A Coordinatively Unsaturated Species with an Agostic C−H Interaction, [(κ^4-Tp^{iPr})Ru(dppe)]OSO_2CF_3, and Its Addition Reaction

Yoshiaki Takahashi, Shiro Hikichi, Munetaka Akita,* and Yoshihiko Moro-oka*

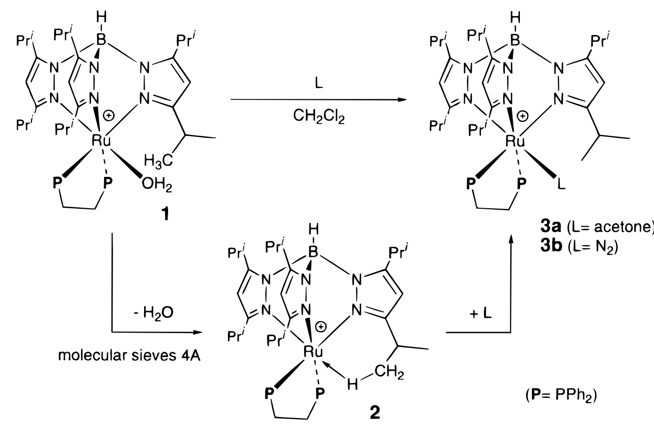
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received April 9, 1999

*Summary: The substitution reaction of the cationic aquo−ruthenium complex [Tp^{iPr}Ru(dppe)(OH_2)]OTf (**1**), giving [Tp^{iPr}Ru(dppe)(L)]OTf (**3**), proceeds by way of the dehydrated intermediate [(κ^4-Tp^{iPr})Ru(dppe)]OTf (**2**), which has an agostic interaction with a methyl C−H bond in the isopropyl substituent of the Tp^{iPr} ligand, as revealed by X-ray crystallography and NMR analysis. Complex **2** is reactive enough to incorporate a N_2 molecule to give the dinitrogen complex [Tp^{iPr}Ru(dppe)-(N_2)]OTf (**3b**).*

Coordinatively unsaturated species are key intermediates in organometallic and inorganic transformations.[1] Ligand substitution reactions of coordinatively saturated complexes usually proceed by way of a dissociation process, and substrates to be transformed are incorporated into the coordination sphere of the resulting transition-metal species. Coordinatively unsaturated species are unstable unless kinetically stabilized by a bulky ligand, and transition-metal species with a lightly stabilizing ligand (e.g. H_2O, THF, acetone, and acetonitrile) are frequently used as their synthetic equivalents. During the course of our systematic synthetic study of transition-metal−dioxygen complexes with the hydrotris(3,5-diisopropylpyrazolyl)borato ligand (Tp^{iPr}),[2,3] we have found that substitution reactions of the labile cationic aquo−ruthenium complex [(κ^3-Tp^{iPr})-Ru(dppe)(OH_2)]OTf (**1**)[4] proceeds via the dehydrated species [(κ^4-Tp^{iPr})Ru(dppe)]OTf (**2**), which has an agostic C−H interaction with a methyl group of the isopropyl substituent.[5]

Scheme 1



The labile nature of the aquo complex **1**[4] was first suggested by its ^{1}H NMR spectrum observed in acetone-d_6, which contained the signal of free water (δ_H 2.79) (Scheme 1). Crystallization of **1** from acetone−hexane gave the acetone complex **3a**, [Tp^{iPr}Ru(dppe)(acetone)]-OTf, as yellow crystals.[6] The shift of the C═O stretching vibration to lower energies (1641 cm^{-1}; cf. free acetone at 1713 cm^{-1}) indicated coordination at the ketonic oxygen atom. Because complex **1** is an octahedral coordinatively saturated species, its substitution reaction is anticipated to proceed by way of a coordinatively unsaturated intermediate. When a $CDCl_3$ solution of **1**

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. J. *Principles and Applications of Organometallic Chemistry*, 2nd ed.; University Science Book: Mill Valley, CA, 1987. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley: New York, 1994. (c) Yamamoto, A. *Organotransition Metal Chemistry*: Wiley: New York, 1986. (d) Elschenbroich, C.; Salzer, A. *Organometallics*, 2nd ed.; VCH: Weinheim, Germany, 1992.

(2) Our recent works based on Tp^R systems are as follows. Rh−diene: (a) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121. Ru−aqua: (b) Takahashi, Y.; Akita, M.; Hikichi, S.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 3186. Ru−diene: (c) Takahashi, Y.; Akita, M.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1998**, *17*, 4884. Pd−OOR: (d) Akita, M.; Miyaji, T.; Hikichi, S.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1998**, 1005. Co−OOR: (e) Hikichi, S.; Komatsuzaki, H.; Akita, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4699. Co, Ni−oxo: (f) Hikichi, S.; Yoshizawa, M.; Sasakura, Y.; Akita, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10567. Fe, Co, Ni−alkyl: (g) Akita, M.; Shirasawa, N.; Hikichi, S.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1998**, 973. (h) Shirasawa, N.; Akita, M.; Hikichi, S.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1999**, 417. Mn−OO(R): (i) Komatsuzaki, H.; Sakamoto, N.; Satoh, M.; Hikichi, S.; Akita, M.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 6554.

(3) Abbreviations used in this paper: Tp^{iPr} = hydridotris(3,5-diisopropylpyrazolyl)borato; Tp = hydridotris(pyrazolyl)borato; pz^{iPr} = 3,5-diisopropylpyrazolyl; OTf = trifluoromethanesulfonate.

(4) The synthesis of **1** was reported in ref 2b.

(5) (a) A closely related labile species with the parent Tp ligand was studied by Kirchner et al. However, the coordinatively unsaturated intermediate could not be detected, presumably due to the lack of substituents which would interact with the unsaturated site. Trimmel, G.; Slugovc, C.; Wiede, P.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Inorg. Chem.* **1997**, *36*, 1076. (b) An agostic C−H interaction was proposed for the related complex TpRu($P^iPr_2Me)_2$Cl, which showed the methyl signal of the isopropyl substituent attached to the phosphorus atom at δ −0.23, but no conclusive evidence was obtained. Tenorio, M. A. J.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1998**, 3601.

(6) Synthesis and spectral data for **3a**: An acetone solution (10 mL) of **1**·THF (209 mg, 0.174 mmol) was stirred for 3 h at ambient temperature. Concentration of the solution under reduced pressure followed by addition of hexane and cooling at −20 °C gave **3a**·acetone as a colorless solid (154 mg, 0.125 mmol, 72% yield). ^{1}H NMR (acetone-d_6; at 25 °C): δ_H 7.8−7.2 (20H, m, Ph), 6.20 (2H, s, pz H), 5.49 (1H, s, pz H), 3.75 (2H, sept, J = 6.8 Hz, C*H*Me$_2$), 3.65 (1H, sept, J = 6.8 Hz, C*H*Me$_2$), 3.34, 3.09 (2H × 2, m × 2, P(CH_2)$_2$P), 2.20 (2H, sept, J = 6.8 Hz, C*H*Me$_2$), 1.30 (1H, sept, J = 6.8 Hz, C*H*Me$_2$), 1.27, 1.22, 1.17, 0.39, 0.29, −0.42 (6H × 6, d × 6, J = 6.8 Hz, CH*Me*$_2$). ^{31}P NMR (acetone-d_6): δ_P 76.9 (s). IR (KBr): 3064 (m), 2966 (vs), 2931 (s, sh), 2540 (w, ν_{B-H}), 1641 cm^{-1} (s, $\nu_{C=O}$). Anal. Calcd for $C_{60}H_{82}BN_6O_5F_3SP_2Ru$ (**3a**·acetone): C, 58.58; H, 6.72; N, 6.83. Found: C, 58.32; H, 6.99; N, 6.99.

10.1021/om990250s CCC: $18.00
Publication on Web 06/17/1999

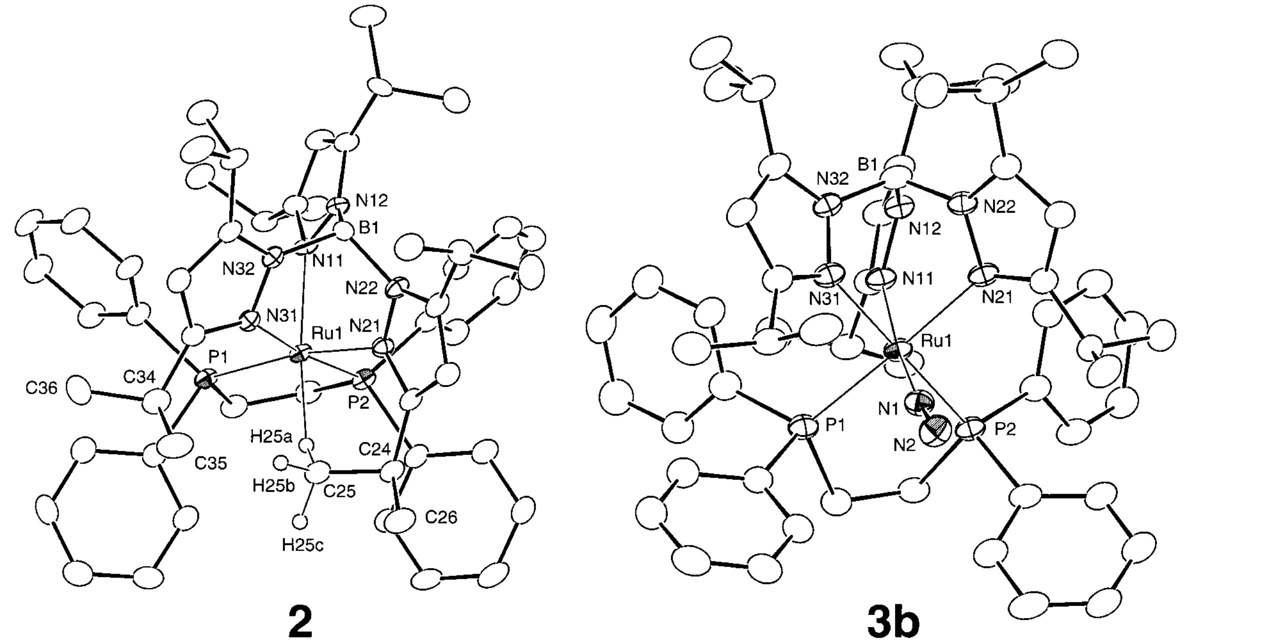


Figure 1. Molecular structures of the cationic parts of **2** and **3b** drawn at the 30% probability level.

was left at room temperature, gradual formation of a new species **2** exhibiting the characteristic signal in high field (δ_H −2.41) was noted and the chemical shift value suggested the occurrence of a C−H agostic interaction.[7] However, the reaction was not completed and was dependent on the solvent, probably because it was an equilibrium reaction accompanying elimination of water. A considerable amount of the intermediate **2** was formed in halogenated solvents such as $CHCl_3$ and CH_2Cl_2, but only a small amount of **2** was detected in benzene, methanol, and THF. Then molecular sieves 4A were added to a CH_2Cl_2 solution of **1** to remove water, and complex **2** was isolated successfully after crystallization from CH_2Cl_2−hexanes.[8]

The intermediate **2** has been characterized by X-ray crystallography (Figure 1).[9] The most striking structural feature is the agostic interaction of the C−H moiety in a methyl group of the isopropyl substituents. The H25a, atom refined isotropically, is located at a distance of 1.83(6) Å from the ruthenium center, and the Ru···C25 separation was 2.627(6) Å.[10] The $Tp^{iPr}Ru$ moiety is considerably distorted due to the chelating agostic interaction, as indicated by the bite angles of the Tp^{iPr} ligand (N11−Ru1−N21, 93.7(2)°; N11−Ru1−N31, 87.0(2)°; N21−Ru1−N31, 77.6(2)°). The difference (16.1°) is substantially larger than the normal values (usually <10°; for example, the difference for **3b** (see below) is 6.2°), and therefore the agostic interaction is a rather strong attractive one so as to distort the $Tp^{iPr}Ru$ backbone.[5] Thus, the Tp^{iPr} ligand is coordinated to the metal center in a κ^4-fashion through the agostic C−H interaction and the three pyrazolyl nitrogen atoms, and the octahedral structure is attained by the additional coordination of the κ^2-dppe ligand.

A ^1H NMR spectrum of an isolated sample of **2** observed at room temperature suggests a C_s-symmetrical structure;[8] the intensity of the agostic methyl signal at δ_H −2.41 is for six protons, and the 4-pz^{iPr} proton signals appear as two singlets in a 1:2 ratio. The inconsistency of the C_1-symmetrical structure determined by X-ray crystallography (Figure 1) with the ^1H NMR data indicates occurrence of a dynamic behavior, which has been studied by variable-temperature ^1H NMR measurements (Figure 2). The signal at δ_H −2.41 is separated into two signals (δ_H 0.26, −5.07; 3H each) at −60 °C. The ^1H NMR change can be best interpreted in terms of the mechanism shown in Scheme 2. The two methyl groups in the isopropyl substituents proximal to the metal center are diastereotopic (labeled as ***a*** and ***b***). Averaging of the two equivalent sites (***a*** and ***a′***) by switching the C−H agostic interactions (**A**−**A′**) would give a ^1H NMR spectrum indicating an apparent mirror symmetry. Rotation of the isopropyl group leading to **B** would be hampered by the steric repulsion among the substituents of the ligands (^iPr and Ph groups). The two signals are assigned to the diastereotopic methyl groups

(7) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(8) Synthesis and spectral data for **2**: A CH_2Cl_2 solution (10 mL) of **1**·THF (204 mg, 0.169 mmol) was stirred for 1 h at ambient temperature in the presence of molecular sieves 4A. After removal of the molecular sieves by filtration, the filtrate was concentrated. Addition of hexane and cooling at −20 °C gave **2** as a colorless solid (45 mg, 0.041 mmol, 25% yield). ^1H NMR ($CDCl_3$; at 25 °C): δ_H 7.44−7.13 (20H, m, Ph), 5.82 (2H, s, pz H), 5.42 (1H, s, pz-H), 3.69 (2H, sept, J = 6.8 Hz, C*H*Me$_2$), 3.52 (6H, m, C*H*Me$_2$ and $P(CH_2)_2P$), 1.45 (2H, sept, J = 6.8 Hz, C*H*Me$_2$), 1.34, 1.33, 1.25, 0.63, −0.24, −2.41 (6H × 6, d × 6, J = 6.8 Hz, CH*Me*$_2$). ^{31}P NMR ($CDCl_3$): δ_P 77.5 (s). IR (KBr): 3057 (m), 2967 (vs), 2932 (s, sh), 2870 (m), 2546 (w, ν_{B-H}) cm^{-1}. Anal. Calcd for $C_{54}H_{70}BN_6O_3F_3SP_2Ru$: C, 58.22; H, 6.33; N, 7.54. Found: C, 57.70; H, 6.22; N, 7.41.

(9) Diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with Mo Kα radiation (λ = 0.710 69 Å) at −60 °C. The structures were solved by a combination of direct methods (SHELXS-86) and Fourier synthesis (DIRDIF). Least-squares refinements were carried out using SHELXL93 linked to teXsan. Crystal data for **2**·CH_2Cl_2: triclinic, $P\bar{1}$, a = 14.475(3) Å, b = 16.736(5) Å, c = 12.273(2) Å, α = 99.99(2)°, β = 107.09(1)°, γ = 86.91(2)°, V = 2799(1) Å^3, Z = 2, D_{calcd} = 1.42 g cm^{-3}, μ = 5.3 cm^{-1}; 10 019 reflections, 9450 observed with $F_o > 4\sigma(F_o)$, 679 parameters; R1 = 0.090, wR2 = 0.252. Crystal data for **3a**·CH_2Cl_2: triclinic, $P\bar{1}$, a = 13.844(5) Å, b = 19.969(3) Å, c = 10.848(6) Å, α = 95.59(3)°, β = 96.76(5)°, γ = 88.77(2)°, V = 2964(2) Å^3, Z = 2, D_{calcd} = 1.38 g cm^{-3}, μ = 5.0 cm^{-1}; 10 788 reflections, 10 150 observed with $F_o > 4\sigma(F_o)$, 697 parameters; R1 = 0.088, wR2 = 0.229.

(10) The second closest interaction between the ruthenium center and the proximal isopropyl groups is Ru1−C24 = 3.331(6) Å, and the others are in the range from 3.918(7) Å (C34) to 5.063(9) Å (C36).

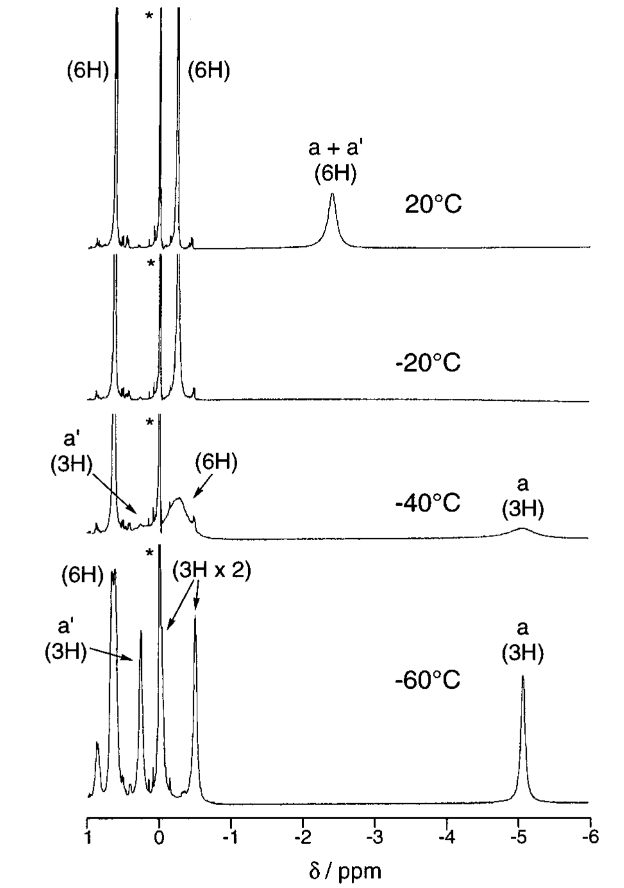
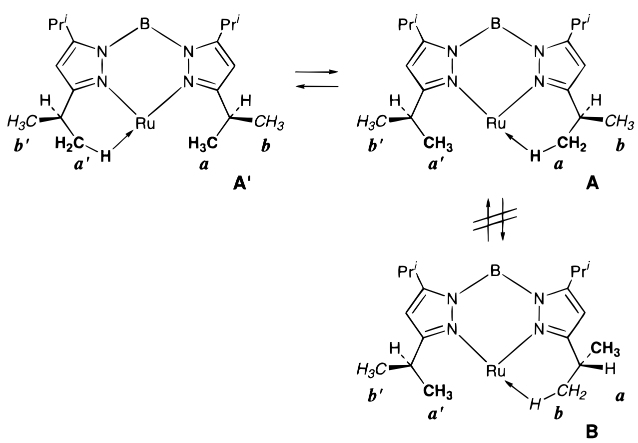


Figure 2. Variable-temperature ^{1}H NMR spectra of **2** observed in $CDCl_3$ at 400 MHz. TMS signals are indicated by asterisks. The assignments are for structure **A** in Scheme 2.

Scheme 2[a]



[a] Only pertinent parts are shown for clarity.

(***a*** and ***a′***) as shown in Figure 2. The rotation of the methyl group cannot be frozen out even at −95 °C (at 400 MHz).[11]

The dehydrated species **2** is found to be very reactive with respect to coordination of an external molecule. Stirring a CH_2Cl_2 solution of **2** under an N_2 atmosphere (1 atm) caused a color change to orange. The intense IR absorption at 2181 cm^{-1} suggests coordination of a N_2 molecule to the ruthenium center, which has been verified by X-ray crystallography (Figure 1).[9,12] The Ru−N−N linkage is essentially linear (175.6(4)°), and the Ru−N (1.923(4) Å) and N−N lengths (1.105(7) Å) are comparable to those for previously reported Ru−N_2 complexes. The structural features are essentially the same as those of the Tp derivatives[3] [TpRu(κ^2-$Ph_2PCH_2CH_2NMe_2$)(N_2)]BPh_4 and [TpRu(PEt_3)$_2$(N_2)]BPh_4, reported recently by Kirchner and Puerta, respectively.[5]

In conclusion, the nonsolvated complex **2** with an agostic C−H interaction, an equivalent to the highly reactive coordinatively unsaturated intermediate, has been successfully isolated and thoroughly characterized. Formation of analogous species is indicated for the $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2PCH{=}CHPPh_2$ (dppene) complexes by the characteristic high-field ^{1}H NMR signals, but they are too unstable to be isolated. The more electron donating dppe ligand would deliver electron density to the metal center to neutralize the cationic charge at the metal center.[13] The agostic interaction is found to be readily replaced by a donor ligand such as N_2, acetone, or H_2O, and it is confirmed that (1) the aquo complex **1** serves as a versatile starting compound for Tp^{iPr}Ru(dppe)X-type compounds and (2) the ligand substitution reaction of **1** proceeds by way of **2**. Reactions of **2** with other substrates, including O_2, are now under study, and the results will be reported in due course.

Acknowledgment. We are grateful to the Ministry of Education, Science, Sports and Culture of the Japanese Government for financial support of this research (Grant-in-Aid for Specially Promoted Scientific Research: 08102006).

Supporting Information Available: Tables giving crystallographic data, positional and thermal parameters, and bond distances and angles and a figure giving the atomic numbering scheme for **2** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990250S

(11) The agostic interaction could not be characterized by IR and ^{13}C NMR (−95 °C) measurements. Although a shielded methyl signal (δ_C ~8.5) was observed at −95 °C, the coupling constants could not be analyzed due to the broad peak shape.

(12) Synthesis and spectral data for **3b**: Complex **2**·CH_2Cl_2 (59 mg, 0.049 mmol) was dissolved in CH_2Cl_2 (5 mL). After the Schlenk tube was evacuated for a short period, N_2 gas was introduced to the Schlenk tube and the mixture was stirred for 5 h under an N_2 atmosphere. The solution changed from red to orange. After concentration under reduced pressure, hexane was added until a small amount of precipitates appeared. Leaving the resultant mixture overnight at ambient temperature gave **3b**·CH_2Cl_2 as pale orange crystals (39 mg, 0.032 mmol, 65% yield). ^{1}H NMR ($CDCl_3$; at 25 °C): δ_H 7.25−6.97 (20H, m, Ph), 5.90 (2H, s, pz H), 5.45 (1H, s, pz H), 3.48 (6H, m, P(CH_2)$_2$P and 2 × C*H*Me_2), 1.97, 1.49 (2H × 2, d × 2, sept, *J* = 6.8 Hz, C*H*Me_2), 1.27, 1.21, 1.12, 0.60, 0.56, −0.25 (6H × 6, d × 6, *J* = 6.8 Hz, CH*Me*$_2$). ^{31}P NMR ($CDCl_3$): δ_P 73.7 (s). IR (KBr) 3059 (m), 2969 (s), 2932 (s, sh), 2870 (m), 2550 (w, ν_{B-H}), 2181 (vs, ν_{NN}) cm^{-1}. Anal. Calcd for $C_{55}H_{72}BN_8O_3F_3SCl_2P_2Ru$ (**3b**·CH_2Cl_2): C, 53.84; H, 5.91; N, 9.13. Found: C, 53.58; H, 5.78; N, 8.92.

(13) The electron-donating abilities of the diphosphine ligands can be estimated by the oxidation potentials of Tp^{iPr}Ru(diphosphine)Cl: 0.064 V (dppe) < 0.198 V (dppm) < 0.245 V (dppene) vs Ag/Ag$^+$ observed in CH_2Cl_2.