

# Hydride and Borohydride Derivatives of (Pentamethylcyclopentadienyl)(tertiary phosphine)ruthenium

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Received November 4, 1986

Reaction of  $\text{NaBH}_4$  with  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2(\text{PR}_3)$  (**1**) in ethanol results in the formation of trihydrides  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PR}_3)$  (**2**,  $\text{R} = \text{PMe}_3, \text{PEt}_3, \text{P}(i\text{-Pr})_3, \text{PCy}_3, \text{PPh}_2\text{Me}, \text{PPh}_3$ ), the last of which is structurally characterized by a single-crystal X-ray diffraction study.  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PPh}_3)$  crystallizes in the triclinic space group  $P\bar{1}$  with two molecules in a unit cell of dimensions  $a = 11.568$  (2) Å,  $b = 13.012$  (2) Å,  $c = 9.169$  (1) Å,  $\alpha = 91.12$  (2)°,  $\beta = 89.72$  (2)°, and  $\gamma = 116.60$  (1)°. The molecule is shown to have pseudo  $C_3$  symmetry. The reaction of **1** with  $\text{NaBH}_4$  in THF yields tetrahydroborate complexes  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PR}_3)(\text{BH}_4)$  (**4**,  $\text{R} = \text{PMe}_3, \text{PEt}_3, \text{PCy}_3, \text{PPh}_2\text{Me}, \text{PPh}_3$ ), which are converted to the trihydrides **2** by treatment with ethanol. Irradiation of **2c** and **2f** with UV light in  $\text{C}_6\text{D}_6$  causes the H/D exchange reaction among the hydrides, the coordinated phosphine, and the solvent.

## Introduction

The chemistry of middle- and late-transition-metal polyhydride complexes has recently received much attention due to the potential applications of these complexes as the precursors of the active catalysts for the H/D exchange reaction and the C-H bond activation.<sup>1</sup>

Since the early 1970s polyhydridoruthenium complexes have been known and some of them were shown to catalyze the H/D exchange reaction with the deuteriated solvents in recent years.<sup>2</sup> In 1983, Davies et al. reported a synthetic method of a thermally stable ruthenium(IV) trihydride  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PPh}_3)$  and proposed that the trihydride possessed the trigonal-bipyramidal structure on the basis of IR and <sup>1</sup>H NMR studies.<sup>3</sup> Recently we reported the synthesis of a novel trihydridoruthenium(IV) complex,  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PPh}_3)$ , starting with the corresponding ruthenium(IV) phosphine complex  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuBr}_3(\text{PPh}_3)$  and the reducing agent  $\text{NaBH}_4$ ;<sup>4</sup> however, this method could not be applicable to the synthesis of trihydride complexes with the bulky phosphine ligand such as  $\text{PCy}_3$ . In a recent communication, Arliguie and Chaudret briefly reported a new route to the trihydrides  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PR}_3)$  ( $\text{R} = \text{Ph}, i\text{-Pr}, \text{and Cy}$ ) by treatment of  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2(\text{PR}_3)$  with  $\text{LiBHET}_3$  in tetrahydrofuran.<sup>5</sup> Bercaw's group has also reported a synthesis of the trihydride  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PMe}_3)$  via hydrogenation of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{CH}_2\text{SiMe}_3)(\text{PMe}_3)_2$ .<sup>6</sup> We established in-

dependently a versatile synthetic method of the trihydridoruthenium(IV) complexes with a variety of phosphine ligands via a reaction of  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2(\text{PR}_3)$  with  $\text{NaBH}_4$  in ethanol.<sup>7</sup> We present here the preparation of the ruthenium(IV) trihydrides  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PR}_3)$  (**2**) and the ruthenium(II) tetrahydroborate  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PR}_3)(\text{BH}_4)$  (**3**). The molecular structure of  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PPh}_3)$  (**2f**) by single-crystal X-ray diffraction and the photoinduced H/D exchange reaction with the trihydrides **2** are also mentioned.

## Experimental Section

**General Methods.** All manipulations were carried out under a dry argon by using standard Schlenk techniques. All solvents were dried by conventional techniques<sup>8</sup> prior to use. Unless otherwise noted, all reagents were obtained from commercial suppliers. Proton and phosphorus-31 NMR spectra were recorded on a JEOL FX-100 or GX-500 spectrometers. All proton chemical shifts are reported as  $\delta$  values in parts per million relative to internal tetramethylsilane. Infrared spectra were recorded on a Hitachi 260-50 grating spectrophotometer. Photolyses of **2c** and **2f** were conducted with an Eiko-sha 300-W high-pressure mercury lamp (Model EHB-W1-300). Elemental analyses were performed by the analytical facility in the Research Laboratory of Resources Utilization at Tokyo Institute of Technology. Ruthenium(III) complexes  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2(\text{PR}_3)$  (**1**) were prepared by the reaction of  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2$  with the corresponding tertiary phosphines.<sup>10</sup>

**$(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PMe}_3)$  (**2a**).** A slurry of 0.496 g (1.29 mmol) of  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2(\text{PMe}_3)$  (**1a**) and 0.343 g (9.07 mmol) of  $\text{NaBH}_4$  in 15 mL of ethanol was allowed to react with stirring for 3 h at ambient temperature. After evaporation of solvent, the brown residue was extracted with the mixed solvent of diethyl ether and pentane (2:1 v/v). Removal of solvents from the extract afforded 0.373 g (92%) of **2a** as an ivory semisolid: IR (KBr) 2970, 2900, 1960, 1479, 1421, 1379, 1279, 950, 932, 746, 589, 372  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{13}\text{H}_{27}\text{PRu}$ : C, 49.51; H, 8.63. Found: C, 49.69; H, 8.74.

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Table I. Yields and Selected Spectral Data of  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}_3(\text{PR}_3)$  (2)

PR <sub>3</sub>	yield, %	<sup>1</sup> H NMR <sup>a</sup>			IR <sup>d</sup> ν(Ru-H), cm <sup>-1</sup>	
		C <sub>5</sub> Me <sub>5</sub> <sup>b</sup>	Ru-H <sup>c</sup>	other assignmts		
2a	PMe <sub>3</sub>	92	2.00 (1.0)	-10.50 (22.5)	1.10 (d, 9 H, <sup>2</sup> J <sub>PH</sub> = 9.3 Hz, P-CH <sub>3</sub> )	1960 <sup>e</sup>
2b	PEt <sub>3</sub>	94	1.99 (1.3)	-10.76 (21.1)	0.89 (dt, 9 H, <sup>3</sup> J <sub>PH</sub> = 15 Hz, <sup>3</sup> J <sub>HH</sub> = 7.8 Hz, P-C-CH <sub>3</sub> ), 1.19 (dq, 6 H, <sup>2</sup> J <sub>PH</sub> = 7.5 Hz, P-CH <sub>2</sub> -)	1976, 1966
2c	P- <i>i</i> -Pr <sub>3</sub>	85	2.01 (1.3)	-11.05 (21.7)	1.03 (dd, 18 H, <sup>3</sup> J <sub>PH</sub> = 12.9 Hz, <sup>3</sup> J <sub>HH</sub> = 7.0 Hz, P-C-CH <sub>3</sub> ), 1.57 (d of sept, 3 H, <sup>2</sup> J <sub>PH</sub> = 8.8 Hz, P-CH-)	1999, 1986
2d	PCy <sub>3</sub>	65	2.07 (1.3)	-11.01 (22.0)	1.21-1.98 (m, 33 H, P-C <sub>6</sub> H <sub>11</sub> )	1991 <sup>e</sup>
2e	PPh <sub>2</sub> Me	58	1.84 (1.3)	-9.98 (20.3)	1.71 (d, 3 H, <sup>2</sup> J <sub>PH</sub> = 8.9 Hz, P-CH <sub>3</sub> ), 6.91-7.70 (m, 10 H, P-C <sub>6</sub> H <sub>5</sub> )	1965 <sup>e</sup>
2f	PPh <sub>3</sub>	85	1.84 (1.3)	-9.72 (20.5)	6.95-7.82 (m, 15 H, P-C <sub>6</sub> H <sub>5</sub> )	1975, 1960 (1974, 1960) <sup>e</sup>

<sup>a</sup> Shifts are in ppm, relative to SiMe<sub>4</sub> at 100 MHz and 30 °C in C<sub>6</sub>D<sub>6</sub>. <sup>b</sup> Number in parentheses is <sup>4</sup>J<sub>PH</sub> in Hz. <sup>c</sup> Number in parentheses is <sup>2</sup>J<sub>PH</sub> in Hz. <sup>d</sup> Measured in C<sub>6</sub>H<sub>6</sub>. <sup>e</sup> Measured in KBr.

**( $\eta^5\text{-C}_5\text{Me}_5$ )RuH<sub>3</sub>(PET<sub>3</sub>) (2b).** The complex was prepared by the same method for 2a, starting from ( $\eta^5\text{-C}_5\text{Me}_5$ )RuCl<sub>2</sub>(PET<sub>3</sub>) (1b) (0.414 g, 0.97 mmol). The complex was isolated in 94% (0.328 g) yield as a pale brown oil: IR (C<sub>6</sub>H<sub>6</sub>) 2963, 2899, 1976, 1966, 1455, 1444, 1377, 1069, 766 cm<sup>-1</sup>. Anal. Calcd for C<sub>16</sub>H<sub>33</sub>PRu: C, 53.76; H, 9.31. Found: C, 54.03; H, 9.27.

**( $\eta^5\text{-C}_5\text{Me}_5$ )RuH<sub>3</sub>[P(*i*-Pr)<sub>3</sub>] (2c).** The preparation is analogous to that for 2a, using ( $\eta^5\text{-C}_5\text{Me}_5$ )RuCl<sub>2</sub>[P(*i*-Pr)<sub>3</sub>] (1c) (0.176 g, 0.38 mmol) as a starting material. The yield of the colorless prisms (mp 58 °C) was 85% (0.127 g): IR (KBr) 2972, 2952, 2905, 2864, 2032, 1999, 1986, 1459, 1378, 1030, 886, 789, 602 cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>39</sub>PRu: C, 57.11; H, 9.84. Found: C, 57.21; H, 10.01.

**( $\eta^5\text{-C}_5\text{Me}_5$ )RuH<sub>3</sub>(PCy<sub>3</sub>) (2d).** The complex was prepared in a similar manner to that for 2a, using ( $\eta^5\text{-C}_5\text{Me}_5$ )RuCl<sub>2</sub>(PCy<sub>3</sub>) (1d) (0.387 g, 0.66 mmol) as a starting material. The colorless prisms (mp 102 °C) were isolated in 65% (0.221 g) yield: IR (KBr) 2908, 2844, 1991, 1446, 1374, 1188, 1025, 1002, 887, 850, 765, 524 cm<sup>-1</sup>. Anal. Calcd for C<sub>28</sub>H<sub>51</sub>PRu: C, 64.71; H, 9.89. Found: C, 64.58; H, 10.13.

**( $\eta^5\text{-C}_5\text{Me}_5$ )RuH<sub>3</sub>(PPh<sub>2</sub>Me) (2e).** The complex was prepared by the same method for 2a, using ( $\eta^5\text{-C}_5\text{Me}_5$ )RuCl<sub>2</sub>(PPh<sub>2</sub>Me) (1e) (0.532 g, 1.05 mmol) as a starting material. The colorless prisms (mp 82 °C) were isolated in 58% (0.268 g) yield: IR (KBr) 3065, 3047, 2950, 2904, 1976, 1956, 1946, 1480, 1435, 1098, 883, 738, 519 cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>31</sub>PRu: C, 62.85; H, 7.11. Found: C, 62.63; H, 7.13.

**( $\eta^5\text{-C}_5\text{Me}_5$ )RuH<sub>3</sub>(PPh<sub>3</sub>) (2f).** A slurry of 0.480 g (0.84 mmol) of ( $\eta^5\text{-C}_5\text{Me}_5$ )RuCl<sub>2</sub>(PPh<sub>3</sub>) (1f) and 0.128 g (3.40 mmol) of NaBH<sub>4</sub> in 10 mL of ethanol was stirred for 24 h at ambient temperature. After evaporation of the solvent, the pale brown residual solid was extracted with three portions of 10 mL of benzene. Removal of the solvent from the combined extract under reduced pressure afforded the ivory microprisms. Recrystallization from 5 mL of diethyl ether at -30 °C gave 0.358 g (85%) of 2f as the colorless prisms: mp 136 °C dec; IR (KBr) 3051, 2976, 2951, 2898, 1974, 1960, 1480, 1435, 1375, 1093, 744, 699, 540, 518 cm<sup>-1</sup>; <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, external PPh<sub>3</sub>) δ 79.3. Anal. Calcd for C<sub>22</sub>H<sub>33</sub>PRu: C, 67.05; H, 6.63. Found: C, 66.92; H, 6.80.

**( $\eta^5\text{-C}_5\text{Me}_5$ )Ru(PMe<sub>3</sub>)(BH<sub>4</sub>) (3a).** A suspension of 0.455 g (1.19 mmol) of ( $\eta^5\text{-C}_5\text{Me}_5$ )RuCl<sub>2</sub>(PMe<sub>3</sub>) (1a) and 0.317 g (8.37 mmol) of NaBH<sub>4</sub> in 15 mL of tetrahydrofuran was stirred for 12 h at ambient temperature. After evaporation of the solvent, the red residual solid was extracted with two portions of 20 mL of pentane. The pentane solution was concentrated to 10 mL and cooled to -30 °C. The orange-red needles that formed were collected on a glass frit and dried under vacuum. The yield was 0.254 g (65%): mp 96-97 °C; IR (KBr) 2979, 2957, 2902, 2436, 2363, 2282, 1479, 1379, 1285, 1151, 956, 935, 731, 673, 592, 373 cm<sup>-1</sup>. Anal. Calcd for C<sub>13</sub>H<sub>22</sub>BPRu: C, 47.72; H, 8.62. Found: C, 47.44; H, 8.57.

**( $\eta^5\text{-C}_5\text{Me}_5$ )Ru(PET<sub>3</sub>)(BH<sub>4</sub>) (3b).** The complex was prepared by the same method for 3a, starting from ( $\eta^5\text{-C}_5\text{Me}_5$ )RuCl<sub>2</sub>(PET<sub>3</sub>) (1b) (0.847 g, 1.99 mmol). The orange-red prisms were isolated in 65% (0.475 g) yield: mp 143-145 °C; IR (KBr) 2965, 2910, 2874, 2433, 2352, 2284, 1453, 1155, 1028, 764, 723, 634, 580, 424 cm<sup>-1</sup>. Anal. Calcd for C<sub>16</sub>H<sub>34</sub>BPRu: C, 52.03; H, 9.28. Found: C, 51.80; H, 9.11.

**( $\eta^5\text{-C}_5\text{Me}_5$ )Ru[P(*i*-Pr)<sub>3</sub>](BH<sub>4</sub>) (3c).** The complex was prepared in a similar manner to that for 3a, using ( $\eta^5\text{-C}_5\text{Me}_5$ )RuCl<sub>2</sub>[P(*i*-Pr)<sub>3</sub>] (1c) (0.548 g, 1.17 mmol) as a starting material.

The red prisms were isolated in 84% (0.294 g) yield: mp 128 °C; IR (KBr) 2955, 2897, 2870, 2393, 2318, 1458, 1379, 1276, 1183, 1023, 888, 645, 539, 429 cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>40</sub>BPRu: C, 55.47; H, 9.80. Found: C, 55.61; H, 10.15.

**( $\eta^5\text{-C}_5\text{Me}_5$ )Ru(PCy<sub>3</sub>)(BH<sub>4</sub>) (3d).** The preparation is analogous to that for 3a, using ( $\eta^5\text{-C}_5\text{Me}_5$ )RuCl<sub>2</sub>(PCy<sub>3</sub>) (1d) (0.329 g, 0.559 mmol) as a starting material. The yield of the orange-red prisms was 98% (0.290 g): mp 132 °C; IR (KBr) 2927, 2849, 2408, 2326, 1449, 1267, 1184, 1024, 1003, 847, 729, 670, 588, 518 cm<sup>-1</sup>. Anal. Calcd for C<sub>28</sub>H<sub>52</sub>BPRu: C, 63.27; H, 9.86. Found: C, 62.98; H, 10.05.

**( $\eta^5\text{-C}_5\text{Me}_5$ )Ru(PPh<sub>2</sub>Me)(BH<sub>4</sub>) (3e).** The complex was prepared by the same method for 3a, using ( $\eta^5\text{-C}_5\text{Me}_5$ )RuCl<sub>2</sub>(PPh<sub>2</sub>Me) (1e) (0.542 g, 1.07 mmol) as a starting material. The red prisms were isolated in 74% (0.359 g) yield: mp 151-152 °C; IR (KBr) 3051, 2980, 2900, 2387, 2297, 2223, 1484, 1434, 1178, 1098, 881, 699, 512 cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>32</sub>BPRu: C, 61.20; H, 7.15. Found: C, 60.97; H, 7.33.

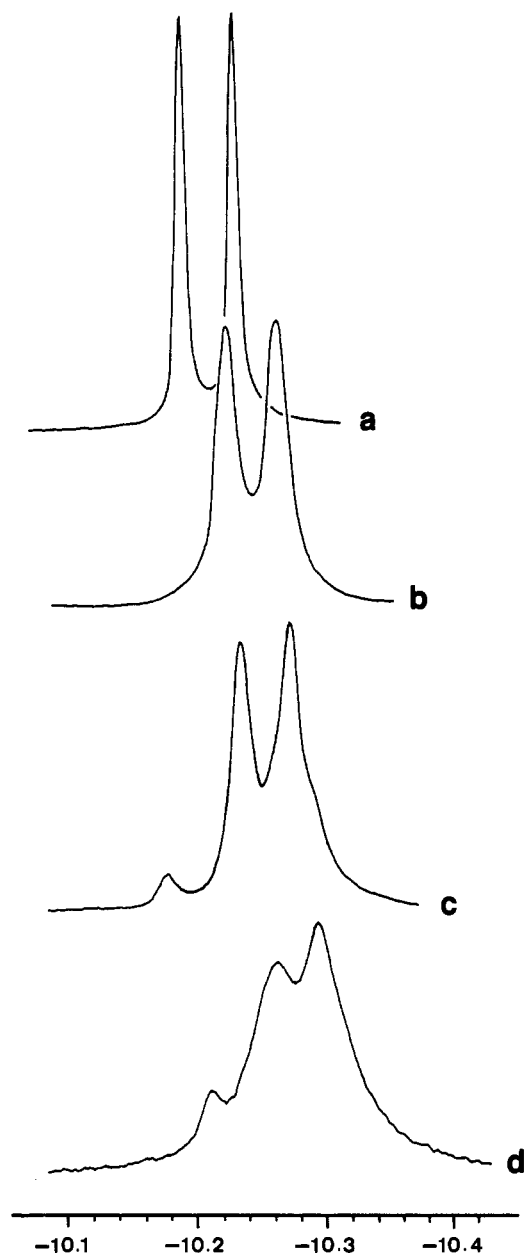
**( $\eta^5\text{-C}_5\text{Me}_5$ )Ru(PPh<sub>3</sub>)(BH<sub>4</sub>) (3f).** The complex was prepared by the same method for 3a, using ( $\eta^5\text{-C}_5\text{Me}_5$ )RuCl<sub>2</sub>(PPh<sub>3</sub>) (1f) (0.323 g, 0.57 mmol) as a starting material. The complex was isolated in 97% (0.331 g) yield as the orange-red prisms: mp 156 °C; IR (KBr) 3051, 2980, 2900, 2450, 2388, 2326, 1479, 1433, 1179, 1089, 1025, 750, 743, 697, 533, 516, 502, 453, 424 cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>34</sub>BPRu: C, 65.51; H, 6.63. Found: C, 65.36; H, 6.87.

**X-ray Data Collection and Structure Determination for 2f.** Crystals of 2f obtained from diethyl ether as described above proved suitable for an X-ray crystal structure determination. Single crystal of 0.15 × 0.38 × 0.55 mm was sealed in a thin-walled glass capillary under argon. Final lattice parameters were determined from a least-squares refinement of ((sin θ)/λ)<sup>2</sup> values for 50 reflections (20° < 2θ < 30°). The crystals are triclinic, space group P $\bar{1}$ , with *a* = 11.568 (2) Å, *b* = 13.012 (2) Å, *c* = 9.169 (1) Å, α = 91.12 (2)°, β = 89.72 (2)°, γ = 116.60 (1)°, *V* = 1233.8 (0) Å<sup>3</sup>, and *Z* = 2. Data were collected at 25 °C on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation using the ω-2θ scan technique (2° < 2θ < 60°).

The structure was solved by Patterson method and refined via standard least-squares and Fourier techniques. Solution and refinement were performed by using the UNICS III system for unique 4648 reflections with *F*<sub>o</sub> > 3σ(*F*<sub>o</sub>). The positions of the ruthenium and the phosphorus atoms were revealed by the inspection of a Patterson map. In a difference Fourier map, calculated following refinement of all non-hydrogen atoms with the anisotropic thermal parameters, the peaks corresponding to the positions of all hydrogen atoms including the hydridic hydrogens bound to the ruthenium atom were found. Final cycle of block-diagonal least-squares refinement of the structure including the anisotropic thermal parameters for the non-hydrogen atoms and isotropic ones for all hydrogen atoms converged at *R* = 0.0283 for 404 variables.

## Results and Discussion

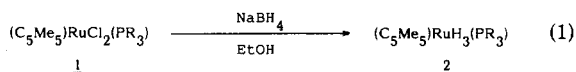
**Synthesis of Trihydride Complexes.** Initial attempt to prepare ( $\eta^5\text{-C}_5\text{Me}_5$ )RuH<sub>3</sub>(PR<sub>3</sub>) (2) starting from the corresponding ruthenium(IV) tribromide ( $\eta^5\text{-C}_5\text{Me}_5$ )RuBr<sub>3</sub>(PR<sub>3</sub>) met with little success. Whereas treatment



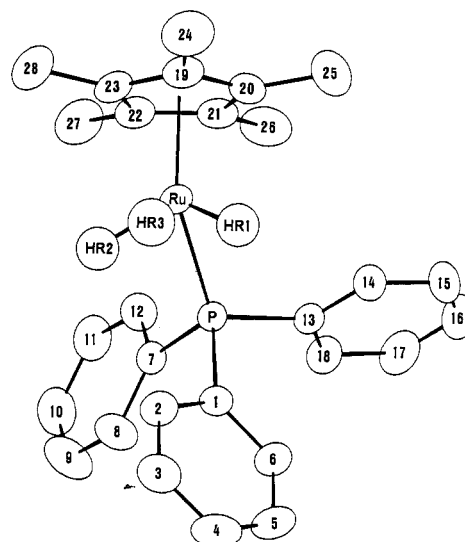
**Figure 1.**  $^1H$  NMR spectra (500 MHz) for **2f** measured in the mixed solvent of THF- $d_6$  and toluene- $d_8$  at various temperatures: (a) at 25 °C, (b) at -80 °C, (c) at -97.2 °C, and (d) at -117.5 °C.

of  $(\eta^5-C_5Me_5)RuBr_3(PPh_3)$  with excess  $NaBH_4$  in ethanol afforded the trihydride  $(\eta^5-C_5Me_5)RuH_3(PPh_3)$  in 18% yield, the tribromides coordinating bulky phosphines such as  $PCy_3$  or  $P(i-Pr)_3$  could not be converted to the trihydrides by reaction with  $NaBH_4$ .<sup>4</sup> The bulky ligands might prevent the access of the hydridic agent to the ruthenium(IV) center. Therefore this reaction was not investigated further, and the reaction of the sterically less congested ruthenium(III) dichlorides  $(\eta^5-C_5Me_5)RuCl_2(PR_3)$  (**1**) with  $NaBH_4$  was attempted.

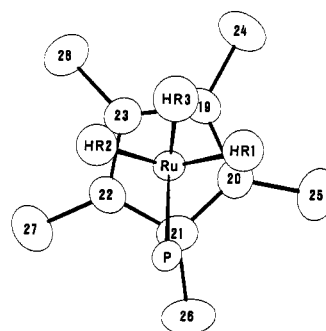
The reaction between  $(\eta^5-C_5Me_5)RuCl_2(PPh_3)$  (**1f**) and  $NaBH_4$  in ethanol proceeds smoothly to produce the colorless trihydride complex  $(\eta^5-C_5Me_5)RuH_3(PPh_3)$  (**2f**) in high yield (eq 1). This method is widely applicable for



$PR_3 = PMe_3, PEt_3, P^iPr_3, PCy_3, PPh_2Me, PPh_3$



**Figure 2.** ORTEP drawing of **2f**. Hydrogen atoms are not shown except for metal hydrides, HR1–HR3.



**Figure 3.** ORTEP drawing of **2f**, viewing approximately along the Ru–Cp' centroid vector.

the synthesis of the trihydridoruthenium(IV) complexes having a variety of phosphine ligands. Even in the reaction of  $(\eta^5-C_5Me_5)RuCl_2(PCy_3)$  with  $NaBH_4$ , trihydride  $(\eta^5-C_5Me_5)RuH_3(PCy_3)$  (**2d**) was isolated in 65% yield. Trihydrides **2a–f** were characterized by standard analytical and spectroscopic methodology. The yields and the selected spectroscopic data of trihydrides **2a–f** are listed in Table I.

The key spectral features of **2** that characterize its structural type are the IR and  $^1H$  NMR parameters associated with the hydride ligands. The IR spectra of the trihydrides reveal the sharp absorptions attributable to the stretching vibration of Ru–H bond in the region of 1960–1999  $cm^{-1}$ . In the  $^1H$  NMR of **2**, the resonances due to ruthenium-bound hydrogen atoms appear at -9.7 to -11.1 ppm as doublet ( $^2J_{PH} = 20$ –22 Hz). In addition, the hydride resonances shift by substitution of the phosphine ligands and the order of the chemical shifts seemed to be consistent with that of electronic parameters of the tertiary phosphines,  $PPh_3 < PPh_2Me < PMe_3 < PEt_3 < P(i-Pr)_3 < PCy_3$ , reported by Tolman.<sup>11</sup>

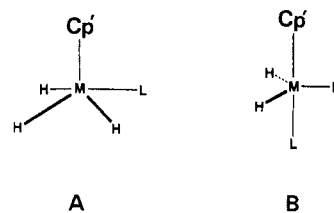
For the seven-coordinate trihydrides  $(\eta^5-C_5Me_5)MH_3(L)$  the following two idealized structures are possible: "four-legged piano stool ( $C_3$ )" (A) and the "trigonal bipyramid ( $C_{3v}$ )" (B). The hydride ligands in the "piano-stool" trihydride A should be distinguished between the magnetically equivalent two cis hydrides and the non-equivalent trans one. Such a structure has been predicted

Table II. Final Positional Parameters with Estimated Standard Deviations for 2f at 25 °C<sup>a</sup>

atom	x	y	z
Ru	0.0073 (0)	0.1760 (0)	0.2538 (0)
P	0.2026 (1)	0.2947 (1)	0.3476 (1)
C(1)	0.3308 (2)	0.2480 (2)	0.3381 (3)
C(2)	0.3419 (3)	0.1907 (3)	0.2129 (3)
C(3)	0.4407 (3)	0.1586 (3)	0.2005 (3)
C(4)	0.5287 (3)	0.1816 (3)	0.3121 (4)
C(5)	0.5172 (3)	0.2372 (3)	0.4371 (4)
C(6)	0.4204 (3)	0.2712 (2)	0.4501 (3)
C(7)	0.2853 (2)	0.4389 (2)	0.2679 (3)
C(8)	0.4079 (3)	0.4834 (3)	0.2087 (4)
C(9)	0.4617 (3)	0.5915 (3)	0.1450 (4)
C(10)	0.3953 (3)	0.6555 (3)	0.1423 (4)
C(11)	0.2738 (3)	0.6131 (3)	0.2034 (3)
C(12)	0.2196 (3)	0.5054 (2)	0.2644 (3)
C(13)	0.2024 (2)	0.3306 (2)	0.5430 (3)
C(14)	0.1329 (3)	0.2411 (3)	0.6366 (3)
C(15)	0.1291 (3)	0.2633 (3)	0.7858 (3)
C(16)	0.1934 (3)	0.3742 (3)	0.8400 (3)
C(17)	0.2620 (3)	0.4629 (3)	0.7494 (3)
C(18)	0.2686 (3)	0.4415 (3)	0.5998 (3)
C(19)	-0.2058 (2)	0.0659 (2)	0.2448 (3)
C(20)	-0.1791 (2)	0.1251 (2)	0.3824 (3)
C(21)	-0.1274 (2)	0.2449 (2)	0.3563 (3)
C(22)	-0.1216 (2)	0.2605 (2)	0.2022 (3)
C(23)	-0.1698 (2)	0.1493 (2)	0.1329 (3)
C(24)	-0.2779 (3)	-0.0626 (3)	0.2213 (4)
C(25)	-0.2141 (3)	0.0708 (3)	0.5293 (4)
C(26)	-0.1017 (3)	0.3354 (3)	0.4723 (4)
C(27)	-0.0928 (3)	0.3694 (3)	0.1246 (4)
C(28)	-0.1965 (3)	0.1246 (3)	-0.0268 (4)
HR(1)	0.037 (3)	0.094 (2)	0.348 (3)
HR(2)	0.095 (3)	0.219 (2)	0.112 (3)
HR(3)	0.038 (3)	0.091 (3)	0.181 (3)
H2	0.280 (3)	0.176 (2)	0.131 (3)
H3	0.440 (3)	0.118 (3)	0.108 (3)
H4	0.595 (3)	0.156 (3)	0.307 (4)
H5	0.574 (3)	0.252 (3)	0.507 (4)
H6	0.418 (3)	0.314 (2)	0.538 (3)
H8	0.460 (3)	0.446 (3)	0.209 (3)
H9	0.549 (3)	0.622 (3)	0.108 (4)
H10	0.434 (3)	0.734 (3)	0.097 (3)
H11	0.227 (3)	0.661 (2)	0.204 (3)
H12	0.138 (3)	0.480 (2)	0.307 (3)
H14	0.086 (3)	0.164 (2)	0.601 (3)
H15	0.076 (3)	0.195 (3)	0.842 (3)
H16	0.187 (3)	0.393 (3)	0.942 (3)
H17	0.307 (3)	0.540 (3)	0.784 (3)
H18	0.320 (3)	0.503 (2)	0.536 (3)
H24(1)	-0.246 (3)	-0.087 (3)	0.132 (4)
H24(2)	-0.258 (3)	-0.099 (3)	0.307 (4)
H24(3)	-0.373 (4)	-0.084 (3)	0.235 (4)
H25(1)	-0.205 (3)	0.004 (3)	0.529 (3)
H25(2)	-0.161 (3)	0.122 (3)	0.601 (4)
H25(3)	-0.305 (3)	0.051 (3)	0.543 (4)
H26(1)	-0.040 (3)	0.341 (3)	0.540 (4)
H26(2)	-0.178 (3)	0.338 (3)	0.500 (4)
H26(3)	-0.057 (3)	0.419 (3)	0.438 (4)
H27(1)	-0.054 (3)	0.433 (3)	0.182 (4)
H27(2)	-0.177 (3)	0.365 (3)	0.081 (4)
H27(3)	-0.039 (3)	0.381 (3)	0.043 (4)
H28(1)	-0.188 (3)	0.057 (3)	-0.057 (3)
H28(2)	-0.287 (3)	0.114 (3)	-0.045 (3)
H28(3)	-0.141 (3)	0.184 (3)	-0.081 (4)

<sup>a</sup> Numbers in parentheses are errors in the last significant digit.

previously for ( $\eta^5\text{-C}_5\text{Me}_5$ )OsH<sub>3</sub>(CO)<sup>12</sup> on the basis of the <sup>1</sup>H NMR study and observed crystallographically for ( $\eta^5\text{-C}_5\text{Me}_5$ )IrH<sub>3</sub>(SnPh<sub>3</sub>).<sup>13</sup> On the other hand, Davies et al. concluded on the basis of the NMR study that ( $\eta^5$ -



$\text{C}_5\text{H}_5$ )RuH<sub>3</sub>(PPh<sub>3</sub>) presumably favored the  $C_{3v}$  structure B by the steric requirement of the bulky triphenylphosphine ligand.<sup>3</sup>

The <sup>1</sup>H NMR parameter for the hydride ligands of 2f measured in the mixed solvent of THF-*d*<sub>3</sub> and toluene-*d*<sub>8</sub> (5:1 v/v) at -80 °C was essentially identical with that measured at 25 °C though the signal was broadened to some extent (Figure 1a,b). When the solution was cooled to -97.2 °C, decoalescence of the signal of the three hydrides was observed (Figure 1c). Although the resonances for the three hydrides could not be well resolved even at -117.5 °C (Figure 1d), these data are in conflict with the  $C_{3v}$  structure B of complex 2f.

**X-ray Crystal Structure Analysis of 2f.** Trihydride complex 2f was prepared by reacting ( $\eta^5\text{-C}_5\text{Me}_5$ )RuCl<sub>2</sub>(PPh<sub>3</sub>) (1f) with excess NaBH<sub>4</sub> in ethanol as described in the Experimental Section. Recrystallization of the crude product from diethyl ether upon cooling at -30 °C yielded the colorless prisms suitable for a structure determination by X-ray diffraction. Complex 2f crystallizes in the space group  $P\bar{1}$ . Two different ORTEP views of the molecule appear in Figures 2 and 3. Final atomic coordinates and anisotropic thermal parameters are given in Tables II and III, respectively. Important bond lengths and angles are given with estimated standard deviations in Table IV according to the atom labeling scheme in Figures 2 and 3.

The molecule adopts a piano-stool configuration in analogy with that of ( $\eta^5\text{-C}_5\text{Me}_5$ )IrH<sub>3</sub>(SnPh<sub>3</sub>)<sup>13</sup> or ( $\eta^5\text{-C}_5\text{Me}_5\text{Et}$ )RuBr<sub>3</sub>(CO).<sup>14</sup> The Ru, P, and HR3 atoms and the Cp' centroid lie in a molecular pseudomirror plane within experimental error. The parameters associated with the ( $\eta^5\text{-C}_5\text{Me}_5$ )Ru fragment of 2f are unexceptional. Thus, the Ru-Cp' centroid distance of 1.91 Å and the average Ru-C(ring) distance of 2.26 Å are typical of the open-sandwich Cp' complexes of group VIII (8-10<sup>18</sup>) metals. The five-membered ring is effectively planar, and the substituent carbon atoms are lying out of the mean plane in a direction away from the ruthenium atom, by an average distance of 0.17 Å. The average Ru-H distance of 1.53 Å is comparable with the values of 1.49 Å in RuH(BH<sub>4</sub>)(PMe<sub>3</sub>)<sub>3</sub>,<sup>15</sup> 1.594 Å in ( $\eta^5\text{-C}_5\text{Me}_5$ )IrH<sub>2</sub>(SiEt<sub>3</sub>)<sub>2</sub>,<sup>16</sup> and 1.53 Å in ( $\eta^5\text{-C}_5\text{Me}_5$ )IrH<sub>3</sub>(SnPh<sub>3</sub>).<sup>13</sup> As observed in the structure of the analogous iridium trihydride ( $\eta^5\text{-C}_5\text{Me}_5$ )IrH<sub>3</sub>(SnPh<sub>3</sub>), the Ru-H bond length of 1.46 Å for the hydrides trans to the phosphine ligand is significantly shorter than those of 1.54 and 1.60 Å for the hydrides cis to the phosphine ligand. Elongation of the Ru-H bond cis to the phosphine ligand would possibly be explained due to the relative trans influence order of PR<sub>3</sub> < H.

**Preparation of Tetrahydroborate Complexes 3.** We attempted the reaction of 1 with NaBH<sub>4</sub> in tetrahydrofuran to clarify the mechanism of formation of the trihydrides 2. Treatment of 1 with an excess of NaBH<sub>4</sub> in

(14) Nowell, I. W.; Tabatabaian, K.; White, C. *J. Chem. Soc., Chem. Commun.* 1979, 547.

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(16) Ricci, J. S., Jr.; Koetzle, T. F.; Fernandez, M.; Maitlis, P. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* 1984, A40, C301.

(12) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* 1982, 104, 3722.

(13) Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* 1985, 107, 3508.

Table III. Anisotropic Temperature Factors of the Non-Hydrogen Atoms in 2f

atom	10 <sup>4</sup> B <sub>11</sub>	10 <sup>4</sup> B <sub>22</sub>	10 <sup>4</sup> B <sub>33</sub>	10 <sup>4</sup> B <sub>12</sub>	10 <sup>4</sup> B <sub>13</sub>	10 <sup>4</sup> B <sub>23</sub>
Ru	50 (0)	47 (0)	78 (0)	21 (0)	-8 (0)	-5 (0)
P	49 (1)	50 (0)	62 (1)	21 (0)	-3 (0)	0 (0)
C(1)	49 (2)	55 (2)	84 (3)	22 (2)	0 (2)	2 (2)
C(2)	71 (3)	84 (3)	100 (4)	42 (2)	-4 (2)	-9 (2)
C(3)	82 (3)	87 (3)	134 (4)	44 (2)	12 (3)	-12 (3)
C(4)	63 (3)	80 (3)	199 (6)	40 (2)	5 (3)	6 (3)
C(5)	94 (3)	97 (3)	147 (5)	42 (2)	-22 (3)	-3 (3)
C(6)	62 (2)	74 (2)	99 (4)	29 (2)	-12 (2)	-5 (2)
C(7)	57 (2)	55 (2)	63 (3)	16 (2)	-5 (2)	-2 (2)
C(8)	70 (3)	78 (3)	148 (5)	29 (2)	24 (3)	27 (3)
C(9)	94 (4)	91 (3)	190 (6)	22 (3)	50 (4)	45 (3)
C(10)	121 (4)	64 (2)	122 (4)	19 (2)	2 (3)	26 (3)
C(11)	114 (4)	66 (2)	113 (4)	40 (2)	-6 (3)	14 (2)
C(12)	79 (3)	65 (2)	103 (4)	31 (2)	5 (3)	10 (2)
C(13)	55 (2)	71 (2)	67 (3)	32 (2)	-4 (2)	1 (2)
C(14)	74 (3)	91 (3)	83 (3)	31 (2)	1 (2)	12 (2)
C(15)	98 (3)	135 (4)	77 (4)	53 (3)	17 (3)	23 (3)
C(16)	122 (4)	160 (4)	70 (3)	90 (4)	1 (3)	-11 (3)
C(17)	114 (4)	112 (3)	96 (4)	66 (3)	-24 (3)	-37 (3)
C(18)	81 (3)	81 (2)	84 (3)	38 (2)	-9 (2)	-12 (2)
C(19)	54 (2)	51 (2)	129 (4)	13 (2)	-13 (2)	-1 (2)
C(20)	50 (2)	72 (2)	105 (4)	18 (2)	7 (2)	10 (2)
C(21)	50 (2)	71 (2)	118 (4)	29 (2)	-3 (2)	-14 (2)
C(22)	56 (2)	57 (2)	120 (4)	27 (2)	-7 (2)	4 (2)
C(23)	56 (2)	69 (2)	105 (4)	28 (2)	-21 (2)	-4 (2)
C(24)	107 (4)	58 (2)	207 (6)	9 (2)	-24 (4)	-5 (3)
C(25)	107 (4)	123 (4)	131 (5)	25 (3)	24 (3)	33 (3)
C(26)	86 (3)	95 (3)	168 (5)	41 (3)	8 (3)	-52 (3)
C(27)	118 (4)	75 (3)	183 (6)	50 (3)	-27 (4)	20 (3)
C(28)	108 (4)	108 (3)	119 (4)	41 (3)	-40 (3)	-16 (3)

Table IV. Selected Lengths (Å) and Angles (deg) for 2f

Bond Lengths			
Ru-HR(1)	1.54 (4)	P-C(13)	1.843 (3)
Ru-HR(2)	1.60 (3)	C(19)-C(24)	1.510 (4)
Ru-HR(3)	1.46 (4)	C(20)-C(25)	1.502 (5)
Ru-C(19)	2.230 (2)	C(21)-C(26)	1.500 (5)
Ru-C(20)	2.282 (3)	C(22)-C(27)	1.497 (5)
Ru-C(21)	2.306 (3)	C(23)-C(28)	1.497 (4)
Ru-C(22)	2.270 (3)	C(19)-C(20)	1.426 (4)
Ru-C(23)	2.218 (3)	C(20)-C(21)	1.422 (4)
Ru-P	2.252 (1)	C(21)-C(22)	1.428 (4)
P-C(1)	1.839 (3)	C(22)-C(23)	1.433 (4)
P-C(7)	1.846 (3)	C(23)-C(19)	1.428 (4)
Bond Angles			
HR(1)-Ru-HR(2)	114.2 (18)	Ru-P-C(1)	118.0 (1)
HR(1)-Ru-HR(3)	61.1 (18)	Ru-P-C(7)	116.5 (1)
HR(2)-Ru-HR(3)	64.5 (17)	Ru-P-C(13)	114.9 (1)
P-Ru-HR(1)	78.3 (9)	C(1)-P-C(7)	101.1 (1)
P-Ru-HR(2)	77.3 (9)	C(1)-P-C(13)	102.2 (1)
P-Ru-HR(3)	100.0 (12)	C(7)-P-C(13)	101.6 (1)

tetrahydrofuran at ambient temperature produced a red-orange solution from which the novel tetrahydroborate complexes ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ru(PR<sub>3</sub>)(BH<sub>4</sub>) (**3a-f**) could be isolated in high yields as the air- and moisture-sensitive orange needles (eq 2). The tetrahydroborate complexes **3**



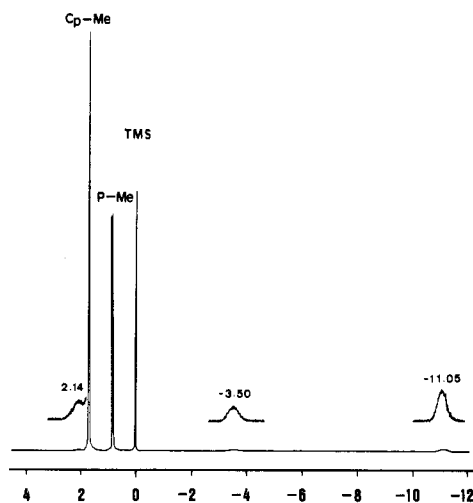
1

3

PR<sub>3</sub> = PMe<sub>3</sub>, PEt<sub>3</sub>, P<sup>i</sup>Pr<sub>3</sub>, PCy<sub>3</sub>, PPh<sub>2</sub>Me, PPh<sub>3</sub>

were characterized by spectroscopic and analytical methodology. The yields and the selected spectroscopic data of the tetrahydroborate complexes **3a-f** are given in Table V.

The IR and <sup>1</sup>H NMR spectra of **3** strongly suggested the incorporation of the tetrahydroborate anion into the com-

Figure 4. <sup>1</sup>H NMR spectrum (500 MHz) for **3a** in C<sub>6</sub>D<sub>6</sub> at 25 °C.

plex. Absorption around 2450–2300 cm<sup>-1</sup> in the IR spectra of **3a-f** are assigned to the B-H(terminal) stretching bands. The coordination of the tetrahydroborate ion via two Ru-H-B bridges in **3** was established by the characteristic <sup>1</sup>H NMR signals. The <sup>1</sup>H NMR spectrum of **3a** measured in C<sub>6</sub>D<sub>6</sub> at 25 °C reveals three resonance peaks for hydride ligands at  $\delta$  2.14 (1 H,  $w_{1/2}$  = 180 Hz), -3.50 (1 H,  $w_{1/2}$  = 145 Hz), and -11.05 (2 H,  $w_{1/2}$  = 115 Hz) (Figure 4). The resonances at  $\delta$  2.14 and -3.50 are due to two nonequivalent B-H nuclei, and the resonance at  $\delta$  -11.05 is due to two equivalent Ru-H-B bridges.

Protonolysis of a solution of **3a-f**, either by reaction with ethanol or by filtration through alumina (Merck Aluminium oxide 90 (Art. 1097)), yields quantitatively the corresponding trihydride complexes **2a-f** (eq 3). Alcoholysis of **3a** with EtOD instead of EtOH affords the monodeuterated complex ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)RuH<sub>2</sub>D(PMe<sub>3</sub>) (**2a-d**).

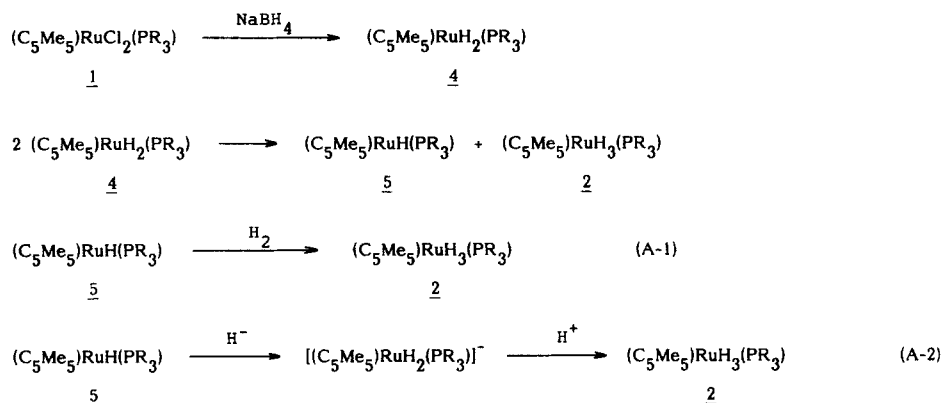
Table V. Yields and Selected Spectral Data of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PR}_3)(\text{BH}_4)$  (3)

PR <sub>3</sub>	yield, %	<sup>1</sup> H NMR <sup>a</sup>			IR <sup>e</sup> ν(RuH <sub>2</sub> BH <sub>2</sub> ), cm <sup>-1</sup>	
		C <sub>5</sub> Me <sub>5</sub> <sup>b</sup>	Ru-H-B <sup>c</sup>	other assignmts		
3a	PMe <sub>3</sub>	65	1.67 (1.2)	-11.05 (-3.50, 2.06) <sup>d</sup>	0.85 (d, 9 H, <sup>2</sup> J <sub>PH</sub> = 9.2 Hz, P-CH <sub>3</sub> )	2438, 2363, 2281
3b	PEt <sub>3</sub>	65	1.69 (1.2)	-11.63 (-3.22, 2.10) <sup>d</sup>	0.84 (dt, 9 H, <sup>3</sup> J <sub>PH</sub> = 15.4 Hz, <sup>3</sup> J <sub>HH</sub> = 7.5 Hz, P-C-CH <sub>3</sub> ), 1.55 (dq, 6 H, <sup>2</sup> H <sub>PH</sub> = 7.8 Hz, P-CH <sub>2</sub> -)	2433, 2352, 2284
3c	P- <i>i</i> -Pr <sub>3</sub>	84	1.68 (1.2)	-12.56	1.09 (dd, 18 H, <sup>3</sup> J <sub>PH</sub> = 12.3 Hz)	2393, 2318
3d	PCy <sub>3</sub>	99	1.73 (1.3)	-12.36	1.20-2.00 (m, 33 H, P-C <sub>6</sub> H <sub>11</sub> )	2408, 2329
3e	PPh <sub>2</sub> Me	74	1.52 (1.5)	-12.00	1.89 (d, 15 H, <sup>2</sup> J <sub>PH</sub> = 8.1 Hz, P-CH <sub>3</sub> ), 6.80-7.70 (m, 10 H, P-C <sub>6</sub> H <sub>5</sub> )	2387, 2292, 2223
3f	PPh <sub>3</sub>	97	1.51 (1.5)	-12.05	6.90-7.80 (m, 15 H, P-C <sub>6</sub> H <sub>5</sub> )	2450, 2388, 2326

<sup>a</sup>Shifts are in ppm, relative to SiMe<sub>4</sub> at 100 MHz and 30 °C in C<sub>6</sub>D<sub>6</sub>. <sup>b</sup>Numbers in parentheses is <sup>4</sup>J<sub>PH</sub> in Hz. <sup>c</sup>Number in parentheses is <sup>2</sup>J<sub>PH</sub> in Hz. <sup>d</sup>Terminal hydrides. <sup>e</sup>Measured in KBr.

## Scheme I

## Path A



## Path B

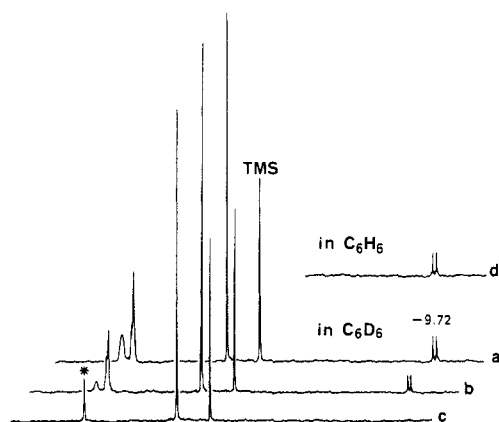
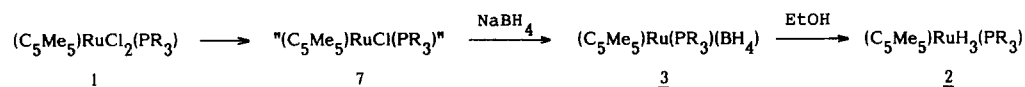
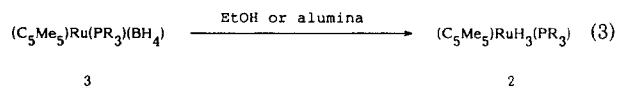


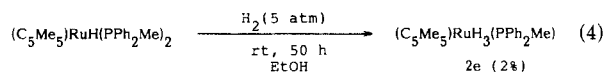
Figure 5. <sup>1</sup>H NMR spectra (100 MHz) for **2f** at 25 °C under irradiation of UV light (300 nm): (a) in C<sub>6</sub>D<sub>6</sub> without irradiation, (b) after irradiation for 15 min, (c) after irradiation for 1 h, and (d) after irradiation for 1 h in C<sub>6</sub>H<sub>6</sub>.



**Mechanism of the Formation of Trihydrides 2.** Two possible mechanisms for the formation of the ruthenium(IV) trihydride complexes **2** starting from the ruthenium(III) dichloride are shown in Scheme I.

The first mechanism (mechanism A) includes the disproportionation of ruthenium(III) dihydride **4**, giving **2** and

monohydride **5**, which would lead to trihydride **2** either by the oxidative addition of dihydrogen evolved in reaction A-1 or by successive addition of hydride and proton (eq A-2). We have examined the oxidative addition of H<sub>2</sub> to a ruthenium(II) monohydride and the reaction of the monohydride with NaBH<sub>4</sub> in ethanol. The reaction of  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}(\text{PPh}_2\text{Me})_2$  with H<sub>2</sub> (5 atm) in ethanol in a pressure bottle gave trihydride **2e** in a 2% yield at most (eq 4). Treatment of  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}(\text{PPh}_2\text{Me})_2$  with

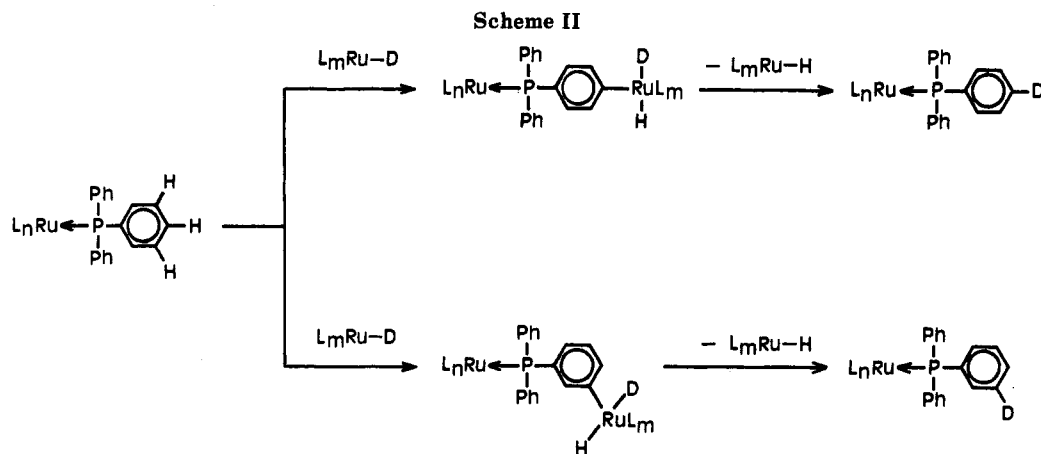


excess NaBH<sub>4</sub> in ethanol resulted in the recovery of the starting monohydride. We cannot yet rule out conclusively the mechanism A from these results because the reactivities of  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}(\text{PPh}_2\text{Me})_2$  might be different from those of the intermediary coordinatively unsaturated monohydride **5**.

The most reasonable pathway from complex **1** to **2** would appear to involve an initial reduction of **1** to the

(17) Monohydride  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuH}(\text{PPh}_2\text{Me})_2$  was derived from the corresponding monochloride by treatment with NaBH<sub>4</sub> in ethanol. Suzuki, H.; Lee, D. H.; Oshima, N.; Narasaka, S.; Xi, Z.; Moro-oka, Y., manuscript in preparation.

(18) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13-18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)



ruthenium(II) species  $(\eta^5-C_5Me_5)RuCl(PR_3)$  (**7**). We previously showed that complex **1** was easily reduced to the ruthenium(II) complexes in ethanol in the presence of varieties of ligands.<sup>10</sup> A nucleophilic displacement of a chloride ion by a tetrahydroborate ion gives **3**, which is immediately converted to trihydride **2** by protonolysis with ethanol as shown above.

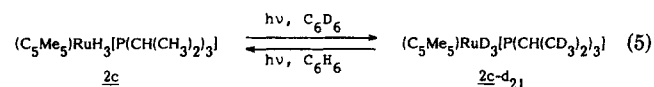
**H/D Exchange Reaction under UV Irradiation.** While the thermal stability of the trihydride complexes **2** is remarkably high with little or no decomposition occurring over a period of hours at 70 °C in toluene, the irradiation of **2c** and **2f** in  $C_6D_6$  solution with ultraviolet light caused the H/D exchange reaction among the solvent, the hydride ligands, and the coordinated phosphine.

The photolysis (>300 nm) of **2f** ( $1.05 \times 10^{-1}$  M in  $C_6D_6$ ) was conducted in a sealed NMR sample tube at 25 °C and monitored by means of  $^1H$  NMR spectroscopy (Figure 5). After 1 h of irradiation, the resonance signals of the coordinated triphenylphosphine and the hydride ligands completely disappeared. Photolysis of **2f** in  $C_6H_6$  in a sealed NMR sample tube at 25 °C for 1 h caused no apparent change in the  $^1H$  NMR spectrum. The result suggests that the product of photolysis in  $C_6D_6$  in a sealed tube is the trideuteride  $(\eta^5-C_5Me_5)RuD_3[P(C_6D_5)_3]$ .

The following two paths, a and b, are possibly proposed for the deuteration of the meta and para positions of the coordinated triphenylphosphine in **2f**: (a) via intermolecular metalation of  $PPh_3$  (Scheme II) and (b) via phosphidorruthenium intermediates. Path a includes intermolecular metalation of coordinated triphenylphosphine at the meta and para positions. Path b proceeds via an oxidative cleavage of the P-C bond of triphenylphosphine. The photolysis of **2f** was conducted in toluene at 25 °C for 5 h to elucidate the mechanism. The reaction path b could be ruled out since no formation of the tolylated or the benzylated phosphine in the photolysis products was confirmed by means of  $^{13}C$  NMR spectroscopy.

The H/D exchange reaction at the  $sp^3$  carbon atom is also observed in the photolysis of the trihydride having

a trialkylphosphine ligand. The irradiation of **2c** with UV light (>300 nm) in  $C_6D_6$  at 25 °C caused the H/D exchange among the solvent, the hydride ligands, and the distal hydrogens of the coordinated triisopropylphosphine to give  $(\eta^5-C_5Me_5)RuD_3[P(CH(CD_3)_2)_3]$  (**2c-d<sub>21</sub>**). The trihydride **2c** was recovered by the photolysis of the deuteriated complex **2c-d<sub>21</sub>** in  $C_6H_6$  at 25 °C (eq 5). The reaction



would proceed via the evolution of dihydrogen, giving a coordinatively unsaturated species,  $(\eta^5-C_5Me_5)RuH[P(i-Pr)_3]$ , followed by the metalation of  $sp^3$ -hybridized terminal C-H bonds of the coordinated phosphine to form a pseudometalacyclobutane intermediate as postulated in the photolysis of  $(\eta^5-C_6H_6)RuH_2[P(i-Pr)_3]$ <sup>2d</sup> or the thermal H/D exchange by  $RuH_4[P(i-Pr)_3]$ .<sup>2b</sup>

**Acknowledgment.** We thank the Instrument Center, Institute for Molecular Science, for the use of X-ray diffractometer (Rigaku AFC-5). We are grateful to Drs. T. Inabe and T. Mori at Institute for Molecular Science for aid of X-ray structural analysis. Financial support for this work was generously provided in part by grants from the Kawakami Memorial Foundation and the Ministry of Education, Science and Culture of the Japanese Government (No. 61225006).

**Registry No.** **1a**, 105711-27-1; **1b**, 108083-33-6; **1c**, 105711-24-8; **1d**, 105711-25-9; **1e**, 108083-35-8; **1f**, 105711-26-0; **2a**, 105744-77-2; **2b**, 108083-32-5; **2c**, 105711-28-2; **2d**, 105711-29-3; **2e**, 108083-34-7; **2f**, 105744-76-1; **3a**, 108083-36-9; **3b**, 108083-37-0; **3c**, 108083-38-1; **3d**, 108083-39-2; **3e**, 108083-40-5; **3f**, 108083-41-6;  $(\eta^5-C_5Me_5)RuH(PPh_2Me)_2$ , 108083-42-7.

**Supplementary Material Available:** Tables of crystal data, interatomic distances, angles, atomic coordinates, and thermal parameters (22 pages); a listing of observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.