Two Isomeric Structures of Hydridoruthenium Complexes Supported by Hydrotrispyrazolylborates, $Tp^RRu(H)$(1,5-cyclooctadiene): An Octahedral Structure with Additional 3-Center-2-Electron Ru−H−B Interaction Is More Stable than a Square-Pyramidal Structure with a κ^2-Tp^R Ligand

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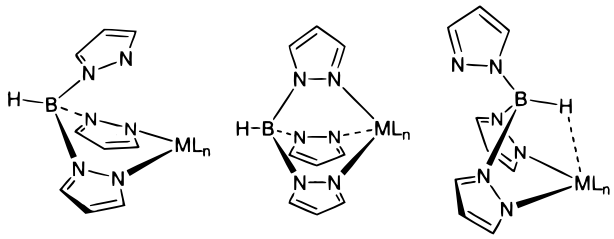
Hydrido-cod-ruthenium complexes containing hydrotris(3,5-diisopropylpyrazolyl)borate (Tp^{iPr}) and its 4-brominated derivative (Tp^{iPrBr}), $Tp^RRu(H)(cod)$, are reported. Spectroscopic and crystallographic analyses reveal the presence of two isomeric structures, a square-pyramidal structure with a κ^2-Tp^R ligand and an octahedral structure with an additional 3-center-2-electron Ru−H−B interaction, and isomerization from the former structure to the latter structure is observed for the first time by means of ^1H NMR analyses.

Introduction

Hydrotrispyrazolylborates (Tp^R) have been used as versatile supporting ligands for a wide range of transition metal complexes.[1−3] Tp^R is a mononegative 6e-donor and is isoelectronic with cyclopentadienyl ligands (η^5-C_5R_5). There are, however, significant differences between those two isoelectronic ligands. One is the occurrence of κ^2-coordination by Tp^R ligands, especially, with 16e square-planar d^8 complexes of group 8 and 9 metals. Recently a comparative study of rhodium diene complexes, $Tp^RRh(diene)$,[2a] showed that the hapticity of the Tp^R ligand (κ^2 (**A**) vs κ^3 (**B**); Chart 1) can be readily differentiated by the values of the ν_{B-H} stretch. During the course of our study on analogous ruthenium-diene complexes,[4] we encountered another structural isomerism (**C**) arising from additional 3-center-2-electron interaction between the free B−H part and the vacant Ru coordination site. (We use the symbol κ^3(BH) for **C**.)

Chart 1



[Substituents of the pz rings are omitted for clarity.]

Herein we report the synthesis and structure of two isomers, the square-pyramidal (κ^2-Tp^R)Ru(H)(cod) (**A**) and the octahedral (κ^3(BH)-Tp^R)Ru(H)(cod) (**C**) (Tp^R = Tp^{iPr}, Tp^{iPrBr}).[3] Although κ^3(BH) coordination **C** has been reported for several related dihydrobis(pyrazolyl)borate complexes, $(H_2Bpz^R_2)MX_n$,[5] examples of hydrotrispyrazolylborate complexes (κ^3(BH)-Tp^R)MX_n are rare,[6] and the relative stability of the two structures [κ^2 (**A**) vs κ^3(BH) (**C**)] has not been ascertained.

Results and Discussion

Synthesis of $Tp^{iPr}Ru(H)(cod)$ (1) and $Tp^{iPrBr}Ru(H)(cod)$ (2). The hydrido-cod-ruthenium complexes

(1) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419. (c) Kitajima, N.; Moro-oka, Y. *Chem. Rev.* **1994**, *94*, 737.

(2) Our recent works based on Tp^R systems. 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. Pd−OOR: (c) Akita, M.; Miyaji, T.; Hikichi, S.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1998**, 1005. Co−OOR: (d) Hikichi, S.; Komatsuzaki, H.; Kitajima, N.; Akita, M.; Mukai, M.; Kitagawa, T.; Moro-oka, Y. *Inorg. Chem.* **1997**, *36*, 266. (e) Hikichi, S.; Komatsuzaki, H.; Akita, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4699. Co, Ni−oxo: (f) Hikichi, S.; Sasakura, Y.; Yoshizawa, M.; Akita, M.; Moro-oka, Y. *J. Am. Chem. Soc.*, in press. Fe, Co, Ni−alkyl: (g) Akita, M.; Shirasawa, N.; Hikichi, S.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1998**, 973. Fe−catecholate: (h) Ogihara, T.; Hikichi, S.; Akita, M.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 2614. Mn−O_2: (i) Komatsuzaki, H.; Nagasu, Y.; Suzuki, K.; Shibasaki, T.; Satoh, M.; Ebina, F.; Hikichi, S.; Akita, M.; Moro-oka, Y. *J. Chem. Soc., Dalton Trans.* **1998**, 511. A short review: (j) Akita, M.; Fujisawa, K.; Hikichi, S.; Moro-oka, Y. *Res. Chem. Intermed.* **1998**, *24*, 291.

(3) Abbreviation used in this paper: Tp^{iPr} = hydrotris(3,5-diisopropylpyrazolyl)borate; Tp^{iPrBr} = hydrotris(4-bromo-3,5-diisopropylpyrazolyl)borate; Tp^{Me} = hydrotris(3,5-dimethylpyrazolyl)borate; Tp = hydrotrispyrazolylborate; Tp^R = substituted Tp derivatives; pz = pyrazolyl group; pz^R = substituted pz groups; cod = 1,5-cyclooctadiene.

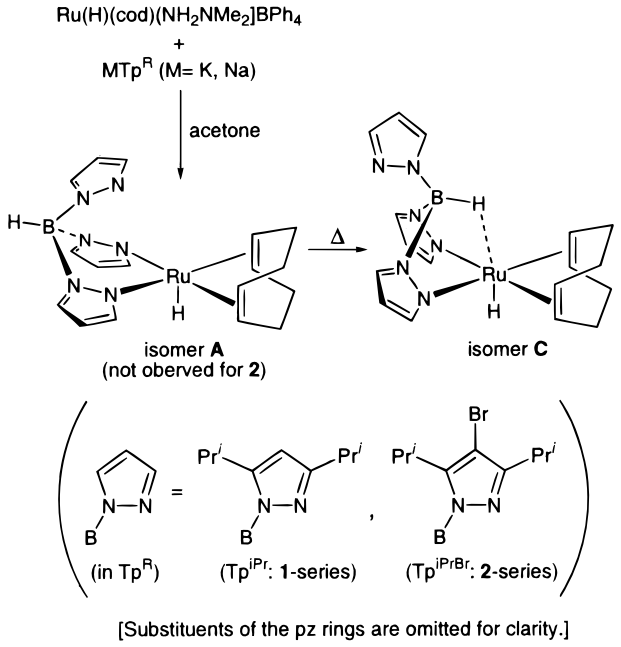
(4) $Tp^RRh(H)(cod)$ complexes were prepared as precursors for the pentahydride complexes Tp^RRuH_5,[6b] which were further converted to cationic aqua complexes by the action of protic acid.[2b]

(5) See, for example: (a) Kosky, C. A.; Ganis, P. Avitabile, G. *Acta Crystallogr.* **1971**, *B27*, 1859. (b) Cotton, F. A.; Jerenic, M.; Shaver, A. *Inorg. Chim. Acta* **1972**, *6*, 543. (c) Reger, D. L.; Swift, C. A.; Lebioda, L. *J. Am. Chem. Soc.* **1983**, *105*, 5343. (d) Albers, M. O.; Crosby, S. F. A.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2014.

(6) (a) (κ^2-Tp)Ru(H)(cod) and (κ^3(BH)-Tp^{Me})Ru(Me)(cod): Corrochano, A. E.; Jalón, F. A.; Otero, A.; Kubicki, M. M.; Richard, P. *Organometallics* **1997**, *16*, 145. (b) TpMeRu(H)(cod) and $Tp^{3-iPr,4-Br}$Ru(H)(cod) were also reported. A short comment on the κ^3(BH)-form of the $Tp^{3-iPr,4-Br}$ derivative was made on the basis of its ν_{BH} value. Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalon, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1995**, *117*, 7441.

10.1021/om980363w CCC: $15.00
Publication on Web 10/08/1998

Scheme 1



$Tp^{iPr}Ru(H)(cod)$ (**1**) and $Tp^{iPrBr}Ru(H)(cod)$ (**2**) were prepared in a manner similar to the synthesis of the nonsubstituted derivative, TpRu(H)(cod), reported by Kirchner et al. (Scheme 1).[7]

Treatment of the cationic hydrido-cod-hydrazine complex, $[Ru(H)(cod)(NH_2NMe_2)]BPh_4$, with KTp^{iPr} [8] in acetone resulted in replacement of the hydrazine ligand to afford the hydrido-cod complex **1A** ($Tp^R = Tp^{iPr}$) in 26% yield. When an NMR sample was left at ambient temperature, gradual conversion to isomer **1C** was observed. Heating a benzene-d_6 solution of **1A** at 70 °C resulted in complete isomerization within 30 min.

^1H and ^{13}C NMR spectra of **1A** contain two sets of the pz^{iPr} signals in a 1:2 ratio and a hydride signal at δ_H −9.61. The ν_{B-H} absorption at 2471 (KBr) and 2471 cm^{-1} (hexane) suggests κ^2-coordination of the Tp^{iPr} ligand (**A**) according to the criterion established by us,[2a] and the Ru−H stretching vibration is located at 2091 (KBr) and 2077 cm^{-1} (hexane). These spectral data are consistent with a square-pyramidal structure where the apical and equatorial sites are occupied by the hydride ligand and the κ^2-Tp^{iPr} and κ^2-cod ligand set, respectively. The structure has been confirmed by X-ray crystallography (see below). NMR data of **1C** also suggest a mirror-symmetrical structure, but the δ_H(Ru−H) signal is shifted toward lower field [δ_H −6.88 (**1C**)]. In addition, a notable shift of the ν_{B-H} vibration [1937 (KBr) and 1926 cm^{-1} (hexane) (**1C**)] to lower energies is observed when compared to **1A** (see above). The shift is due to a 3-center-2-electron B−H−Ru interaction, as discussed below.

In contrast to the reaction of the Tp^{iPr} complex **1** mentioned above, reaction with the 4-bromo derivative ($NaTp^{iPrBr}$) afforded a product **2C**, which showed spectral features (δ_H −7.12; ν_{B-H} 1944 (KBr) and 1931 cm^{-1} (hexane)) similar to those of **1C**. Although ν_{Ru-H} could not be detected for **1C**, a weak absorption at 2094 (KBr) and 2078 cm^{-1} (hexane) assignable to ν_{Ru-H} was observed for **2C**. An **A**-type isomer could not be detected despite careful monitoring of the reaction by ^1H NMR.

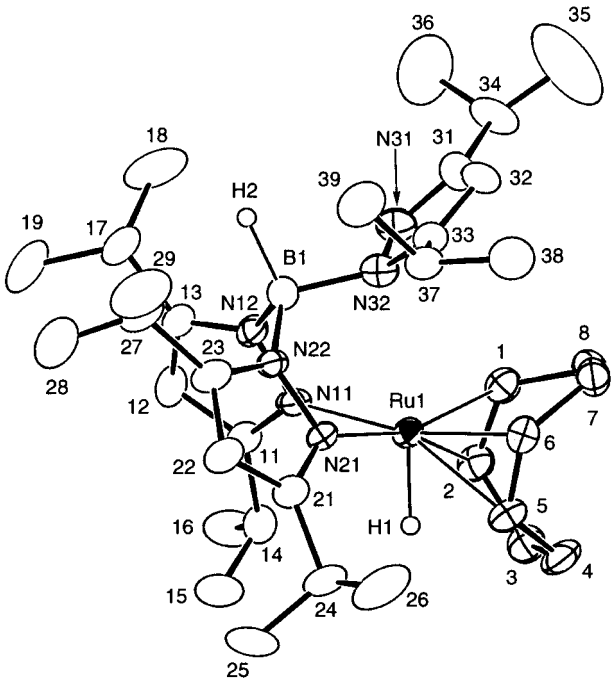


Figure 1. Molecular structure of **1A** drawn at the 30% probability level. (Labels without atom names are for carbon atoms.)

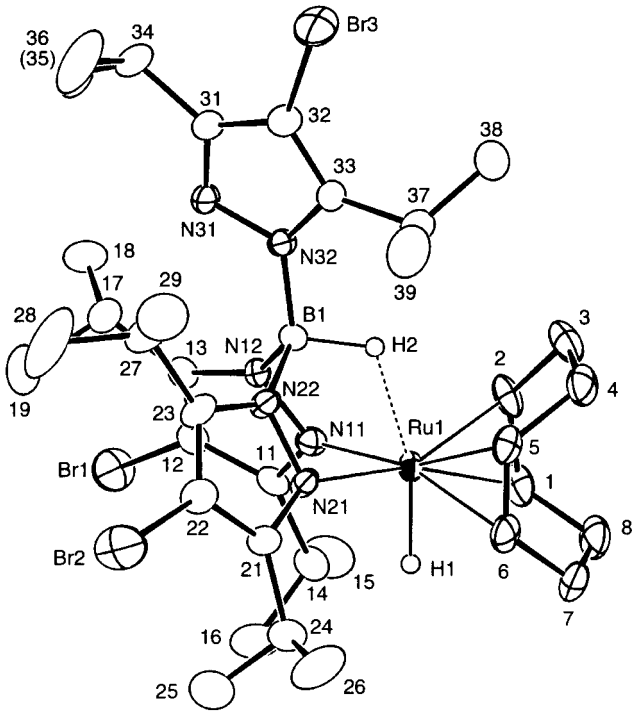


Figure 2. Molecular structure of **2C** drawn at the 30% probability level. (Labels without atom names are for carbon atoms.)

Molecular Structures of 1A and 2C. ORTEP views of **1A** and **2C** are shown in Figures 1 and 2, and their structural parameters are compared in Table 1.

Complex **1A** (Figure 1) adopts a typical square-pyramidal structure with the cod−N11−N21 basal

(7) Gemel, C.; Trimmel, G.; Slugovc, C.; Kremel, S.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 3998. TpRu(H)(cod) was generated as a precursor of the halo complexes, TpRu(X)(cod).

(8) Any notable change was not observed when sodium salt, $NaTp^{iPr}$, was used in place of the potassium salt.

Table 1. Selected Structural Parameters for 1A[a]

1A		2C	
Ru1−N11	2.125(5)	Ru1−N11	2.089(5)
Ru1−N21	2.114(5)	Ru1−N21	2.136(5)
Ru1···N31	3.329(5)	Ru1···N31	5.185(5)
Ru1−C1	2.178(6)	Ru1−C1	2.201(6)
Ru1−C2	2.166(6)	Ru1−C2	2.165(6)
Ru1−C5	2.172(6)	Ru1−C5	2.165(6)
Ru1−C6	2.172(6)	Ru1−C6	2.177(6)
Ru1−H1	1.46(4)	Ru1−H1	1.56(6)
Ru1···H2	4.29(5)	Ru1···H2	1.96(5)
Ru1···B1	3.024(7)	Ru1···B1	2.706(7)
B1−H2	1.31(5)	B1−H2	1.25(4)
C1−C2	1.356(9)	C1−C2	1.40(1)
C5−C6	1.369(8)	C5−C6	1.38(1)
N11−Ru1−N21	82.3(2)	N11−Ru1−N21	84.0(2)
N11−Ru1−H1	104(2)	N11−Ru1−H1	89(2)
N21−Ru1−H1	91(2)	N21−Ru1−H1	94(2)
Ru1−N11−N12	115.1(4)	Ru1−N11−N12	111.3(4)
Ru1−N21−N22	113.8(3)	Ru1−N21−N22	108.1(3)
N11−N12−B1	116.2(5)	N11−N12−B1	108.9(4)
N21−N22−B1	118.5(5)	N21−N22−B1	111.3(5)
N31−N32−B1	111.9(5)	N31−N32−B1	120.3(5)
N12−B1−N22	106.7(5)	N12−B1−N22	107.9(5)
N12−B1−N32	107.6(5)	N12−B1−N32	121.2(5)
N22−B1−B32	109.5(5)	N22−B1−B32	113.6(5)
N12−B1−H2	106(2)	N12−B1−H2	109(2)
N22−B1−H2	124(2)	N22−B1−H2	100(2)
N32−B1−H2	102(2)	N32−B1−H2	103(2)

plane. The third pyrazolyl ring does not interact with the ruthenium center as judged by the Ru1···N31 distance [3.024(7) Å] and is bent back away from the Ru center, as shown from the dihedral angle B1−N32−N31−C31 [145.3(5)°; cf. B1−N12−N11−C11, 162.5(5)°; B1−N22−N21−C21, 170.2(6)°], to reduce steric repulsions with the cod ligand. The hydrido ligand refined isotropically is located in the space trans to the uncoordinated pz^{iPr} ring and projects virtually perpendicularly (N11−Ru1−H1, 103(1)°; N21−Ru1−H1, 90(1)°) to the basal plane of the square pyramid. The 1:2 pattern of the ^{1}H NMR signals of the pz^{iPr} rings indicates that the solid-state structure is retained in a solution. The overall structure is quite similar to that of the isoelectronic Rh complex, Tp^{iPr}Rh(cod), which was previously reported by us.[2a]

Complex **2C** (Figure 2) contains an octahedral Ru core with the additional Ru−H−B interaction. The basal plane consists of the cod−N11−N21 donor set in a manner similar to **1A**, but the BH hydrogen atom (H2) is located trans to the hydrido ligand at a distance of 1.96(5) Å from the Ru center, indicating a 3-center-2-electron interaction. As a result, the RuNNBNN boat structure is inverted when compared with that of **1A** and the Ru1···H2 interaction causes shortening of the Ru1···B1 distance [2.706(7) Å; cf. **1A**, 3.024(7) Å] as well as making the B−N−N and Ru−N−N angles slightly more acute than those in **1A**. The shift of the δ_H(Ru−H) signal compared with the **A** isomer indicates that the 3c-2e interaction is retained in solution. SimilarRu−H−B interaction has been frequently noted for analogous dihydrobis(pyrazolyl)borate complexes,(H_2-Bpz^R_2)MX_n.[5] Jalón and Otero reported the closely related methyl complexes, Tp^RRu(Me)(cod), and found the κ^3(BH)-form **C** for the Tp^{Me} complex but not for the non-

substituted Tp complex.[6a] The κ^3(BH)-coordination was indicated for another 4-bromo derivative, $Tp^{3-iPr,4-Br}$Ru(H)(cod), on the basis of the lack of a ν_{BH} absorption.[6b]

Isomerization from the Square-Pyramidal κ^2-Tp^R Structure (1A) to the Octahedral κ^3(BH)-Tp^R Structure (1C). Analysis of the isomerization process from **1A** to **1C** by means of ^{1}H NMR revealed first-order kinetics. The isomerization rates observed in toluene-d_8 were 4.45×10^{-5} sec^{-1} (50 °C), 1.20×10^{-4} s^{-1} (65 °C), 2.32×10^{-4} s^{-1} (69 °C), 4.71×10^{-4} s^{-1} (76 °C), 6.64×10^{-4} s^{-1} (80 °C), and 1.05×10^{-3} s^{-1} (85 °C), and activation parameters were estimated as follows: $\Delta H^{\ddagger} = 20.0(6)$ kcal·mol^{-1}, $\Delta S^{\ddagger} = -16.8(16)$ cal·deg^{-1}·mol^{-1}. Several examples of κ^3(BH)-coordination of H_2-Bpz^R_2 and Tp^R ligands are reported as mentioned above, but the relative stability of the two isomers **A** and **C** has not been examined, because the conversion from the κ^2-Tp^R isomer to the κ^2(BH)-Tp^R isomer has not been observed previously. The present result suggests that a κ^3(BH)-Tp^R structure (**C**) is more stable than a κ^2-Tp^R structure (**A**).

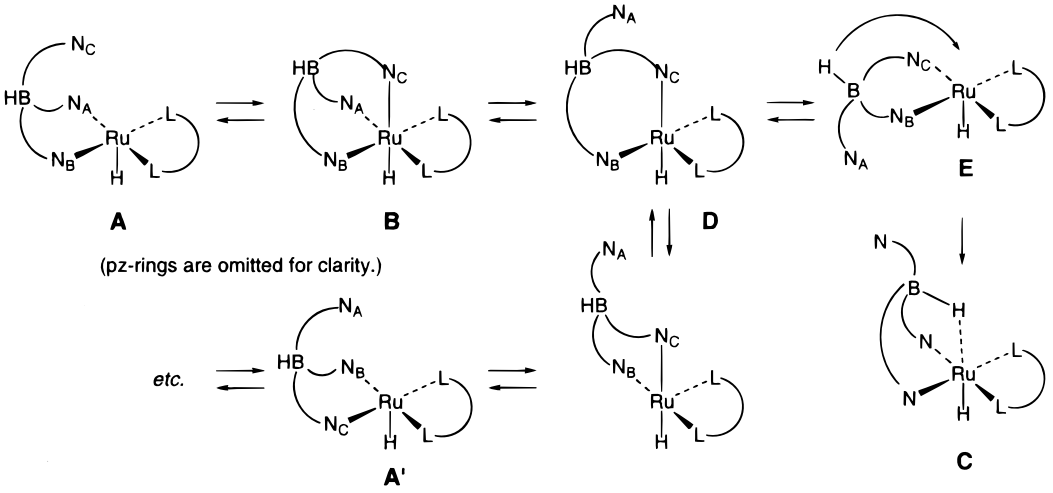
Dynamic behavior of a Tp^R ligand via interconversion between κ^2- and κ^3-coordination is a well-documented process.[9] The slightly broad pz ring proton signals of **1A** observed at room temperature suggest occurrence of such a process in addition to the isomerization. As was anticipated, the pz signals became sharp at low temperatures and coalesced into a single resonance above 45 °C. It should be noted that the two kinds of the olefinic hydrogen atoms of the cod ligand (separated by 0.37 ppm at room temperature) above and below the basal plane remained inequivalent even at a higher temperature where the pz signals (separated by 0.48 ppm at room temperature) coalesced. This observation indicated that the Ru(H)(cod) partial structure was rigid in the observed temperature range. A possible mechanism for the coalescence taking into account this point is shown in Scheme 2. Coordination of the free pz ring (NC) to the vacant site in **A** forms an octahedral κ^3-intermediate **B**. Dissociation of an equatorial pz ring (NA) gives another square-pyramidal species (**D**), and subsequent migration of the remaining pz rings (NB and then NC) furnishes structure **A′** equivalent to **A**. Migration of NC (from **D**) may give another isomeric structure **E**. If the reverse process regenerating **D** is faster than the NMR time scale, the results of variable ^{1}H NMR measurements can be explained in terms of a combination of these processes. This mechanism is consistent with the X-ray structure of **1A**, in which the vacant coordination site trans to the hydrido ligand accommodates the lone pair electrons of the free pz ring, facilitating the dynamic process via simple coordination leading to **B**.

A key step of the isomerization from **A** to **C** is inversion of the six-membered BN_2RuN_2 boat structure at the stage of intermediate **E**. The steric repulsion among the isopropyl substituents attached to the pz rings may hinder the inversion to make isomer **A** observable. In accord with this consideration, the $\Delta G^{\ddagger}$ value for the dynamic process at the coalescence temperature (45 °C) can be estimated to be 18.6 kcal·mol^{-1},[10] which is substantially smaller than the $\Delta G^{\ddagger}$ value (25.3-

(9) The Tp^RRhL_2 system is the most studied one. See, for example: Bucher, U. E.; Currao, A.; Nesper, R.; Rüegger, H.; Venanzi, L. M.; Younger, E. *Inorg. Chem.* **1995**, *34*, 66. See also references cited in ref 2a.

(10) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic: San Diego, CA, 1988.

Scheme 2



(6) kcal·mol^{-1}) for the isomerization process calculated from the above-mentioned kinetic data. The driving force of the isomerization should be (1) relief of steric repulsion arising from the bulky isopropyl groups attached to the noncoordinated pz ring and (2) the stable Ru−H−B 3-center-2-electron interaction in isomer **C**.

In contrast to the dynamic behavior of **1A**, isomer **1C** gave sharp signals in the temperature range of room temperature (rt) to 85 °C, indicating the rigid octahedral structure with the robust Ru−H−B interaction.

In the case of the 4-bromo derivative **2**, we have no evidence for **2A**. Electronic effects of the pz^R substituents (R) on the properties of the Tp^R ligand are still a matter of controversy, and the reason for the absence of **2A** is not clear at the moment.

In summary, we report that (1) isomerization from **A** to **C** is observed for the first time and (2), in the Tp^R-Ru(H)(cod) system, the κ^3(BH)-Tp^R structure **C** with the Ru−H−B interaction is more stable than the κ^2-Tp^R structure **A**.

Experimental Section

General Methods. All manipulations were carried out under an inert atmosphere by using standard Schlenk techniques. Ether (Na−K alloy), acetone ($KMnO_4$ molecular sieves), and MeCN (CaH_2) were treated with appropriate drying agents, distilled, and stored under argon. ^{1}H and ^{13}C NMR spectra were recorded on JEOL EX400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) and GX500 (^{1}H, 500 MHz) spectrometers. Solvents for NMR measurements containing 0.5% TMS were dried over molecular sieves, degassed, distilled under reduced pressure, and stored under Ar. IR and FD-MS spectra were obtained on a JASCO FT/IR 5300 spectrometer and a Hitachi M80 mass spectrometer, respectively. [Ru(H)(cod)(NH_2NMe_2)$_3$]-BPh_4 was prepared according to the reported method.[12]

Synthesis of NaTp^{iPrBr}. NaTp^{iPrBr} was prepared by the reaction between $NaBH_4$ and 3,5-diisopropyl-4-bromopyrazole (pz^{iPrBr}−H), which was obtained by bromination of 3,5-diisopropylpyrazole (pz^{iPr}−H) following the procedure reported for analogous compounds.[11]

Bromination of pz^{iPr}−H. To a CH_2Cl_2 solution (20 mL) of pz^{iPr}−H[13] (2.92 g, 19.2 mmol) was added a slight excess amount of Br_2 (1.0 mL, 19.4 mmol) dropwise. After the mixture was stirred for 30 min at room temperature, an aqueous solution (50 mL) of Na_2SO_3 (5 g) and $KHCO_3$ (5 g) was added in portions. The organic phase was separated and washed with 1 M NaOH aqueous solution, water, and then brine. The organic phase was dried over $MgSO_4$, and volatiles were removed under reduced pressure. Crystallization from MeCN at −30 °C gave pz^{iPrBr}−H (3.58 g, 15.5 mmol, 81% yield) as colorless plates. pz^{iPrBr}−H: ^{1}H NMR ($CDCl_3$) δ_H 9.90 (1H, br, NH), 3.07 (2H, sept, J = 7.0 Hz, C*H*Me$_2$), 1.31 (12H, d, J = 7.0 Hz, CH*Me*$_2$); IR (KBr) 3157 (s), 3088 (s), 2969 (vs), 2932 (s), 2874 (s), 2812 (m), 1570 (w), 1483 (m), 1468 (m), 1366 (w), 1271 (m), 1073 (m), 1042 (w), 1009 (s), 883 (w), 824 (w). Anal. Calcd for $C_9H_{15}N_2Br$: C, 46.77; H, 6.54; N, 12.12; Br, 34.57. Found: C, 46.55; H, 6.45; N, 12.53; Br, 34.04.

Synthesis of NaTp^{iPrBr}. A mixture of $NaBH_4$ (194 mg, 5.13 mmol) and pz^{iPrBr}−H (3.58 g, 15.5 mmol) was placed in a 10 mL flask filled with Ar, which was connected to a gas-collecting bottle. The flask was heated in an oil bath, and the temperature was gradually raised to 240 °C. Heating was continued at 240 °C until 350 mL of hydrogen gas was evolved. Then the flask was cooled to room temperature, and the solid was extracted with CH_2Cl_2 and passed through a Celite pad to remove insoluble materials. After removal of the volatiles under reduced pressure the product was extracted with MeCN. Filtration though a filter paper followed by cooling at −30 °C gave NaTp^{iPrBr} as colorless needles (3.22 g, 9.90 mmol, 64% yield). NaTp^{iPrBr}: ^{1}H NMR ($CDCl_3$) δ_H 3.60, 2.97 (3H × 2, sept × 2, J = 7.0 Hz, C*H*Me$_2$), 1.25, 1.18 (18H × 2, d × 2, J = 7.0 Hz, CH*Me*$_2$); IR (KBr) 2965 (vs), 2933 (s), 2871 (s), 2493 (w, ν_{BH}), 1647 (m), 1515 (s), 1460 (s), 1436 (s), 1381 (s), 1284 (s), 1167 (vs), 1142 (s), 1086 (s), 1024 (vs), 791 (m), 670 (m). Anal. Calcd for $C_{27}H_{43}BN_6Br_3Na$: C, 44.72; H, 5.98; N, 11.59; Br, 33.06. Found: C, 44.41; H, 5.98; N, 11.42; Br, 33.12.

Synthesis of 1A,C. An acetone solution (30 mL) of [Ru(H)(cod)(NH_2NMe_2)$_3$]BPh_4 (3.00 g, 4.23 mmol) and KTp^{iPr13} (2.13 g, 4.22 mmol) was stirred for 30 min at room temperature. After removal of the volatiles under reduced pressure products were extracted with ether (50 mL) and passed through a Celite pad to remove inorganic salts. The filtrate was concentrated under reduced pressure, and acetonitrile (10 mL) was added. The insoluble materials were removed by filtration through a Celite pad. Concentration and cooling at −20 °C gave **1A** (738 mg, 1.09 mmol, 26% yield) as orange crystals. Heating a benzene solution of **1A** at 80 °C caused complete isomerization to pale yellow **1C** within 30 min. Spectral data for **1A**: ^{1}H NMR (toluene-d_8; at −20 °C) δ_H 6.31

(11) Trofimenko, S.; Calabrese, J. C.; Domaille, P. J.; Thompson, J. S. *Inorg. Chem.* **1989**, *28*, 1091.

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Table 2. Crystallographic Data for 1A and 2C

	1A	2C
formula	$C_{35}H_{59}BN_6Ru$	$C_{35}H_{56}BN_6RuBr_3$
fw	675.8	912.5
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	*Pbca*
a/Å	10.955(4)	19.324(4)
b/Å	17.606(8)	30.66(2)
c/Å	10.083(4)	13.542(3)
α/deg	101.55(4)	
β/deg	94.42(3)	
γ/deg	77.12(5)	
V/Å^3	1856(1)	8022(4)
Z	2	8
d_{calcd}/g·cm^{-3}	1.21	1.51
μ/cm^{-1}	4.5	34.2
max 2*θ*/deg	55.2	53.7
no. of data collected	6300	7941
no. of unique data with $I > 3\sigma(I)$	5516	5299
no. of params refined	396	423
R	0.073	0.051
R_w	0.078	0.055

(1H, s, pz), 5.83 (2H, s, pz), 4.06 (2H, m, CH═), 3.70 (2H, sept, J = 7.0 Hz, C*H*Me$_2$), 3.69 (2H, m, ═CH), 3.35 (2H, sept, J = 7.0 Hz, C*H*Me$_2$), 3.24 (1H, sept, J = 7.3 Hz, C*H*Me$_2$), 2.28 (2H, m, CH$_2$ in cod), 2.21 (1H, sept, J = 7.6 Hz, C*H*Me$_2$), 2.05 (2H, m, CH$_2$ in cod), 1.76 (2H, m, CH$_2$ in cod), 1.54 (2H, m, CH$_2$ in cod), 1.38 (6H, d, J = 6.7 Hz, CH*Me*$_2$), 1.26 (6H, d, J = 6.4 Hz, CH*Me*$_2$), 1.25 (6H, d, J = 6.7 Hz, CH*Me*$_2$), 1.21 (6H, d, J = 7.0 Hz, CH*Me*$_2$), 1.19 (6H, d, J = 7.3 Hz, CH*Me*$_2$), 1.06 (6H, d, J = 7.0 Hz, CH*Me*$_2$), −9.61 (1H, s, Ru−H); ^{13}C NMR (toluene-d_8; at −20 °C) δ_C 167.3, 164.1, 161.8, 155.6 (s × 4, 3- and 5-pz), 104.1 (d, J = 167 Hz, 4-pz), 98.2 (d, J = 169 Hz, 4-pz), 72.8 (d, J = 156 Hz, ═CH), 33.1, 28.3 (t × 2, J = 129 Hz, CH$_2$ in cod), 29.2, 28.6, 27.2, 26.7 (d × 4, J = 127 Hz, *C*HMe$_2$), 24.6, 24.3, 23.8, 23.4, 23.1, 22.9 (q, J = 128 Hz, CH*Me*$_2$); IR (KBr) 2964 (vs), 2928 (s), 2868 (s), 2838 (m), 2471 (m, ν_{B-H}), 2091 (w, ν_{Ru-H}), 1538 (s), 1461 (s), 1382 (s), 1363 (s), 1304 (m), 1171 (vs), 1132 (s), 1051 (s), 789 (s); MS (FD) 676 (M$^+$ for the ^{101}Ru isotopomer). Anal. Calcd for $C_{35}H_{59}BN_6Ru$: C, 62.21; H, 8.80; N, 12.44. Found: C, 61.71; H, 8.43; N, 12.32. Spectral data for **1C**: ^{1}H NMR (toluene-d_8; at −20 °C) δ_H 6.18 (1H, s, pz), 5.76 (2H, s, pz), 4.22 (2H, sept, J = 7.1 Hz, C*H*Me$_2$), 4.15 (2H, sept, J = 7.1 Hz, C*H*Me$_2$), 3.74 (2H, m, CH═), 3.46 (4H, m, ═CH and 2·C*H*Me$_2$), 3.19 (1H, sept, J = 7.1 Hz, C*H*Me$_2$), 2.46, 2.39, 1.88, 1.78 (2H × 4, m, CH$_2$ in cod), 1.46 (6H, d, J = 7.1 Hz, CH*Me*$_2$), 1.30 (6H, d, J = 7.1 Hz, CH*Me*$_2$), 1.21 (6H, d, J = 6.4 Hz, CH*Me*$_2$), 1.16 (6H, d, J = 6.4 Hz, CH*Me*$_2$), 1.07 (12H, d, J = 7.1 Hz, CH*Me*$_2$), −6.88 (1H, s, Ru−H); ^{13}C NMR (toluene-d_8; at −20 °C) δ_C 160.6, 159.1, 158.5, 157.1 (s × 4, 3- and 5-pz), 100.0 (d, J = 169 Hz, 4-pz), 98.5 (d, J = 171 Hz, 4-pz), 71.0 (d, J = 156 Hz, ═CH), 70.5 (d, J = 154 Hz, ═CH), 33.1, 30.6 (t × 2, J = 127 Hz, CH$_2$ in cod), 28.8, 28.3, 26.4, 25.7 (d × 4, J = 127 Hz, *C*HMe$_2$), 24.9, 24.4, 24.0, 23.9, 23.43, 23.39 (q, J = 127 Hz, CH*Me*$_2$); IR (KBr) 2964 (vs), 2867 (s), 2836 (m), 1937 (br s, ν_{Ru-H-B}), 1540 (s), 1472 (s), 1380 (s), 1301 (s), 1220 (m), 1180 (m), 1156 (s), 1051 (s), 840 (m), 789 (s), 735 (m), 716 (m), 670 (m); MS (FD) 676 (M$^+$ for the ^{101}Ru isotopomer). Anal. Calcd for $C_{35}H_{59}BN_6Ru$: C, 62.21; H, 8.80; N, 12.44. Found: C, 61.74; H, 8.95; N, 12.51.

Synthesis of 2C. Stirring an acetone solution (20 mL) of [Ru(H)(cod)(NH$_2$NMe$_2$)$_3$]BPh$_4$ (0.99 g, 1.39 mmol) and KTp^{iPr} (1.01 g, 1.39 mmol) for 90 min at room temperature gave an orange-red solution. After removal of the volatiles under reduced pressure products were extracted with ether (40 mL) and passed through a Celite pad to remove inorganic salts. The volatiles were removed again under reduced pressure, and acetonitrile (10 mL) was added. Then ether was added to dissolve the solid completely. Concentration and cooling at −30 °C gave **2C** (207 mg, 0.227 mmol, 16% yield) as yellow crystals. **2C**: ^{1}H NMR (C_6D_6; at rt) δ_H 4.30 (1H, sept, J = 7.1 Hz, C*H*Me$_2$), 4.12 (2H, sept, J = 7.1 Hz, C*H*Me$_2$), 3.66 (2H, sept, J = 7.1 Hz, C*H*Me$_2$), 3.32 (1H, sept, J = 6.9 Hz, C*H*Me$_2$), 3.55, 3.29 (2H × 2, m, CH═), 2.30, 2.25, 1.76, 1.66 (2H × 4, m, CH$_2$ in cod), 1.49, 1.41, 1.39, 1.36, 1.34, 1.30 (6H × 6, J = 7 Hz, CHMe$_2$), −7.12 (1H, s, Ru−H); ^{13}C NMR (toluene-d_8; at −20 °C) δ_C 157.8, 156.5, 153.7, 151.4 (s × 4, 3- and 5-pz), 93.3, 89.3 (s × 2, 4-pz), 72.3, 71.7 (d × 2, J = 154 Hz, ═CH), 32.9, 30.3 (t × 2, J = 128 Hz, CH$_2$ in cod), 29.9, 27.0, 26.4, 25.3 (d × 4, J = 127 Hz, *C*HMe$_2$), 22.2, 20.9, 20.8, 20.7, 20.54, 20.47 (q × 6, J = 128 Hz, CH*Me*$_2$); IR (KBr) 2969 (vs), 2871 (s), 2836 (m), 2094 (w, ν_{Ru-H}), 1944 (vs, ν_{Ru-H-B}), 1516 (m), 1478 (m), 1438 (s), 1393 (m), 1384 (m), 1304 (m), 1279 (s), 1213 (s), 1174 8s), 1139 (m), 1092 (s), 1023 (s), 876 (w), 847 (m), 797 (s), 778 (m), 716 (m), 684 (m). MS (FD) 910 (M$^+$: the most intense peak). Anal. Calcd for $C_{35}H_{56}BN_6Br_3Ru$: C, 46.07; H, 6.19; N, 9.21; Br, 26.27. Found: C, 45.89; H, 6.11; N, 9.03; Br, 26.56.

X-ray Crystallography. Singles crystals of **1A** and **2C** were obtained by recrystallization from acetone−ether and mounted on glass fibers.

Diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with Mo Kα radiation (λ = 0.710 59 Å). All the data collections were carried out at rt. 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 6° (**1A**), 2° (**2C**); the number of oscillation images 22 (**1A**), 40 (**2C**); the exposed time 45 min (**1A**), 50 min (**2C**). Readout was performed with the pixel size of 100 μm × 100 μm.

The structural analysis was performed on an IRIS O2 computer using teXsan structure solving program system obtained from the Rigaku Corp., Tokyo, Japan. Neutral scattering factors were obtained from the standard source.[14] In the reduction of data, Lorentz and polarization corrections were made. An empirical absorption correction was also made.[15] Crystallographic data for **1A** and **2C** are listed in Table 2.

The structures were solved by a combination of the direct methods (SHELXL 87) and Fourier synthesis (DIRDIF). Non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms except the Ru−H and B−H atoms (refined isotropically) were fixed at the calculated positions (C−H = 0.95 Å) and were not refined.

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Note Added in Proof. After submission of our manuscript, Parkin et al. reported the κ_3(BH) structure of a BpCo complex, (H$_2$Bpz$^R_2$)$_2$Co. Ghosh, P.; Bonnano, J. B.; Parkin, J. *J. Chem. Soc., Dalton Trans.* **1998**, 2779.

Supporting Information Available: Structural parameters for **1A** and **2B** (8 pages). Ordering information is given on any current masthead page.

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