

**New Alkyl Organo Complexes of Ruthenium: X-ray  
Molecular Structure of a  
[Hydridotris(pyrazolyl)borato]methylruthenium  
Complex, [RuTp\*(CH<sub>3</sub>)(cod)] (Tp\* =  
Hydridotris(3,5-dimethylpyrazolyl)borate, cod =  
1,5-Cyclooctadiene), Containing an Unusual  
Three-Center B(μ-H)Ru Bond**

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Received May 21, 1996<sup>®</sup>

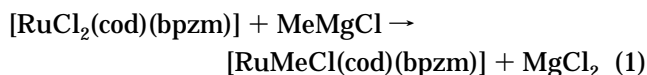
*Summary:* The reaction of [RuCl<sub>2</sub>(cod)(bpzm)] (**1**; cod = 1,5-cyclooctadiene, bpzm = bis(pyrazol-1-yl)methane) with MeMgCl gives [RuMeCl(cod)(bpzm)] (**2**). This complex reacts with AgCF<sub>3</sub>SO<sub>3</sub>, affording [RuMe(CF<sub>3</sub>SO<sub>3</sub>)(cod)(bpzm)] (**3**) and AgCl. [RuTp\*Me(cod)] (**4**) and [RuTp\*Me(cod)] (**5**) were prepared from the reaction of **3** with KTp (Tp = hydridotris(pyrazolyl)borate) and KTp\* (Tp\* = hydridotris(3,5-dimethylpyrazolyl)borate), respectively. Compound **5** was characterized by X-ray diffraction. The molecule shows unusual coordination of the hydridotris(3,5-dimethylpyrazolyl)borate ligand, where a three-center B(μ-H)Ru bond was found.

### Introduction

Recently we studied the chemistry of ruthenium complexes with N-donor ligands such as poly(pyrazol-1-yl)methane<sup>1</sup> and poly(pyrazol-1-yl)borate.<sup>2</sup> We subsequently became interested in the behavior of [RuCl<sub>2</sub>(cod)(bpzm)] (**1**), prepared from the reaction of the polymeric compound [RuCl<sub>2</sub>(cod)]<sub>n</sub> with bpzm (bis(pyrazolyl)methane), in alkylation reactions, in search of a general entry into N-donor-ligand-containing alkylruthenium complexes. This paper focuses on the preparation and structural details of some methyl[bis(pyrazolyl)methane]ruthenium and methyl[hydridotris(pyrazolyl)borato]ruthenium complexes, and we report an interesting example of a [hydridotris(pyrazolyl)borato]ruthenium(II) complex with only two coordinated pyrazolyl groups, where a strong interaction with the B–H bond of the ligand and the unsaturated ruthenium center is preferred to the N-coordination of the third pyrazolyl ring.

### Results and Discussion

[RuCl<sub>2</sub>(cod)(bpzm)] (**1**) reacts with MeMgCl, giving rise to the alkyl complex [RuMeCl(cod)(bpzm)] (**2**) (eq 1). Complex **2** crystallizes as an air-sensitive crystalline material from methanol. Attempts to prepare similar

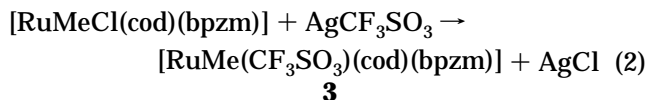


complexes by reaction with other Grignard reagents, such as EtMgCl and BzMgCl, were not successful, and intractable mixtures of products were obtained.

The IR spectrum of **2** shows the different absorption characteristics of the bpzm, Me, and cod ligands. The <sup>1</sup>H and <sup>13</sup>C NMR spectra exhibited only one set of pyrazol-1-yl resonances, indicating that the two pyrazolyl rings are equivalent (see Experimental Section). The H<sup>3</sup> and H<sup>5</sup> pyrazole resonances were assigned on the basis of the coupling constant criterion for pyrazoles where <sup>3</sup>J(H<sup>4</sup>,H<sup>5</sup>) > <sup>3</sup>J(H<sup>3</sup>,H<sup>4</sup>).<sup>3</sup> The CH<sub>2</sub> protons of the bpzm ligand are diastereotopic and appear as an AX system. The assignment of the C<sup>3</sup> and C<sup>5</sup> pyrazole resonances was made on the basis of the observation for free pyrazoles, where <sup>1</sup>J(C<sup>5</sup>,H<sup>5</sup>) > <sup>1</sup>J(C<sup>3</sup>,H<sup>3</sup>).<sup>4</sup> In addition, the <sup>1</sup>H and <sup>13</sup>C NMR spectra show the resonances for the methyl and the cod ligands, the signals for the latter concurring with the expected C<sub>s</sub> local symmetry within the molecule<sup>5</sup> (see Experimental Section).

The spectroscopic results agree with an octahedral environment for **2** (Figure 1) with a bpzm ligand located in the equatorial plane.

The reaction of **2** with silver triflate, AgCF<sub>3</sub>SO<sub>3</sub>, affords the triflate-containing complex [RuMe(CF<sub>3</sub>SO<sub>3</sub>)(cod)(bpzm)] (**3**) (eq 2). Complex **3** was isolated as an air-sensitive crystalline solid from acetone.



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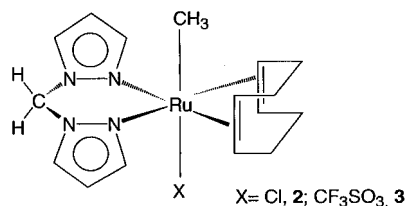
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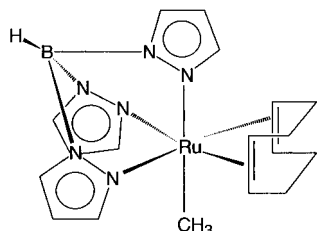
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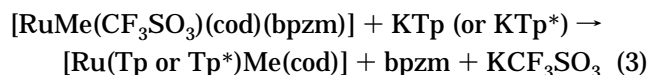
**Figure 1.** Proposed structure for complexes **2** and **3**.



**Figure 2.** Proposed structure for complex **4**.

In the IR spectrum of complex **3** the presence of several bands (see Experimental Section) corresponding to a coordinated triflate<sup>6</sup> is noteworthy. Again, the <sup>1</sup>H and <sup>13</sup>C NMR spectra indicated the equivalence of the two pyrazolyl rings in the bpzp ligand, and the corresponding resonances for H<sup>3</sup>, H<sup>5</sup>, C<sup>3</sup>, and C<sup>5</sup> were assigned by using the criteria previously described for complex **2** (see Experimental Section). For the CH<sub>2</sub> group an AB system was observed in the <sup>1</sup>H NMR spectrum. In addition, the <sup>1</sup>H and <sup>13</sup>C spectra display resonances corresponding to the Me, cod, and CF<sub>3</sub>SO<sub>3</sub> ligands (see Experimental Section). An octahedral environment for complex **2** is proposed on the basis of the spectroscopic data (see Figure 1).

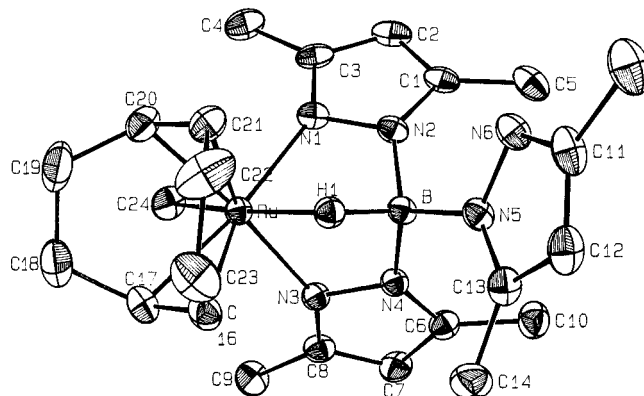
Moreover, **3** reacts with 1 equiv of KTp or KTp\* in acetone at room temperature to give the complexes [RuTpMe(cod)] (**4**) and [RuTp\*Me(cod)] (**5**), respectively (eq 3). The trans effect of the methyl group probably



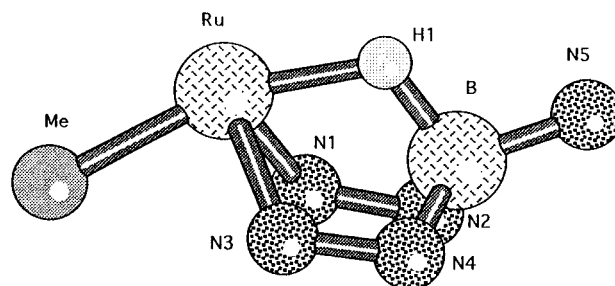
promotes the triflate displacement, as was previously observed in the reaction of the hydride derivative [RuHCl(bpzm)(cod)] with KTp.<sup>2</sup> Complexes **4** and **5** were isolated as air-sensitive crystalline solids from diethyl ether.

The IR spectrum of **4** shows a characteristic band at 2450 cm<sup>-1</sup>, which corresponds to ν(B–H). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **4** show the expected resonances for two distinct sets of pyrazole rings, and their assignment was carried out by comparison with the spectrum for [RuHCl(bpzm)(cod)].<sup>2</sup> Furthermore, the methyl signals and those corresponding to a cod group, bonded with C<sub>s</sub> symmetry, are present (see Experimental Section). Finally, the <sup>11</sup>B NMR spectrum displays a doublet at –3.62 ppm (<sup>1</sup>J(B,H) = 125.1 Hz), the signal appearing at a higher field than in KTp (<sup>1</sup>J(B,H) = 108.4 Hz). The data are in agreement with an octahedral environment, as depicted in Figure 2.

The IR spectrum of **5** exhibits a band at 1870 cm<sup>-1</sup>, which is ascribed to ν(Ru–H–B), and the <sup>1</sup>H and <sup>13</sup>C NMR spectra show the signals of one Tp\* ligand where



**Figure 3.** ORTEP drawing (50% probability level) of [RuTp\*Me(cod)] (**5**) with the atom-drawing scheme. Selected distances (Å): Ru–B, 2.632(4); Ru–H(1), 1.77(3); Ru–C(24), 2.159(4); Ru–N(1), 2.142(3); Ru–N(3), 2.173(3); B–H(1), 1.33(3); B–N(2), 1.536(5); B–N(4), 1.537(4); B–N(5), 1.505(4). Selected angles (deg): Ru–H(1)–B, 115.0(2); N(1)–Ru–N(3), 87.8(1); C(24)–Ru–H(1), 162.0(1); N(2)–B–N(4), 108.1(3); N(5)–B–H(1), 105.0(1).



**Figure 4.** Boat structure found in complex **5**.

two of the three pyrazolyl rings are equivalent. The spectra also show the characteristic resonances for the methyl and cod ligand, the latter being bonded with C<sub>s</sub> local symmetry, as well as the signal for the BH group, which shows up as a quadruplet at 1.47 ppm (<sup>1</sup>J(B,H) = 71 Hz) (see Experimental Section). The <sup>11</sup>B NMR spectrum displays a doublet at –3.56 ppm (<sup>1</sup>J(B,H) = 71 Hz), appearing at lower field than in KTp\* (<sup>1</sup>J(B,H) = 108.6 Hz). The lower value found for the coupling constant compared with that for KTp\* agrees with a decrease in the B–H interaction.<sup>7</sup>

An X-ray crystal structure determination was carried out for **5**, and the obtained structure corresponds to the proposed compound with a Ru–H–B interaction. An ORTEP drawing is shown in Figure 3. The molecule contains a six-membered B(μ-pz)<sub>2</sub>Ru ring typical of poly(pyrazolyl)borate complexes and adopts the usual boat structure (Figure 4).<sup>8</sup> The depth of the boat is measured by the Ru,N(1),N(3)/N(1),N(2),N(3),N(4) and B,N(2),N(4)/N(1),N(2),N(3),N(4) dihedral angles, which are equal to 126.4 and 111.6°, respectively.

Compared to other known “homoscorpionates” of the type RB(pz)<sub>3</sub>M, there is an unprecedented feature in this structure. Our HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>(Tp\*) scorpionate “stings” the ruthenium atom with its hydrogen atom and not with the nitrogen atom of the third pz fragment, as is generally observed. An analogous type of bonding, B(μ-pz)<sub>2</sub>(μ-H)M, has already been found in Ru,<sup>9</sup> Ni,<sup>10</sup> Mo,<sup>11</sup>

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Ta,<sup>7</sup> and Zr<sup>12</sup> complexes, but the scorpionate ligand in all these compounds is H<sub>2</sub>B(pz)<sub>2</sub>.

The Ru–N bond lengths of 2.142(3) and 2.173(3) Å are slightly longer than those reported for the [H( $\mu$ -H)B(3,5-Me<sub>2</sub>pz)<sub>2</sub>Ru(cod)H] structure (~2.11 Å).<sup>9</sup> This is probably due to the smaller size of the H<sub>2</sub>B(3,5-Me<sub>2</sub>pz)<sub>2</sub> ligand compared to that of our HB(3,5-Me<sub>2</sub>pz)<sub>3</sub> ligand. However, the Ru–B separation in **5** (2.632(4) Å) is significantly shorter than the analogous separation (2.673(2) Å) in [H( $\mu$ -H)B(3,5-Me<sub>2</sub>pz)<sub>2</sub>Ru(cod)H].<sup>9</sup> Moreover, the Ru–H(1) bond in **5** (1.77(3) Å) is also shorter than the agostic Ru···H interaction (2.06(2) Å) in [H( $\mu$ -H)B(3,5-Me<sub>2</sub>pz)<sub>2</sub>Ru(cod)H]. This may be related to the different ligands trans to the Tp, namely Me and H, and their respective trans-influence effects. Thus, the B–H–Ru linkage in the structure reported here, in terms of valence bond, is a two-electron–three-center bond. It is worth noting that the B( $\mu$ -H)···M bonding in all the other complexes cited above containing the H<sub>2</sub>B(pz)<sub>2</sub> ligand<sup>9–12</sup> is also of an agostic nature. Thus, the three-center B( $\mu$ -H)M bonding observed in **5** is unique. For the moment, the only explanation for this behavior is the presence of the third pz substituent on the HB(3,5-Me<sub>2</sub>pz)<sub>3</sub> ligand, but we do not know why the system is not of the type HB( $\mu$ -pz)<sub>3</sub>Ru, although the third pyrazolyl ring would have trouble coordinating to the metal center for steric reasons. It is also noteworthy that the analogous complex Tp\**Ru*H(cod)<sup>13</sup> exhibits the Tp\* classically linked by three pyrazolyl groups, and the different structural situation can be ascribed to the different trans-influence effects of both Me and H ligands. The B–N(2) and B–N(4) distances involving the bridging pyrazolyl substituents in **5** (1.537 Å) are the same as those (1.536 Å) observed in [H( $\mu$ -H)B(3,5-Me<sub>2</sub>pz)<sub>2</sub>Ru(cod)H] and in (C<sub>5</sub>H<sub>5</sub>)Ru(HBpz<sub>3</sub>),<sup>14</sup> but the B–N(5) bond to the dangling pz substituent is significantly shorter (1.505(4) Å).

### Experimental Section

All operations were performed under an inert atmosphere using standard vacuum line (Schlenk) techniques. Solvents were purified by distillation from appropriate drying agents before use. NMR spectra were recorded on a Varian Unity FT-300 instrument. IR spectra were recorded as Nujol mulls between CsI plates (in the region between 4000 and 200 cm<sup>-1</sup>) on a Perkin-Elmer PE 883 IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 microanalyzer. Potassium tris(pyrazol-1-yl)borates<sup>15</sup> and the ruthenium compound [RuCl<sub>2</sub>(cod)(bpzm)]<sup>1</sup> were prepared as previously reported.

**[RuMeCl(cod)(bpzm)] (2).** A solution of MeMgCl (3.0 M in THF; 0.97 mL, 2.92 mmol) was added to a THF solution (25 mL) of [RuCl<sub>2</sub>(cod)(bpzm)] (**1**; 1.00 g, 2.33 mmol) at –78 °C. The reaction mixture was stirred and warmed to room temperature over a period of 2 h. After the ivory colored solution was stirred for 30 min at 25 °C, the THF was removed

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and the precipitate was washed with 5 mL of Et<sub>2</sub>O. Crystallization from methanol yielded 819 mg of **2** (86% yield). <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>):  $\delta$  7.99 (d, 2H, <sup>3</sup>J<sub>45</sub> = 2.2 Hz, H<sup>5</sup>), 7.38 (AX system, 2H, J<sub>AX</sub> = 13.2 Hz, CH<sub>2</sub>), 7.28 (d, 2H, <sup>3</sup>J<sub>34</sub> = 2.0 Hz, H<sup>3</sup>), 6.42 (pt, 2H, H<sup>4</sup>), 3.80 (br s, 2H, olefinic H of cod), 3.18 (br s, 2H, olefinic H of cod), 2.87 (m, 2H, H<sup>exo</sup> of cod), 2.36 (m, 2H, H<sup>exo</sup> of cod), 1.84 (d, 2H, J<sub>gem</sub> = 6.8 Hz, H<sup>endo</sup> of cod), 1.72 (d, 2H, J<sub>gem</sub> = 7.4 Hz, H<sup>endo</sup> of cod), 0.99 (s, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>OD):  $\delta$  144.11 (C<sup>3</sup>), 135.63 (C<sup>5</sup>), 108.69 (C<sup>4</sup>), 86.16 (sp<sup>2</sup> C of cod), 80.73 (sp<sup>2</sup> C of cod), 63.06 (CH<sub>2</sub>, bpzm), 30.90 (sp<sup>3</sup> C of cod), 29.53 (sp<sup>3</sup> C of cod), 8.94 (Me). Anal. Calcd for C<sub>16</sub>H<sub>23</sub>N<sub>4</sub>ClRu: C, 47.11; H, 5.68; N, 13.74. Found: C, 46.73; H, 5.59; N, 13.57.

**[RuMe(CF<sub>3</sub>SO<sub>3</sub>)(cod)(bpzm)] (3).** A solution of **2** (0.5 g, 1.23 mmol) in acetone (50 mL) was cooled to –78 °C, and the stoichiometric quantity of AgCF<sub>3</sub>SO<sub>3</sub> (0.33 g, 1.23 mmol) was added. The mixture was stirred for 15 h. A green solution was obtained, which was filtered and evaporated to dryness. The complex **3** was obtained as a green-yellow solid. Yield: 595 mg (93%). <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>):  $\delta$  8.20 (d, 2H, <sup>3</sup>J<sub>45</sub> = 2.4 Hz, H<sup>5</sup>), 7.62 (d, 2H, <sup>3</sup>J<sub>34</sub> = 2.2 Hz, H<sup>3</sup>), 6.70 (AB system, 2H, J<sub>AB</sub> = 13.5 Hz, CH<sub>2</sub>), 6.58 (pt, 2H, H<sup>4</sup>), 4.19 (br s, 2H, olefinic H of cod), 3.64 (br s, 2H, olefinic H of cod), 2.57 (m, 2H, H<sup>exo</sup> of cod), 2.41 (m, 2H, H<sup>exo</sup> of cod), 1.98 (d, 2H, J<sub>gem</sub> = 7.4 Hz, H<sup>endo</sup> of cod), 1.91 (d, 2H, J<sub>gem</sub> = 8.0 Hz, H<sup>endo</sup> of cod), 1.39 (s, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>OD):  $\delta$  144.36 (C<sup>3</sup>), 135.83 (C<sup>5</sup>), 121.75 (c, <sup>1</sup>J<sub>CF</sub> = 1269 Hz, CF<sub>3</sub>SO<sub>3</sub>), 108.78 (C<sup>4</sup>), 86.72 (sp<sup>2</sup> C of cod), 80.80 (sp<sup>2</sup> C of cod), 63.01 (CH<sub>2</sub>, bpzm), 30.94 (sp<sup>3</sup> C of cod), 29.36 (sp<sup>3</sup> C of cod), 8.39 (Me). Anal. Calcd for C<sub>17</sub>H<sub>23</sub>N<sub>4</sub>O<sub>3</sub>F<sub>3</sub>SRu: C, 39.15; H, 4.45; N, 10.74. Found: C, 39.80; H, 4.16; N, 11.26.

**[RuTpMe(cod)] (4) and [RuTp\*Me(cod)] (5).** The salt KTp or KTp\* (0.20 or 0.27 g, respectively, 0.80 mmol) was added to an acetone solution (40 mL) of **3** (0.40 g, 0.77 mmol). The mixture was stirred for 15 h. The resulting solution was filtered and evaporated to dryness. The remaining solid contains the complex **4** or **5** and the ligand bpzm. Complex **4** was obtained as a green microcrystalline solid by crystallization from diethyl ether. Yield: 235 mg (70%). For **5**, the bpzm ligand was sublimed under vacuum at 100 °C. Orange crystals of **5** for the X-ray structural analysis were then obtained by crystallization from a saturated diethyl ether solution. Yield: 340 mg (85%). For **4**: <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$  8.44 (d, 1H, <sup>3</sup>J<sub>3,4</sub> = 2.0 Hz, H<sup>3</sup>), 7.84 (d, 1H, <sup>3</sup>J<sub>45</sub> = 2.2 Hz, H<sup>5</sup>), 7.72 (d, 2H, <sup>3</sup>J<sub>45</sub> = 1.8 Hz, H<sup>2</sup>), 7.35 (d, 2H, <sup>3</sup>J<sub>34</sub> = 2.2 Hz, H<sup>5</sup>), 6.37 (pt, 1H, H<sup>4</sup>), 6.18 (pt, 2H, H<sup>4</sup>), 3.42 (br s, 2H, olefinic H of cod), 3.15 (br s, 2H, olefinic H of cod), 2.77 (m, 2H, H<sup>exo</sup> of cod), 2.54 (m, 2H, H<sup>exo</sup> of cod), 1.98 (d, 2H, J<sub>gem</sub> = 8.11 Hz, H<sup>endo</sup> of cod), 1.94 (d, 2H, J<sub>gem</sub> = 7.40 Hz, H<sup>endo</sup> of cod), 1.49 (s, 3H, Me); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  143.21 (C<sub>A</sub><sup>3</sup>), 139.18 (C<sub>B</sub><sup>3</sup>), 105.73 (C<sub>A</sub><sup>4</sup>), 105.66 (C<sub>B</sub><sup>4</sup>), 135.63 (C<sub>A</sub><sup>5</sup>), 134.51 (C<sub>B</sub><sup>5</sup>), 82.13 (sp<sup>2</sup> C of cod), 74.72 (sp<sup>2</sup> C of cod), 30.45 (sp<sup>3</sup> C of cod), 30.26 (sp<sup>3</sup> C of cod), 14.75 (Me); IR (KBr, cm<sup>-1</sup>) 2450  $\nu$ (B–H). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>N<sub>6</sub>RuB: C, 48.67; H, 5.59; N, 18.70. Found: C, 49.44; H, 5.76; N, 19.22. For **5**: <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$  6.03 (s, 1H, H<sup>4</sup>), 5.67 (s, 2H, H<sup>4</sup>), 3.50 (br s, 2H, olefinic H of cod), 3.25 (br s, 2H, olefinic H of cod), 2.83 (m, 4H, H<sup>exo</sup> of cod), 2.44 (s, 3H, Me<sup>3</sup> or <sup>5</sup>), 2.45 (s, 6H, Me<sup>3</sup> or <sup>5</sup>), 2.23 (s, 3H, Me<sup>3</sup> or <sup>5</sup>), 2.25 (s, 6H, Me<sup>3</sup> or <sup>5</sup>), 1.87 (d, 2H, J<sub>gem</sub> = 7.8 Hz, H<sup>endo</sup> of cod), 1.80 (d, 2H, J<sub>gem</sub> = 7.8 Hz, H<sup>endo</sup> of cod), 1.47 (q, 1H, BH), 1.39 (s, 3H, Me); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  150.98 (C<sub>A</sub><sup>3</sup>), 149.48 (C<sub>B</sub><sup>3</sup>), 144.75 (C<sub>A</sub><sup>5</sup>), 143.56 (C<sub>B</sub><sup>5</sup>), 108.51 (C<sub>A</sub><sup>4</sup>), 107.82 (C<sub>B</sub><sup>4</sup>), 77.55 (sp<sup>2</sup> C of cod), 75.23 (sp<sup>2</sup> C of cod), 31.81 (sp<sup>3</sup> C of cod), 29.89 (sp<sup>3</sup> C of cod), 14.22 (Me<sub>A</sub><sup>3</sup> or <sup>5</sup>), 12.51 (Me<sub>B</sub><sup>3</sup> or <sup>5</sup>), 13.17 (Me<sub>A</sub><sup>3</sup> or <sup>5</sup>), 12.89 (Me<sub>B</sub><sup>3</sup> or <sup>5</sup>), 10.61 (Ru–Me); IR (KBr, cm<sup>-1</sup>) 1870  $\nu$ (Ru–H–B). Anal. Calcd for C<sub>24</sub>H<sub>43</sub>N<sub>6</sub>RuB: C, 55.29; H, 6.98; N, 16.35. Found: C, 55.28; H, 7.15; N, 16.12.

**X-ray Data Collection, Structure Determination, and Refinement of [RuTp\*Me(cod)] (5).** Crystal data: monoclinic, space group *P2<sub>1</sub>/c* (No. 14), *a* = 11.400(2) Å, *b* = 12.178(1) Å, *c* = 17.826(2) Å,  $\beta$  = 94.20(1)°, *V* = 2468 Å<sup>3</sup>, *d*<sub>calcd</sub> = 1.404 g cm<sup>-3</sup>, *Z* = 4,  $\mu$  = 6.45 cm<sup>-1</sup>. A deep red crystal with

the approximate dimensions  $0.4 \times 0.2 \times 0.15$  mm was sealed in a capillary and mounted on an Enraf-Nonius CAD4 diffractometer. The unit cell was determined and refined from 25 randomly selected reflections. Intensities were collected at room temperature and corrected for Lorentz and polarization effects. A linear decay correction ( $-5.6\%$ ) was performed. The structure was solved by means of a direct method (SHELXS) and subsequent least-squares and difference Fourier synthesis. After isotropic refinement of heavy atoms, some hydrogen atoms, including the bridging one (H(1)), were located on a difference Fourier synthesis map. The remaining hydrogen atoms were included in the structure factor calculation at their calculated positions, with the exception of those of the methyl group bound to the ruthenium atom. All non-hydrogen atoms were refined anisotropically. The final refinement led to the

following residuals:  $R = 0.039$ ,  $R_w = 0.043$ , and  $GOF = 1.44$ . Atomic coordinates are given in Supporting Information.

**Acknowledgment.** A.E.C., F.A.J., and A.O. gratefully acknowledge financial support from the DGICYT (Grant No. PB 92-0715) of Spain.

**Supporting Information Available:** Tables of crystallographic data, complete bond distances and angles, positional parameters of hydrogen atoms, and general displacement parameter expressions ( $B$ ) (6 pages). Ordering information is given on any current masthead page. A list of structure factors is available upon request from the authors.

OM960395O