexanes gave **5** as brown plates (110 mg, 0.097 mmol, 47% yield): IR 3600−3000 (br maximum at 3131, ν_{OH}), 2972 (vs), 2933 (s), 2870 (s), 2553 (m, ν_{BH}), 1626 (s), 1595 (s), 1539 (s), 1472 (s), 1450 (s), 1429 (m), 1394 (s), 1365 (m), 1297 (vs), 1241 (vs), 1169 (vs), 1053 (s), 1030 (s), 899 (w), 796 (m), 764 (s), 698 (m), 662 (m), 638 (s), 583 (w), 517 (w). Anal. Calcd for $C_{45}H_{67}BN_7O_5F_3SRu$ (**5**·THF): C, 54.76; H, 6.84; N, 9.93. Found: C, 54.73; H, 6.99; N, 9.45.

Preparation of Tp^{iPr}Ru(NCMe)$_3$·(OTf) (6a). **2**·THF (256 mg, 0.25 mmol) was dissolved in 5 mL of acetonitrile. After 30 min of stirring at room temperature, the solution color changed from yellow to colorless. After removal of the volatiles, the product was recrystallized from acetone−hexanes. **6a**: 158 mg, 0.19 mmol, 77% yield; IR 2966 (vs), 2933 (s), 2869 (s), 2541 (w, ν_{BH}), 2273 (w, ν_{CN}), 1541 (m), 1471 (s), 1431 (m), 1401 (s), 1383 (s), 1634 (m), 1269 (vs), 1225 (s), 1179 (vs), 1053 (s), 1032 (vs), 789 (m), 767 (m), 724 (w), 714 (w), 663 (m), 640 (s), 574 (w), 518 (m). Anal. Calcd for $C_{34}H_{55}BN_9O_3F_3SRu$ (**6a**): C, 48.68; H, 6.61; N, 15.03. Found: C, 48.40; H, 6.14; N, 14.52.

Preparation of Tp^{iPr}Ru(py)$_3$·(OTf) (6b). To a 10 mL acetone solution of **2**·THF (149 mg, 0.143 mmol) was added pyridine (50 *μ*L, 0.62 mmol). After the mixture was stirred for 30 min at room temperature, the volatiles were removed under reduced pressure. The resultant yellow solids were washed with ether and recrystallized at −20 °C from acetone−hexanes to give **6b** (57 mg, 0.060 mmol, 44% yield) as yellow solids: IR 3084 (w), 2971 (vs), 2933 (s), 2871 (m), 2553 (w, ν_{BH}), 1538 (s), 1483 (s), 1444 (s), 1425 (m), 1389 (s), 1366 (m), 1306 (m), 1263 (vs), 1222 (s), 1189 (s), 1177 (s), 1153 (vs), 1051 (s), 1031 (vs), 797 (s), 765 (s), 707 (vs), 663 (w), 638 (vs), 518 (w). Anal. Calcd for $C_{43}H_{61}BN_9O_3F_3SRu$ (**6b**): C, 54.20; H, 6.45; N, 13.23. Found: C, 54.01; H, 6.45; N, 13.21.

Preparation of Tp^{iPr}Ru(dppe)Cl (7a). To an acetone solution (10 mL) of **2**·THF (290 mg, 0.241 mmol) was added LiCl (50 mg, 1.2 mmol), and the resultant mixture was stirred for 2 h at room temperature. After evaporation of the volatiles, products were extracted with ether and passed through an alumina pad. Crystallization from THF and hexanes gave **7a** (114 mg, 0.114 mmol, 47% yield) as yellow crystals: IR 3060 (m), 2966 (vs), 2866 (m), 2528 (w, ν_{BH}), 1541 (s), 1469 (s), 1459 (s), 1433 (vs), 1384 (s), 1362 (m), 1304 (m), 1198 (s), 1178 (s), 1096 (m), 1044 (m), 790 (s), 747 (m), 698 (vs), 663 (m), 525 (s), 491 (w); δ_P ($CDCl_3$) 81.1 (s). Anal. Calcd for $C_{53}H_{70}BN_6ClP_2Ru$ (**7a**): C, 63.63; H, 7.05; N, 8.40. Found: C, 63.89; H, 6.78; N, 8.62.

Preparation of Tp^{iPr}Ru(dppe)I (7b). A mixture of **2**·THF (92 mg, 0.076 mmol) and NaI (50 mg, 0.33 mmol) dissolved in acetone (10 mL) was stirred for 12 h at room temperature. The solution color changed from yellow to brown. After removal of the volatiles under reduced pressure, the products were extracted with ether and passed through a Celite plug. Crystallization from THF−MeOH at −20 °C gave **7b** (41 mg, 0.038 mmol, 49% yield): IR 3056 (m), 2961 (vs), 2865 (s), 2525 (w, ν_{B-H}), 1541 (s), 1458 (s), 1433 (s), 1377 (s), 1360 (m), 1304 (m), 1262 (s), 1200 (s), 1177 (m), 1096 (vs), 1042 (vs), 791 (vs), 745 (m), 700 (vs), 660 (s), 527 (s), 490 (m), 434 (w); δ_P 83.5 (s). Anal. Calcd for $C_{53}H_{70}BN_6P_2RuI$ (**7b**): C, 58.30; H, 6.46; N, 7.70. Found: C, 57.95; H, 6.33; N, 7.68.

Experimental Procedure for X-ray Crystallography. Suitable single crystals were obtained from recrystallization from THF (**2**, **3b**,**c**, **4c**, and **5**) and ether (**7a**) and mounted on glass fibers.

Diffraction measurements of **2**, **3c**, **4c**, and **5** were made on a Rigaku RAXIS IV imaging plate area detector with Mo Kα radiation (*λ* = 0.710 69 Å). Indexing was performed from three oscillation images which were exposed for 4 min. The crystal-to-detector distance was 110 mm. Data collection parameters were as follows. The detector swing angle: 2° (**2**), 2.5° (**3c**), 4° (**3e**), 5.5° (**4a**), 4° (**5**), 3.5° (**7a**); number of oscillation images: 42 (**2**), 40 (**3c**), 40 (**3e**), 16 (**4a**), 40 (**5**), 22 (**7a**). Exposure duration: 30 min (**2**), 50 min (**3c**), 30 (**3e**), 110 min (**4a**), 30 min (**5**), 60 min (**7a**). The data collections except for **7a** (at room temperature) were carried out at −60 °C. Readout was performed with a pixel size of 100 *μ*m × 100 *μ*m. The data processing was performed on an IRIS Indy computer. In the reduction of data, Lorentz and polarization corrections and an empirical absorption correction[26] were made.

Diffraction measurement of **3b** was made on a Rigaku AFC-5S automated four-circle diffractometer by using graphite-monochromated Mo Kα radiation (*λ* = 0.710 59 Å). The data collection was carried out at −60 °C. The unit cell was determined and refined by a least-squares method using 20 independent reflections (2*θ* ∼ 20°). Data were collected with an *ω* scan technique. If *σ*(*F*)/*F* was more than 0.1, a scan was repeated up to three times and the results were added to the first scan. Three standard reflections were monitored at every 100 measurements. The data processing (data collection) was performed on a FACOM A-70 computer. In the reduction of data, Lorentz and polarization corrections and an empirical absorption correction (Ψ scan) were made.

Crystallographic data and the results of refinements are summarized in Table 2. Structure analysis was performed on an IRIS O2 computer (structure analysis) by using the teXsan structure solving program system obtained from the Rigaku Corp., Tokyo, Japan. Neutral scattering factors were obtained from the standard source.[27] The

(26) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

structures were solved by a combination of direct methods (SHELXS-86 and SIR93) and Fourier synthesis (DIRDIF). Unless otherwise stated, non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were fixed at the calculated positions (C−H = 0.95 Å) and were not refined. The disordered part of the THF ligand in **2** was refined isotropically with two components (C5: C5a = 0.61:0.39). The highly disordered THF solvates except those in **5**·2THF were refined by using the rigid pentagonal model.

Acknowledgment. We are grateful to the Ministry of Education, Science, Sports and Culture of the Japanese Government for financial support of the research (Grant-in-Aid for Specially Promoted Scientific Research: No. 08102006).

(27) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1975; Vol. 4.

Note Added in Proof. After submission of our manuscript we noticed a recent report by Prof. Kirchner, where synthesis of $TpRuL_1L_2Cl$-type compounds with the nonsubstituted Tp ligand was disclosed (Slugovc, C.; Sapunov, V. N.; Wiede, P.; Mereiter, K.; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1997**, 4209).

Supporting Information Available: Tables of ^1H and ^{13}C NMR data (6 pages). X-ray crystallographic files in CIF format for the structure determinations of **2**, **3b**,**c**, **4a**, **5**, and **7a**) are available on the Internet only. Ordering and access information is given on any current masthead page.

IC9801802