

# TpRu Hydride and Dihydrogen Complexes Bearing Bidentate Phosphinoamine Ligands. NMR Study of Proton Transfer to [TpRuH(L)] (L = *R,R*-dippach, dippae; Tp = Hydrotris(pyrazolyl)borate)

Manuel Jiménez-Tenorio, M. Dolores Palacios, M. Carmen Puerta, and Pedro Valerga\*

Departamento de Ciencia de Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain

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The diastereomerically pure complexes [TpRuX(*R,R*-dippach)] (X = Cl (**1a**), H (**2a**); *R,R*-dippach = (*R,R*)-1,2-bis((diisopropylphosphino)amino)cyclohexane) as well as the nonchiral derivatives [TpRuX(dippae)] (X = Cl (**1b**), H (**2b**); dippae = 1,2-bis((diisopropylphosphino)amino)ethane) have been prepared and characterized. The reaction of either **1a** or **1b** with H<sub>2</sub> and NaBAR'<sub>4</sub> (Ar' = 3,5-bis(trifluoromethyl)phenyl) in fluorobenzene yields the corresponding stable dihydrogen complexes [TpRu(H<sub>2</sub>)(*R,R*-dippach)][BAR'<sub>4</sub>] (**3a**) and [TpRu(H<sub>2</sub>)(dippae)][BAR'<sub>4</sub>] (**3b**). No significant intramolecular interaction between the amino protons and the hydrogen atoms bound to the metal has been observed in any of these compounds. Both **3a** and **3b** react readily with dinitrogen, furnishing the complexes [TpRu(N<sub>2</sub>)(*R,R*-dippach)][BAR'<sub>4</sub>] (**4a**) and [TpRu(N<sub>2</sub>)(dippae)][BAR'<sub>4</sub>] (**4b**). The X-ray crystal structures of **3b** and **4b** were determined. The proton-transfer processes over the monohydrides **2a** and **2b** with HBF<sub>4</sub>·OEt<sub>2</sub> have been studied by NMR spectroscopy. Dicationic dihydrogen complexes [TpRu(H<sub>2</sub>)(*R,R*-dippachH)]<sup>2+</sup> (**5a**) and [TpRu(H<sub>2</sub>)(dippaeH)]<sup>2+</sup> (**5b**) result from the protonation of **2a** and **2b** at one of the NH groups of the respective phosphinoamine ligands by an excess (>10 equiv) of HBF<sub>4</sub>. These species undergo slow tautomerization to their monohydride isomers [TpRuH(*R,R*-dippachH<sub>2</sub>)]<sup>2+</sup> (**5a**) and [TpRuH(dippaeH<sub>2</sub>)]<sup>2+</sup> (**5b**). Intermediates having short hydride (*T*<sub>1</sub>)<sub>min</sub> values have been detected in the course of the proton transfer reactions, which possibly involve the formation of dihydrogen-bonded complexes and/or contact ion pairs between the monohydride complex and the proton donor. Finally, the reaction of **2a** with less than 1 equiv of HBF<sub>4</sub> at –80 °C generates a hydride species having an extremely short (*T*<sub>1</sub>)<sub>min</sub> value of 0.5 ms at –62 °C and 400 MHz. The causes for this fast relaxation phenomenon are so far unknown.

## Introduction

The protonation of neutral hydride complexes is a well-established procedure for the preparation of dihydrogen complexes.<sup>1–3</sup> The protonation reactions of half-sandwich ruthenium hydride systems of the type [(C<sub>5</sub>R<sub>5</sub>)RuHLL'] (R = H, Me; L, L' = tertiary phosphine, CO) have been particularly well-studied.<sup>4–10</sup> In these sys-

tems, dihydrogen complexes of the formula [(C<sub>5</sub>R<sub>5</sub>)Ru(H<sub>2</sub>)LL']<sup>+</sup> are always the kinetic products resulting from the protonation reaction at the hydride site. In most cases, these dihydrogen derivatives rearrange to their corresponding thermally more stable dihydride tautomers [(C<sub>5</sub>R<sub>5</sub>)Ru(H)<sub>2</sub>LL']<sup>+</sup>, although there are systems in which dihydrogen–dihydride equilibrium has been observed.<sup>11</sup>

It has been shown recently that the proton-transfer reaction from a donor HX to a hydride HML<sub>n</sub> is a stepwise process,<sup>12</sup> which is preceded by the formation of the dihydrogen-bonded complex HX⋯HML<sub>n</sub>.<sup>13–15</sup> The

\* To whom correspondence should be addressed. E-mail: pedro.valerga@uca.es. Tel: +34 956 016340. Fax: +34 956 016288.

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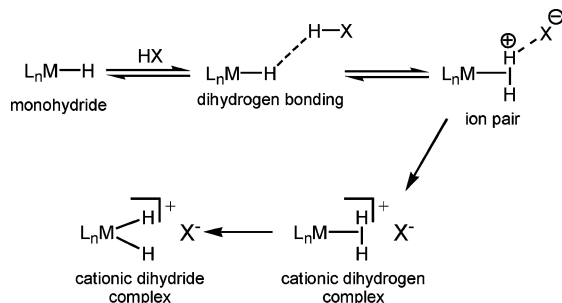
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term “unconventional hydrogen bond” was introduced to refer to this sort of interaction.<sup>14</sup> The dihydrogen-bonded species is converted to a dihydrogen complex forming a contact ion pair stabilized by hydrogen bonding with the anion  $L_nM(H_2)^+ \cdots X^-$ , prior to the formation of the free  $[L_nM(H_2)]^+$  and  $X^-$  ions as reaction products. Afterward, the dihydrogen complex undergoes slow isomerization to its dihydride tautomer.<sup>2</sup>



Under suitable conditions it is possible to detect intermediates in the proton transfer reactions by techniques such as IR and NMR spectroscopy, especially by varying the concentration and strength of the proton donor and/or the polarity of the solvent. Thus, the proton transfer to  $[CpRuH(CO)(PCy_3)_3]$  has been experimentally studied in detail by low-temperature IR and NMR spectroscopy<sup>5</sup> and theoretically treated by DFT calculations, taking into consideration the influence of the media on the protonation.<sup>16</sup> The results obtained support the proposed steps in the proton-transfer process, including the identification by NMR of the dihydrogen-bonded intermediates.

In relation to this, the use of Cp ligands with tethered amino groups has allowed the study of the role of the intramolecular interactions with NH groups in the proton-transfer process from an acid to neutral hydride complexes of ruthenium.<sup>17–20</sup> Thus, Lau and co-workers have shown the occurrence of  $NH \cdots HRu$  dihydrogen bonding in the complexes  $[(\eta^5-C_5H_4(CH_2)_nNMe_2H^+)RuH(dppm)]$  ( $n = 2, 3$ ;  $dppm = 1,2$ -bis(diphenylphosphino)methane) and the proton/hydride exchange in these systems through the intermediacy of dihydrogen complexes  $[(\eta^5-C_5H_4(CH_2)_nNMe_2)Ru(H_2)(dppm)]^+$ .<sup>17</sup> Chaudret and co-workers found similar results when studying the proton transfer in the system  $[(\eta^5-C_5H_4(CH_2)_2NMe_2)RuH(PPh_3)_2]$  using proton donors of different strengths.<sup>19</sup> Furthermore, it has been suggested that the formation of dihydrogen-bonded species triggers the catalytic activity of certain hydride complexes.<sup>17,18,21</sup>

It has been established that, at variance with the metastable character of cationic CpRu or Cp\**Ru* dihydrogen complexes, the formally homologous derivatives

containing hydrotris(pyrazolyl)borate (Tp) as coligand form stable dihydrogen complexes which do not undergo dihydrogen to dihydride tautomerization.<sup>22–24</sup> This makes of these systems good candidates for the study of proton transfer reactions without the additional complications derived from the interference of the dihydrogen to dihydride rearrangement in which CpRu or Cp\**Ru* derivatives are most often involved. On the other hand, the use of phosphinoamine ligands allows the study of the interactions of the NH groups with hydride, as well as their role in the proton transfer processes. In addition, bidentate phosphinoamine ligands are very versatile, being relatively easy to prepare.<sup>25,26</sup> In contrast with standard bidentate phosphines, the availability of enantiopure 1,2-diamines allows the synthesis on a multigram scale of chiral phosphinoamine ligands which have been used in stereoselective organic transformations mediated mainly by Rh complexes.<sup>27</sup>

In this work we describe the synthesis and characterization of a series of TpRu hydride, dihydrogen, and related complexes containing either the enantiopure phosphinoamine ligand (*R,R*)-1,2-bis((diisopropylphosphino)amino)cyclohexane (*R,R*-dippach) or the nonchiral 1,2-bis((diisopropylphosphino)amino)ethane (dippae) and the study by VT-NMR spectroscopy of the proton transfer reactions of the neutral monohydrides in an attempt to identify the intermediate species in these processes.

## Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40–60 °C) were distilled from the appropriate drying agents. Toluene and fluorobenzene were of anhydrous quality and used as received. All solvents were deoxygenated immediately before use. The complex  $[TpRuCl(PPh_3)_2]$  was obtained according to the literature.<sup>28</sup> The ligands (*R,R*)-1,2-bis((diisopropylphosphino)amino)cyclohexane (*R,R*-dippach) and 1,2-bis((diisopropylphosphino)amino)ethane (dippae) were prepared following suitable adaptations of published procedures.<sup>26,29–32</sup>  $HBf_4$ ,  $CF_3COOH$ , and benzoic acid were used as supplied by Aldrich. IR spectra were recorded as Nujol mulls on a Perkin-Elmer SPECTRUM 1000 FTIR spectrometer. NMR spectra were taken on a Varian Unity 400 MHz or Varian Gemini 300 MHz equipment. Chemical shifts are given in ppm from  $SiMe_4$  ( $^1H$  and  $^{13}C\{^1H\}$ ) or 85%  $H_3PO_4$  ( $^{31}P\{^1H\}$ ). Longitudinal relaxation times ( $T_1$ ) measurements were carried

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out by the inversion–recovery method. Optical rotations were measured on a Perkin-Elmer 341 polarimeter. Microanalysis was performed on a LECO CHNS-932 elemental analyzer at the Servicio Central de Ciencia y Tecnología, Universidad de Cádiz.

**[TpRuCl(*R,R*-dippach)] (1a).** To a solution of [TpRuCl(PPh<sub>3</sub>)<sub>2</sub>] (1.8 g, 2.0 mmol) in toluene (20 mL) was added *R,R*-dippach (0.8 mL, 2.0 mmol). The mixture was stirred for 1 h at 80 °C. Then the solvent was removed under vacuum and the residue washed three times with petroleum ether. A microcrystalline yellow solid was formed, which was dried in vacuo. Yield: 0.9 g, 70%. Anal. Calcd for C<sub>27</sub>H<sub>50</sub>N<sub>8</sub>BCIP<sub>2</sub>Ru: C, 46.5; H, 7.24; N, 16.1. Found: C, 42.8; H, 7.01; N, 15.7. [α]<sub>D</sub><sup>25</sup> = −23° (c = 1). IR (Nujol): ν(BH) 2471 cm<sup>−1</sup>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ −0.39, 0.19, 0.59, 1.04, 1.32, and 1.42 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.56, 1.92, and 2.02 (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 1.76 (m, 2 H, NH), 2.33 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 3.08 (m, 2 H, CHCH), 6.02, 6.12, 6.14, 7.62, 7.64, 7.69, 7.89, 8.02, and 8.19 (m, 1 H each, HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161.89 MHz, CD<sub>2</sub>-Cl<sub>2</sub>, 298 K): δ 105.7 (d, J<sub>PP</sub> = 44 Hz), 110.4 (d, J<sub>PP</sub> = 44 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 18.5, 18.8, 18.9, 19.8, 19.9, 21.7, 21.8, and 22.6 (s, PCH(CH<sub>3</sub>)<sub>2</sub>), 22.9, 23.1, 37.8, and 38.5 (s, (CH<sub>2</sub>)<sub>4</sub>), 29.4, 29.6, 30.5, and 30.6 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 59.8 and 60.8 (s, CHCH), 106.3, 106.7, 106.8, 136.3, 136.5, 138.4, 145.7, 146.1, and 149.7 (s, HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>).

**[TpRuCl(dippae)] (1b).** To a solution of [TpRuCl(PPh<sub>3</sub>)<sub>2</sub>] (1.8 g, 2.0 mmol) in toluene (20 mL) was added dippae (0.6 mL, 2.0 mmol). The mixture was stirred for 1 h at 80 °C. Then the solvent was removed under vacuum and the residue washed three times with petroleum ether. A microcrystalline yellow solid was obtained, which was dried in vacuo. Yield: 0.9 g, 70%. Anal. Calcd for C<sub>23</sub>H<sub>44</sub>N<sub>8</sub>BCIP<sub>2</sub>Ru: C, 43.0; H, 6.91; N, 17.4. Found: C, 42.8; H, 7.01, N, 17.8. IR (Nujol): ν(BH) 2468 (s) cm<sup>−1</sup>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ −0.42, 1.12, 1.31, and 1.52 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.80 (m, 2 H, NH), 2.37 and 3.31 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 3.22 and 3.39 (m, 4 H, (CH<sub>2</sub>)<sub>2</sub>), 5.87 (s br, 2 H), 6.19 (s br, 1 H), 7.55 (s br, 2 H), 7.78 (s br, 1 H), 7.91 (s br, 2 H), 8.22 (d, 1 H) (all HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161.89 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 110.3 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 16.4 and 19.7 (s, PCH(CH<sub>3</sub>)<sub>2</sub>), 18.9 and 20.3 (t, <sup>2</sup>J<sub>CP</sub> = 3.01 Hz, PCH(CH<sub>3</sub>)<sub>2</sub>), 27.1 and 33.2 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 45.4 (s, (CH<sub>2</sub>)<sub>2</sub>), 104.4, 105.2, 134.9, 136.4, 144.3, and 147.7 (s, HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>).

**[TpRuH(*R,R*-dippach)] (2a).** To a solution of **1a** (1.0 g, 1.4 mmol) in ethanol (15 mL) was added KBH<sub>4</sub> (0.15 g, excess). The mixture was heated under reflux for 15 min. The solution was cooled to room temperature, and a white microcrystalline solid precipitated. The solid was filtered and dried in vacuo. Yield: 0.5 g, 58%. Anal. Calcd for C<sub>27</sub>H<sub>51</sub>N<sub>8</sub>BP<sub>2</sub>Ru: C, 49.0; H, 7.77; N, 16.9. Found: C, 48.8; H, 7.85; N, 16.7. [α]<sub>D</sub><sup>25</sup> = −60° (c = 0.1). IR (Nujol): ν(RuH) 1980 cm<sup>−1</sup>, ν(BH) 2476 cm<sup>−1</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ −15.2 (dd, J<sub>HP</sub> = 28.3 Hz, J<sub>HP'</sub> = 35.6 Hz, RuH, (T<sub>1</sub>)<sub>min</sub> = 397 ms (238 K, toluene-*d*<sub>8</sub>), 0.12, 0.71, 0.80, 0.87, 1.29, and 1.47 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.75 (m, 2 H, NH), 1.87 and 2.69 (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 2.15 and 2.29 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 2.87 and 3.51 (m, 2 H, CHCH), 5.90, 6.22, 7.05, 7.56, 7.59, 7.78, 7.89, 7.99, and 8.53 (m, 9 H, HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161.89 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 118.3 (d, J<sub>PP</sub> = 51 Hz), 120.6 (d, J<sub>PP</sub> = 51 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 17.6, 17.7, 17.9, 18.4, 18.7, 19.2, 20.5, and 20.7 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 25.1, 25.7, 32.9, and 35.6 (s, (CH<sub>2</sub>)<sub>4</sub>), 28.4, 31.2, 35.8, and 36.2 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 56.0 and 61.6 (s, CHCH), 104.0, 104.4, 104.7, 134.3, 134.9, 135.1, 145.2, 145.6, and 146.3 (s, HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>).

**[TpRuH(dippae)] (2b).** This compound was obtained in a fashion analogous to that for **2a**, starting from **1b** (1.0 g, 1.6 mmol). Yield: 0.6 g, 61%. Anal. Calcd for C<sub>23</sub>H<sub>45</sub>N<sub>8</sub>BP<sub>2</sub>Ru: C, 45.4; H, 7.46; N, 18.4. Found: C, 45.8; H, 7.35, N, 18.8. IR (Nujol): ν(RuH) 1973 cm<sup>−1</sup>, ν(BH) 2468 cm<sup>−1</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ −15.8 (t, J<sub>HP</sub> = 31.6 Hz, RuH, (T<sub>1</sub>)<sub>min</sub> = 373 ms (213 K, toluene-*d*<sub>8</sub>), 0.48, 0.67, 1.37, and 1.44 (m, 24

H, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.85 (m, 2 H, NH), 2.30 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 2.67 and 3.34 (m, 4 H, (CH<sub>2</sub>)<sub>2</sub>), 5.87 (s br, 2 H), 6.19 (s br, 1 H), 7.55 (s br, 1 H), 7.78 (s br, 2 H), 7.91 (s br, 1 H), 8.22 (d, 2 H) (all HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161.89 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 118.9 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 17.4, 18.3, 19.3, and 20.1 (s, PCH(CH<sub>3</sub>)<sub>2</sub>), 29.7 and 32.8 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 46.2 (s, (CH<sub>2</sub>)<sub>2</sub>); 104.5, 104.7, 134.9, 135.2, 144.9, and 145.8 (s, HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>).

**[TpRu(H<sub>2</sub>)(*R,R*-dippach)][Bar'<sub>4</sub>] (3a).** To a solution of **1a** (0.6 g, 0.8 mmol) in fluorobenzene (15 mL) under hydrogen was added solid NaBar'<sub>4</sub> (0.7 g, 0.8 mmol). An H<sub>2</sub> stream was bubbled through the mixture for 2 min. Then, it was stirred for a further 30 min at room temperature under hydrogen. Sodium chloride was removed by filtration through Celite. The filtrate was concentrated using reduced pressure, layered with petroleum ether, and left undisturbed at room temperature. Colorless crystals were obtained, which were separated from the supernatant liquor, washed with petroleum ether, and dried using an argon stream. Yield: 0.7 g, 57%. Anal. Calcd for C<sub>59</sub>H<sub>64</sub>N<sub>8</sub>B<sub>2</sub>P<sub>2</sub>F<sub>24</sub>Ru: C, 46.4; H, 4.23; N, 7.34. Found: C, 46.2; H, 4.32; N, 7.36. [α]<sub>D</sub><sup>25</sup> = −68° (c = 0.1). IR (Nujol): ν(BH) 2476 cm<sup>−1</sup>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ −9.52 (t br, J<sub>HP</sub> = 7.3 Hz, Ru(H<sub>2</sub>), (T<sub>1</sub>)<sub>min</sub> = 19 ms at 218 K), −0.24, −0.36, 0.09, 0.42, 0.86, and 1.32 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.51 and 2.47 (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 1.78 (m, 2 H, NH), 2.15 and 2.43 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 2.92 and 3.08 (m, 2 H, CHCH), 6.19, 6.41, 7.62, 7.68, 7.81, 7.86, 7.91, 8.30, and 8.54 (m, 9 H, HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161.89 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 118.3 (d, J<sub>PP</sub> = 51 Hz), 120.6 (d, J<sub>PP</sub> = 51 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 15.9, 16.7, 17.5, 19.4, 19.7, 19.9, 20.2, and 21.7 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 26.1, 26.7, 31.7, and 34.8 (s, (CH<sub>2</sub>)<sub>4</sub>), 28.1, 32.2, 34.6, and 36.4 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 55.4 and 60.6 (s, CHCH), 104.2, 104.5, 105.1, 134.7, 135.7, 135.9, 145.3, 144.9, and 147.1 (s, HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>).

**[TpRu(H<sub>2</sub>)(dippae)][Bar'<sub>4</sub>] (3b).** This compound was obtained by following the same procedure used for **3a**, starting from **1b** (0.6 g, 0.8 mmol) and NaBar'<sub>4</sub> (0.7 g, 0.8 mmol). It was isolated as a solvate containing one molecule of fluorobenzene of crystallization per formula **3b**·C<sub>6</sub>H<sub>5</sub>F. Yield: 0.8 g, 65%. Anal. Calcd for C<sub>61</sub>H<sub>63</sub>B<sub>2</sub>F<sub>25</sub>N<sub>8</sub>P<sub>2</sub>Ru: C, 46.7; H, 4.05; N, 7.15. Found: C, 46.7; H, 4.00, N, 7.1. IR (Nujol): ν(BH) 2458 cm<sup>−1</sup>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273 K): δ −9.96 (br, 2 H, Ru(H<sub>2</sub>), (T<sub>1</sub>)<sub>min</sub> = 15.8 ms at 219 K), −0.21, 0.96, 1.29, and 1.45 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 2.21 and 2.39 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.96 (s br, 2 H, NH), 3.22 and 3.37 (m, 4 H, (CH<sub>2</sub>)<sub>2</sub>), 6.20 (s, 2 H), 6.27 (s br, 1 H), 7.66 (s br, 1 H), 7.69 (s br, 2 H), 7.82 (s br, 1 H), 8.32 (d, 2 H) (all HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161.89 MHz, CD<sub>2</sub>-Cl<sub>2</sub>, 298 K): δ 107.3 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CDCl<sub>3</sub>, 298 K): δ 16.3, 16.5, 17.7, and 18.9 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 27.4 and 37.5 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 44.2 (s, (CH<sub>2</sub>)<sub>2</sub>), 106.1, 106.6, 136.6, 137.5, 142.9, and 145.3 (s, HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>).

**[TpRu(N<sub>2</sub>)(*R,R*-dippach)][Bar'<sub>4</sub>] (4a).** To a solution of **1a** (0.6 g, 0.8 mmol) in fluorobenzene (15 mL) under a N<sub>2</sub> atmosphere was added solid NaBar'<sub>4</sub> (0.7 g, 0.8 mmol). The mixture was stirred for 30 min at room temperature. Sodium chloride was removed by filtration through Celite. The filtrate was concentrated using reduced pressure and then layered with petroleum ether and left undisturbed at room temperature. Red crystals were obtained, which were separated from the supernatant liquor, washed with petroleum ether, and dried in vacuo. Yield: 0.5 g, 54%. Anal. Calcd for C<sub>59</sub>H<sub>62</sub>N<sub>10</sub>B<sub>2</sub>P<sub>2</sub>F<sub>24</sub>Ru: C, 45.6; H, 4.23; N, 7.34. Found: C, 46.2; H, 4.32; N, 7.36. [α]<sub>D</sub><sup>25</sup> = −120° (c = 0.01). IR (Nujol): ν(N<sub>2</sub>) 2160 cm<sup>−1</sup>, ν(BH) 2474 cm<sup>−1</sup>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ −0.33, 0.44, 1.09, 1.47, and 1.59 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.59 and 2.06 (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 1.79 (m, 2 H, NH), 2.21, 2.39, and 2.80 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 2.94 and 3.08 (m, 2 H, (CH)<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>), 6.19, 6.41, 7.62, 7.68, 7.81, 7.86, 7.91, 8.30, and 8.54 (m, 9 H, HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161.89 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 99.4 (d, J<sub>PP</sub> = 36 Hz), 103.6 (d, J<sub>PP</sub> = 36 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 15.9, 16.7, 17.8, 18.8, 19.1, 19.5, and

**Table 1. Summary of Crystallographic Data for 3b and 4b**

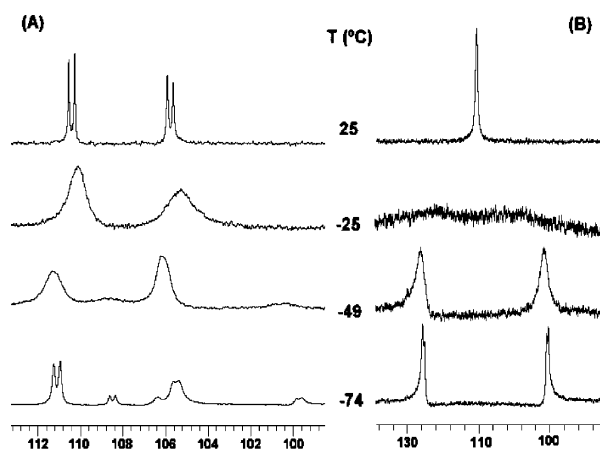
	3b·C <sub>6</sub> H <sub>5</sub> F	4b
formula	C <sub>61</sub> H <sub>63</sub> B <sub>2</sub> F <sub>25</sub> -N <sub>8</sub> P <sub>2</sub> Ru	C <sub>55</sub> H <sub>56</sub> B <sub>2</sub> F <sub>24</sub> -N <sub>10</sub> P <sub>2</sub> Ru
fw	1567.82	1497.73
T (K)	100(2)	100(2)
cryst size (mm)	0.57 × 0.22 × 0.12	0.34 × 0.27 × 0.19
cryst syst	triclinic	monoclinic
space group	P $\bar{1}$ (No. 2)	P <sub>2</sub> /c (No. 14)
cell params		
a (Å)	12.6791(13)	19.0967(15)
b (Å)	14.0536(13)	18.5933(15)
c (Å)	19.250(2)	18.3316(15)
α (deg)	86.926(2)	
β (deg)	79.169(2)	
γ (deg)	87.394(2)	108.191(2)
V (Å <sup>3</sup> )	3361.9(6)	6183.7(9)
Z	2	4
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.549	1.609
μ(Mo Kα) (cm <sup>-1</sup> )	3.96	4.25
F(000)	1588	3024
max and min transmissn factors	1.00–0.74	1–0.88
θ range for data collectn	1.08 < θ < 25.14	1.60 < θ < 25.04
no. of rflns collected	16 013	42 526
no. of unique rflns	11 061 (R <sub>int</sub> = 0.0409)	10 870 (R <sub>int</sub> = 0.0769)
no. of obsd rflns (I > 2σ <sub>I</sub> )	8792	9551
no. of params	906	855
final R1, wR2 values (I > 2σ <sub>I</sub> )	0.0545, 0.1147	0.0657, 0.1299
final R1, wR2 values (all data)	0.0724, 0.1232	0.0801, 0.1377
residual electron density peaks (e Å <sup>-3</sup> )	+0.903, -0.498	+0.702, -0.662

20.4 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 24.6, 24.7, 28.0 and 35.5 (s, (CH<sub>2</sub>)<sub>4</sub>), 29.1, 33.6, 35.5 and 36.4 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 58.4 and 59.5 (s, (CH)<sub>2</sub>-(CH<sub>2</sub>)<sub>4</sub>), 106.3, 107.0, 107.1, 136.7, 137.1, 138.5, 142.9, 143.1, and 146.2 (s, HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>).

**[TpRu(N<sub>2</sub>)(dippae)][Bar<sup>-</sup><sub>4</sub>] (4b).** This compound was obtained in a fashion analogous to that for **4a**, starting from **1b** (0.5 g, 0.8 mmol) and NaBar<sup>-</sup><sub>4</sub> (0.7 g, 0.8 mmol). Yield: 0.8 g, 60%. Anal. Calcd for C<sub>55</sub>H<sub>56</sub>B<sub>2</sub>F<sub>24</sub>N<sub>10</sub>P<sub>2</sub>Ru: C, 44.1; H, 3.77; N, 9.35. Found: C, 44.5; H, 3.68, N, 9.15. IR (Nujol): ν(N<sub>2</sub>) 2157 (s) cm<sup>-1</sup>, ν(BH) 2462 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>-Cl<sub>2</sub>, 298 K): δ -0.35, 1.13, 1.39, and 1.54 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 2.24 and 2.83 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.94 (bs, 2 H, NH), 3.35 and 3.43 (m, 4 H, (CH<sub>2</sub>)<sub>4</sub>), 6.21 (s, 1 H), 6.34 (s, 2 H), 7.78 (s, 2 H), 7.81 (s, 2 H), 8.19 (d, 2 H); <sup>31</sup>P{<sup>1</sup>H} NMR (161.89 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 102.8 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CD<sub>2</sub>-Cl<sub>2</sub>, 298 K): δ 15.9, 17.6, 18.7, and 19.9 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 27.5 and 35.6 (m, PCH(CH<sub>3</sub>)<sub>2</sub>), 44.6 (s, (CH<sub>2</sub>)<sub>2</sub>), 106.5, 107.3, 137.2, 138.4, 143.6, and 146.2 (s, HB(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>3</sub>).

**NMR Study of Proton-Transfer Reactions.** Solutions of the respective monohydride complexes **2a** and **2b** in CD<sub>2</sub>Cl<sub>2</sub>, prepared under an argon atmosphere in NMR tubes, were frozen by immersion into liquid N<sub>2</sub>. The corresponding amount of HBF<sub>4</sub> or of other acid was added via syringe or micropipet. The solvent was allowed to melt. Then, the tubes were shaken, to mix the reagents, and stored in an ethanol/liquid N<sub>2</sub> bath. The samples prepared in this way were studied by NMR at low temperatures. The sample was removed from the bath and inserted into the precooled probe of the Varian UNITY-400 spectrometer at 185 K. Once shims were adjusted, the probe was warmed to the desired temperature. The NMR temperature controller was previously calibrated against a methanol sample, the reproducibility being ±0.5 °C.

**X-ray Structure Determinations.** Crystal data and experimental details are given in Table 1. X-ray diffraction data were collected on a Bruker SMART APEX three-circle diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å) with CCD area detector at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Hemispheres of the reciprocal space were measured by ω scan



**Figure 1.** VT <sup>31</sup>P{<sup>1</sup>H} NMR spectra (161.89 MHz) in CD<sub>2</sub>-Cl<sub>2</sub> of (A) **1a** and (B) **1b**.

frames with δ(ω) = 0.30°. Correction for absorption and crystal decay (insignificant) were applied by semiempirical methods from equivalents using the program SADABS.<sup>33</sup> The structures were solved by direct methods, completed by subsequent difference Fourier synthesis, and refined on F<sup>2</sup> by full-matrix least-squares procedures using the program SHELXTL.<sup>34</sup> The dihydrogen ligand was refined using constraints. The program ORTEP-3<sup>35</sup> was used for plotting.

## Results and Discussion

**Preparation and Characterization of Complexes 1–4.** The complexes [TpRuCl(*R,R*-dippach)] (**1a**) and [TpRuCl(dippae)] (**1b**) were obtained by thermal displacement of PPh<sub>3</sub> from [TpRuCl(PPh<sub>3</sub>)<sub>2</sub>] by either *R,R*-dippach or dippae in refluxing toluene. The NMR spectral properties of **1b** are essentially consistent with those previously observed by us for other derivatives of the type [TpRuCl(P)<sub>2</sub>] bearing bulky <sup>i</sup>Pr substituents at the phosphorus atoms. However, the presence of the enantiomerically pure phosphinoamine ligand *R,R*-dippach in **1a** renders the phosphorus atoms inequivalent, and hence, a two-doublet pattern corresponding to an AM spin system is observed in its <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. All the protons of the pyrazole rings of the Tp ligand as well as those of the methyl groups of the <sup>i</sup>Pr substituents on the phosphorus atoms are inequivalent, giving rise respectively to nine and eight separate resonances. Only one diastereomer is observed in solution. When the temperature is lowered, decoalescence of the <sup>31</sup>P{<sup>1</sup>H} NMR resonances to two sets of doublets in the approximate intensity ratio 4:1 is observed (Figure 1A). Signals corresponding to other species in smaller amounts are also present at the lowest temperature.

This has been interpreted in terms of freezing the equilibrium between rapidly exchanging conformers in solution.<sup>25</sup> A value of 48 kJ/mol has been calculated by means of NMR line shape fitting for the free energy of activation ΔG<sup>‡</sup> of this process. A similar process has been observed for **1b**. The decoalescence of the <sup>31</sup>P{<sup>1</sup>H} NMR resonance to two doublets when the temperature

(33) Sheldrick, G. M. SADABS; University of Göttingen, Göttingen, Germany, 2001.

(34) Sheldrick, G. M. SHELXTL version 6.10, Crystal Structure Analysis Package; Bruker AXS, Madison, WI, 2000.

(35) Farruggia, L. J. ORTEP-3 for Windows, version 1.076. *J. Appl. Crystallogr.* **1997**, *30*, 565.

is lowered (Figure 1B) indicates the nonequivalence of the phosphorus atoms, which may also arise from freezing out different conformations around single Ru–P and P–C bonds.<sup>23,25</sup> The free energy of activation in this case has been estimated to be 41.5 kJ/mol, a value similar to that found for **1a**.

The monohydride complexes [TpRuH(*R,R*-dippach)] (**2a**) and [TpRuH(dippae)] (**2b**) were prepared by reaction of either **1a** or **1b** with KBH<sub>4</sub> in refluxing ethanol. These white, air-sensitive compounds display strong  $\nu$ -(RuH) bands near 1980 cm<sup>-1</sup> in their IR spectra. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **2a** shows a two-doublet pattern corresponding to a AB spin system, whereas the spectrum of **2b** consists of one sharp singlet resonance. The signals in these spectra get slightly broader when the temperature is lowered, but no decoalescence occurs. The resonance for the hydride proton in **2a** appears as a doublet of doublets (X part of a ABX spin system) in its <sup>1</sup>H NMR spectrum. In the case of **2b**, one triplet resonance is observed for the hydride proton. One of the reasons for using phosphinoamine ligands is to establish whether weak NH⋯HRu interactions might be present. The minimum longitudinal relaxation time ( $T_1$ )<sub>min</sub> for the hydride signal in **2a** and **2b** has a value of 373 and 397 ms, respectively, at 400 MHz in toluene-*d*<sub>8</sub>. These values are relatively short for a monohydride complex of ruthenium and indicate a significant dipole–dipole interaction with neighboring atoms contributing to relaxation. However, NOE NMR experiments in which the hydride signal or the NH signal was irradiated did not show any evidence for significant contacts among these atoms. Furthermore, contacts were found between the hydride proton and protons of the isopropyl groups and even with protons of pyrazole rings. These observations suggest that apparently there is no significant NH⋯HRu interaction in these complexes. The bidentate character of both *R,R*-dippach and dippae involves the formation of a seven-membered ring. It seems likely that, in order to adopt the most stable conformation, the NH groups in these rings are forced to point away from the hydride ligand, preventing any intramolecular interaction. Thus, the contribution to the relaxation of the hydride, apart from the direct effect of the ruthenium atom, comes mainly from contacts with protons from isopropyl and pyrazole groups rather than with NH protons.

Both **1a** and **1b** react with H<sub>2</sub> and NaBAR'<sub>4</sub> in fluorobenzene, yielding the corresponding dihydrogen complexes [TpRu(H<sub>2</sub>)(*R,R*-dippach)][BAR'<sub>4</sub>] (**3a**) and [TpRu(H<sub>2</sub>)(dippae)][BAR'<sub>4</sub>] (**3b**). The latter was isolated in crystalline form as a solvate containing one fluorobenzene molecule, **3b**·C<sub>6</sub>H<sub>5</sub>F. The dihydrogen ligands in these complexes appear as a broad resonance near -10 ppm in their respective <sup>1</sup>H NMR spectra. These signals have characteristically short ( $T_1$ )<sub>min</sub> values of 19 ms for **3a** and 15.8 ms for **3b** at 400 MHz in CD<sub>2</sub>Cl<sub>2</sub>. Taking into consideration the effects that the metal and other atoms, particularly hydrogens, present in each of the cations have on the relaxation of the dihydrogen ligand, it is possible to obtain a corrected value for ( $T_1$ )<sub>min</sub> which accounts for the relaxation due to the H–H interaction only, using the expression<sup>3,36</sup>

$$\frac{1}{T_1(\text{H}_2)_{\text{obsd}}} = \frac{1}{T_1(\text{H}_2)_{\text{true}}} + \frac{1}{T_1(\text{H})_{\text{obsd}}} \quad (1)$$

The term  $1/T_1(\text{H})_{\text{obsd}}$  in eq 1 corresponds to the value of ( $T_1$ )<sub>min</sub> measured for the hydride resonance of either **2a** or **2b**, considering that the contribution to the relaxation of the hydride ligand in these complexes comes mainly from dipole–dipole interactions with the metal and through space with all the remaining atoms, as has already been mentioned. The resulting corrected values for ( $T_1$ )<sub>min</sub> of the dihydrogen protons are 20 ms for **3a** and 16.5 ms for **3b**. This indicates that the interactions of the dihydrogen ligands with other atoms within the cation complex contribute less than 5% to the overall relaxation. These values lead to the calculation of H–H separations of 0.89 and 1.12 Å for **3a** in the fast rotation and slow rotation regimes of the H<sub>2</sub> ligand, respectively, and 0.86 and 1.08 Å in the case of **3b**.<sup>3,37</sup> The coupling constants <sup>1</sup>J<sub>HD</sub> measured in the isotopomers [TpRu(HD)(*R,R*-dippach)]<sup>+</sup> (30 Hz) and [TpRu(HD)(dippae)]<sup>+</sup> (29 Hz) are consistent with the values found in the literature for other dihydrogen complexes. Using the equation developed by Morris and co-workers,<sup>37</sup> the H–H bond distance can be also obtained from <sup>1</sup>J<sub>HD</sub> data. In our case, separations of 0.92 and 0.94 Å are obtained for **3a** and **3b**, respectively. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3b** consists of one singlet, whereas two doublets (AB spin system) are present in the case of **3a**, as expected. When the temperature is lowered, the single phosphorus resonance in the spectrum of **3b** decoalesces to two broad signals, in a fashion similar to that for compound **1b**. The free energy of the activation barrier ΔG<sup>‡</sup> has been estimated as 35 kJ/mol in this case. At variance with this, the resonances in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3a** undergo broadening at low temperature, but no decoalescence has been observed, suggesting that again in this case only one diastereomer is present in solution.

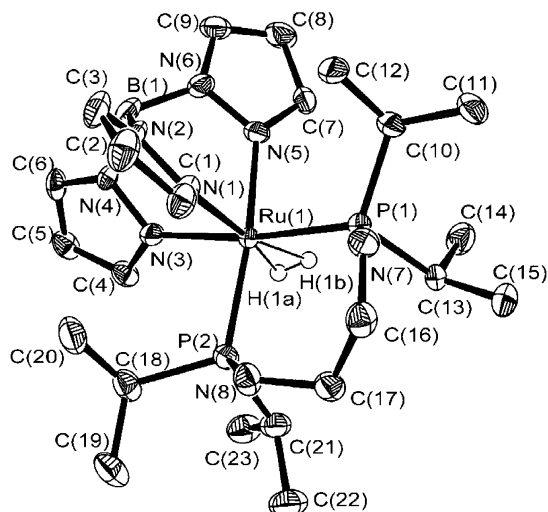
The dihydrogen complexes **3a** and **3b** are stable both in the solid state and in solution under argon at room temperature. They are deprotonated by KOBu<sup>t</sup> in THF, furnishing the corresponding neutral monohydride **2a** or **2b**. As for other cationic TpRu derivatives of the type [TpRu(H<sub>2</sub>)(P)<sub>2</sub>]<sup>+</sup> ((P)<sub>2</sub> = 1,2-bis(diisopropylphosphino)ethane (dippe); P = PPh<sub>3</sub>, PET<sub>3</sub>, PMe<sup>i</sup>Pr<sub>2</sub>),<sup>22–24</sup> irreversible isomerization to the ruthenium(IV) dihydride form has not been observed, at variance with what commonly happens in related CpRu or Cp\*<sup>+</sup>Ru systems.

The dihydrogen ligand in **3a** and **3b** is labile and is readily replaced by dinitrogen in solution, furnishing the dinitrogen complexes [TpRu(N<sub>2</sub>)(*R,R*-dippach)][BAR'<sub>4</sub>] (**4a**) and [TpRu(N<sub>2</sub>)(dippae)][BAR'<sub>4</sub>] (**4b**). These dark red materials display one strong  $\nu$ (N≡N) band in their respective IR spectra, at 2160 cm<sup>-1</sup> for **4a** and 2157 cm<sup>-1</sup> for **4b**. Such values for  $\nu$ (N≡N) compare well with those found for other [TpRu(N<sub>2</sub>)(P)<sub>2</sub>]<sup>+</sup> derivatives and indicate a very small degree of activation for the N≡N bond.<sup>22–24</sup>

The crystal structures of **3b**·C<sub>6</sub>H<sub>5</sub>F and **4b** were determined. ORTEP views of the complex cations [TpRu(H<sub>2</sub>)(dippae)]<sup>+</sup> and [TpRu(N<sub>2</sub>)(dippae)]<sup>+</sup> are shown in

(36) Desrosiers, P. J.; Cai, L.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173–4184.

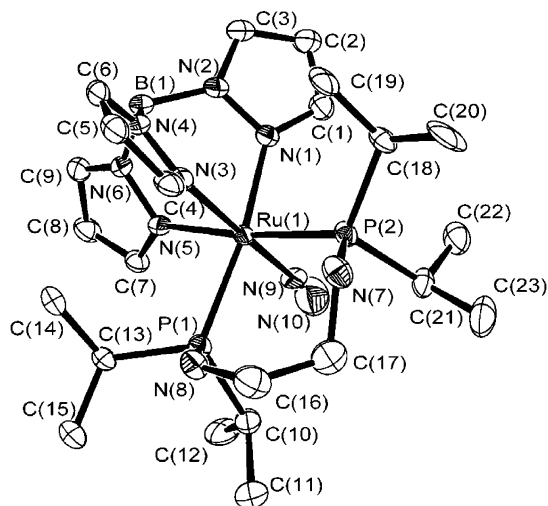
(37) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396–5407.



**Figure 2.** ORTEP drawing (50% thermal ellipsoids) of the cation  $[\text{TpRu}(\text{H}_2)(\text{dippae})]^+$  in complex **3b**. Hydrogen atoms, except dihydrogen, have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ru1–N1, 2.085(3); Ru1–N3, 2.167(3); Ru1–N5, 2.154(3); Ru1–P1, 2.3323(11); Ru1–P2, 2.2932(11); Ru1–H1a, 1.685(19); Ru1–H1b, 1.66(4); H1a–H1b, 0.69(4); P2–N8, 1.680(3); P1–N7, 1.675(3); N1–Ru1–N5, 88.12(13); N1–Ru1–N3, 86.92(13); N5–Ru1–N3, 79.96(12); N1–Ru1–P2, 91.61(10); N5–Ru1–P2, 172.84(10); N3–Ru1–P2, 92.89(9); N1–Ru1–P1, 89.77(10); N5–Ru1–P1, 93.27(9); N3–Ru1–P1, 172.55(9); P2–Ru1–P1, 93.88(4).

Figures 2 and 3, respectively, together with a listing of selected bond lengths and angles.

Both compounds exhibit distorted-octahedral geometries around the ruthenium atom, with ruthenium–pyrazole separations being fully consistent with values previously reported in the literature.<sup>22,23,38</sup> The distances Ru1–N1 in **3b** and Ru1–N3 in **4b** are almost 0.1 Å shorter than the other Ru–pyrazole bond distances found in these complexes and reflect the trans influence of the dihydrogen and dinitrogen ligands, respectively. An electron density peak located in the final difference Fourier map of **3b** was assigned to the dihydrogen ligand. This group was refined with restraints, yielding the final Ru1–H1a and Ru1–H1b separations of 1.685(19) and 1.66(4) Å, respectively, and a short H1a–H1b bond distance of 0.69(4) Å. Even considering the experimental error in the determination of these parameters by X-ray crystallography, these results are fully consistent with the presence of one dihydrogen molecule bound in a side-on manner to the ruthenium atom. The conformation of the chelate ring formed by the bidentate phosphinoamine and the metal forces the hydrogen atoms of the NH groups to point away from the dihydrogen, so that no intramolecular N–H···H interactions are expected. In case of compound **4b**, the conformation adopted by the chelate ring is also very similar to that observed in **3b**. The dinitrogen ligand is linearly assembled to ruthenium, as indicated by the angle Ru1–N9–N10 of 170.2(6)°. The Ru–N9 and N9–N10 bond distances of 1.933(4) and 0.999(8) Å, respectively, are similar to those found in other TpRu dinitrogen



**Figure 3.** ORTEP drawing (50% thermal ellipsoids) of the cation  $[\text{TpRu}(\text{N}_2)(\text{dippae})]^+$  in complex **4b**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ru1–N1, 2.159(4); Ru1–N3, 2.079(4); Ru1–N5, 2.165(4); Ru1–P1, 2.2563(13); Ru1–P2, 2.3449(13); Ru1–N9, 1.933(4); N9–N10, 0.999(8); P1–N8, 1.679(4); P2–N7, 1.669(4); Ru1–N9–N10, 170.2(6); N9–Ru1–N3, 175.30(18); N9–Ru1–N1, 89.30(17); N3–Ru1–N1, 87.35(15); N9–Ru1–N5, 87.56(17); N3–Ru1–N5, 88.63(15); N1–Ru1–N5, 80.11(15); N9–Ru1–P2, 92.26(14); N3–Ru1–P2, 91.23(12); N1–Ru1–P2, 93.58(11); N5–Ru1–P2, 173.69(11); N9–Ru1–P1, 93.11(13); N3–Ru1–P1, 89.79(11); N1–Ru1–P1, 171.95(11); N5–Ru1–P1, 92.32(11); P2–Ru1–P1, 93.99(5).

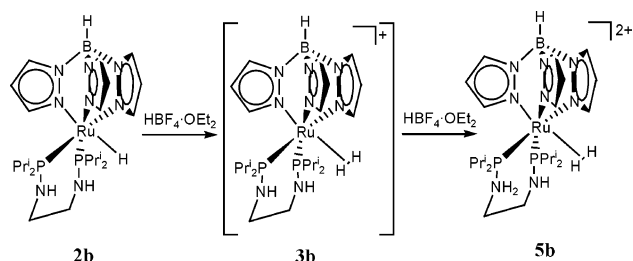
complexes, such as  $[\text{TpRu}(\text{N}_2)(\text{PEt}_3)_2][\text{BPh}_4]$  (Ru–N = 1.91(2) Å, N–N = 1.01(2) Å)<sup>28</sup> and  $[\text{TpRu}(\text{N}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)][\text{CF}_3\text{SO}_3]$  (Ru–N = 1.943(4) Å, N–N = 1.097(5) Å).<sup>38</sup> The fact that the N–N separation in the dinitrogen ligand is essentially identical with that in the free dinitrogen molecule is a characteristic feature of these TpRu dinitrogen complexes.

**Study of Proton-Transfer Reactions of 2a and 2b.** We have studied by VT  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy the protonation reactions of **2a** and **2b** with  $\text{HBF}_4$  using different acid-to-complex ratios.

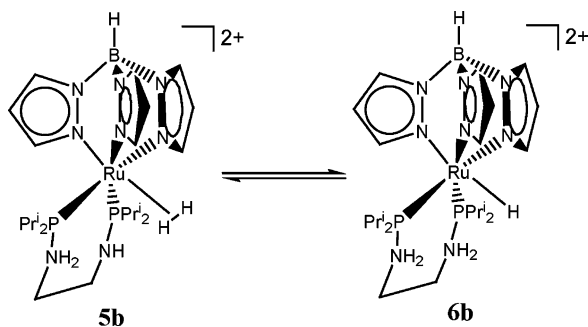
Both **2a** and **2b** react with 1 equiv of  $\text{HBF}_4$  at  $-80^\circ\text{C}$  and slow warming to  $25^\circ\text{C}$ , forming quantitatively the corresponding dihydrogen complexes **3a** and **3b**. However, the addition of a large excess of  $\text{HBF}_4$  ( $>10$  equiv) to a solution of **2b** in  $\text{CD}_2\text{Cl}_2$  at  $-80^\circ\text{C}$  and subsequent warming to  $25^\circ\text{C}$  causes a major change in the position of the  $^{31}\text{P}\{^1\text{H}\}$  NMR signal of the expected dihydrogen complex **3b** from 107 to 134 ppm. This resonance reversibly broadens as the temperature is lowered. At  $-74^\circ\text{C}$  the signal almost merges into the baseline, but no decoalescence is observed. Likewise, the  $^1\text{H}$  NMR spectrum shows one broad resonance centered at  $-8.5$  ppm, with a  $(T_1)_{\text{min}}$  value of 19 ms, which is consistent with the presence of one dihydrogen ligand. The same results are obtained upon treatment of **3b** with an excess of  $\text{HBF}_4$  in  $\text{CD}_2\text{Cl}_2$ . These observations have been interpreted in terms of the protonation of one of the NH groups of the dippae ligand to yield the dicationic dihydrogen complex  $[\text{TpRu}(\text{H}_2)(\text{dippaeH})][\text{BF}_4]_2$  (**5b**).

The rapid exchange between NH and  $\text{NH}_2$  protons renders the phosphorus atoms equivalent on the NMR time scale, and hence, one singlet which gets broader

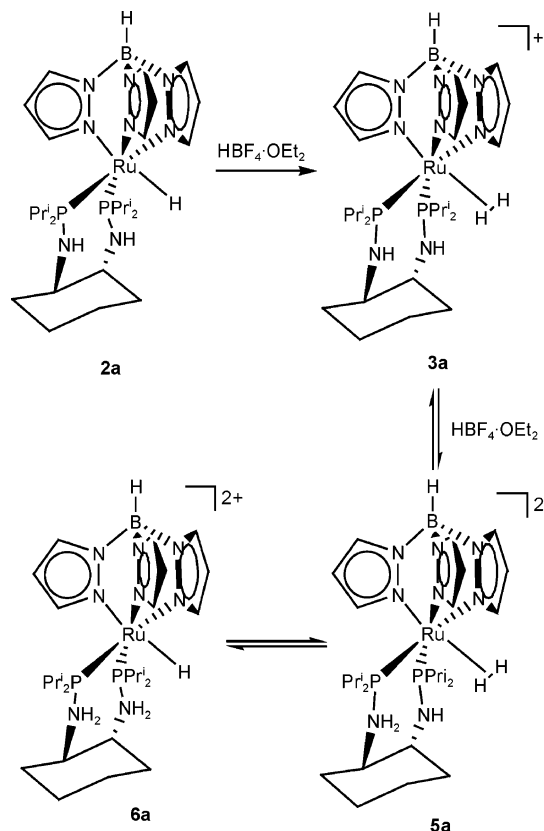
(38) Trimmel, G.; Slugovc, G.; Wiede, P.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Inorg. Chem.* **1997**, *36*, 1076.



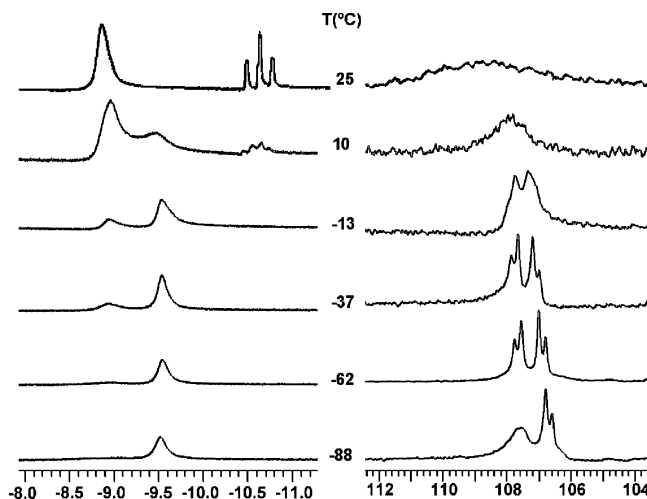
as the temperature is lowered is observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. On standing at 25 °C, a new hydride signal slowly arises at  $-10.7$  ppm (triplet,  $^2J_{\text{HP}} = 35.6$  Hz) in the  $^1\text{H}$  NMR spectrum. This new hydride signal has a long  $T_1$  value of 510 ms at 25 °C. Concomitantly, one singlet signal at 147.5 ppm begins to grow in intensity in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, until an equilibrium is apparently reached. We have attributed these signals to the species  $[\text{TpRuH}(\text{dippaeH}_2)]\text{[BF}_4\text{]}_2$  (**6b**), resulting from the irreversible isomerization of **5b** via deprotonation of the acidic dihydrogen ligand by the nonprotonated NH group of the phosphinoamine ligand, which hence acts as an internal base.



The results of analogous experiments performed with either **2a** or **3a** plus an excess of  $\text{HBF}_4$  in  $\text{CD}_2\text{Cl}_2$  were essentially similar. At variance with the protonation of **2b** or **3b**, in which no trace of the monocationic dihydrogen complex  $[\text{TpRu}(\text{H}_2)(\text{dippae})]^+$  was observed, in this case the formation of the dicationic derivative  $[\text{TpRu}(\text{H}_2)(R,R\text{-dippach})][\text{BF}_4]_2$  (**5a**) is gradual and slower, depending on the temperature. Along with the dihydrogen signal for  $[\text{TpRu}(\text{H}_2)(R,R\text{-dippach})]^+$ , another broad resonance at  $-8.9$  ppm gradually appears in the  $^1\text{H}$  NMR as the temperature is raised. The process is reversible with temperature. The  $(T_1)_{\text{min}}$  values measured for both signals were essentially the same and equal to 16 ms, suggesting a fast proton exchange between the monocationic and dicationic species in solution and the averaging of the  $T_1$  values of the two species. On standing at room temperature, as also occurs in the protonation of **2b/3b**, a new resonance with a  $T_1$  value of 580 ms at 25 °C arises at  $-10.5$  ppm ( $^2J_{\text{HP}} = 42.8$  Hz) in the  $^1\text{H}$  NMR spectrum, whereas the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum becomes featureless at 25 °C. This is indicative of the rearrangement of the dicationic dihydrogen complex to the dicationic monohydride complex  $[\text{TpRuH}(R,R\text{-dippachH}_2)][\text{BF}_4]_2$  (**6a**). The latter species participates most likely in a rapid proton-exchange equilibrium with the dihydrogen complex  $[\text{TpRu}(\text{H}_2)(R,R\text{-dippach})]^+$ , accounting additionally for the observed featureless  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 25 °C.



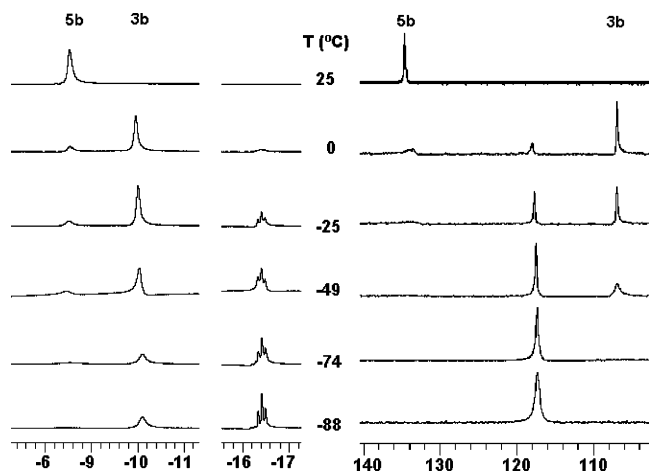
Some dicationic dihydrogen complexes of Ru and Os have been reported.<sup>39</sup> These species are exceedingly acidic, being capable of protonating diethyl ether. Most often dicationic dihydrogen complexes of ruthenium decompose at ambient temperature.<sup>39a</sup>



**Figure 4.** VT  $^1\text{H}$  NMR (left, hydride region, 400 MHz) and VT  $^{31}\text{P}\{^1\text{H}\}$  NMR (right, 161.89 MHz) of a sample made up by addition of an excess  $\text{HBF}_4$  to a  $\text{CD}_2\text{Cl}_2$  solution of **2a**.

The addition of an excess of  $\text{HBF}_4$  to a frozen solution of either **2a** or **2b** below  $-90$  °C followed by transfer to the precooled NMR probe to  $-88$  °C has allowed the observation in situ of intermediate species in the proton-transfer process. Figure 5 shows the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$

(39) (a) Luther, T. A.; Heinekey, D. M. *Inorg. Chem.* **1998**, *37*, 127–132. (b) Schlaf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270–2278.



**Figure 5.** VT  $^1\text{H}$  NMR (left, hydride region, 400 MHz) and VT  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.89 MHz) monitoring of a sample made up by addition of an excess  $\text{HBF}_4$  to a frozen  $\text{CD}_2\text{Cl}_2$  solution of **2b** below  $-90^\circ\text{C}$  followed by subsequent warming to the indicated temperatures.

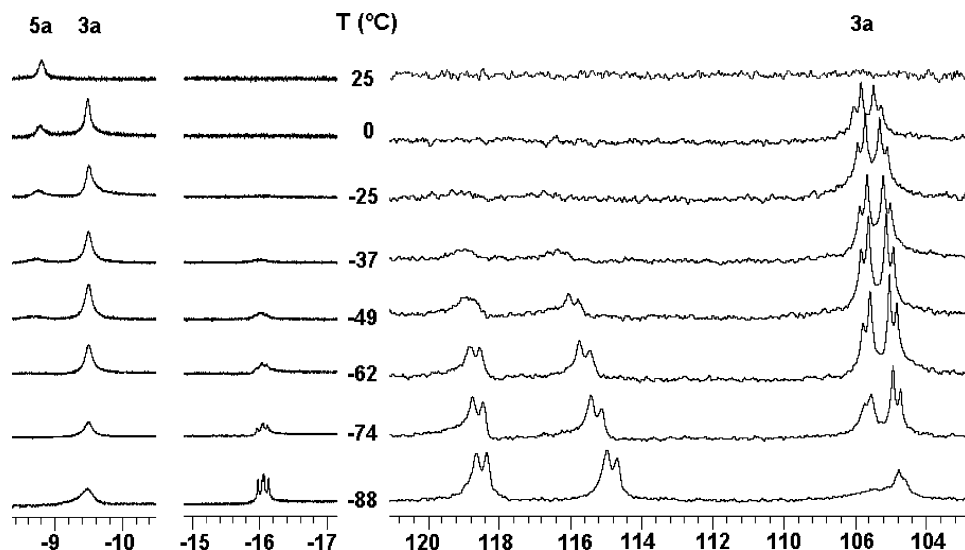
NMR spectra of a sample made up by addition of an excess of  $\text{HBF}_4$  to a frozen solution of **2b**, at temperatures ranging from  $-88$  to  $25^\circ\text{C}$ .

The  $^1\text{H}$  NMR spectrum at  $-88^\circ\text{C}$  shows already the presence of the dihydrogen complex **3b**, plus one triplet resonance at  $-16.4$  ppm, resembling that for the hydride ligand in **2b**. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum consists of one rather broad signal at  $117.3$  ppm. At this temperature, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3b** is essentially featureless, due to its dynamic behavior (vide supra). When the temperature is raised, the triplet resonance gets broader and gradually disappears along with the phosphorus signal at  $117.3$  ppm, whereas the resonances attributable to the dihydrogen complex **3b** grow in intensity. These changes in the spectra are irreversible. At  $25^\circ\text{C}$ , the only species present visible by NMR spectroscopy is the dicationic complex **5b**.  $T_1$  measurements performed on the hydridic resonances yielded the expected values for both **3b** and **5b**. However, the triplet resonance showed a short  $(T_1)_{\text{min}}$  value of  $27$  ms, in sharp contrast with the value of  $373$  ms found for the

hydride in **2b**. An analogous experiment performed with a sample of **2a** yielded similar results (Figure 6).

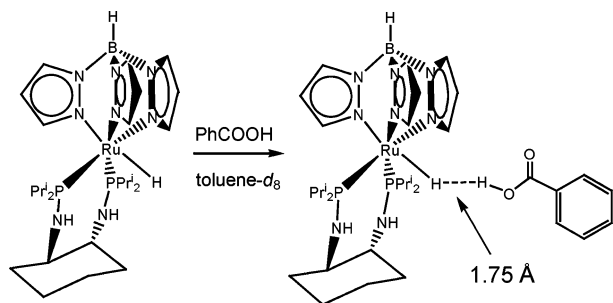
In this case, at  $-88^\circ\text{C}$  the dihydrogen complex **3a** is present, along with another species that resembles the monohydride **2a**, which shows one doublet of doublets signal at  $-16.03$  ppm. The latter species displays two doublet resonances at  $115$  and  $118.4$  ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, with  $^2J_{\text{PP}} = 48.8$  Hz. The changes observed in the spectra when the temperature is raised match those observed for **2b**, including the formation of the dicationic dihydrogen complex **5a** when the temperature reaches  $25^\circ\text{C}$ . The observed value  $(T_1)_{\text{min}}$  of  $29$  ms for the resonance at  $-16.03$  ppm is also short compared to that for the hydride in **2a**. In fact, the values of  $(T_1)_{\text{min}}$  for the high-field resonances observed in the course of the protonation of both **2a** and **2b** are too short to be attributable to dihydrogen-bonded species, being more similar in magnitude to those of dihydrogen complexes such as **3a** and **3b**. When a dihydrogen bond is formed, a decrease in the value of  $(T_1)_{\text{min}}$  is expected with respect to the parent hydride complex, the new value for  $(T_1)_{\text{min}}$  being consistent with H–H separations between  $1.7$  and  $2.1$  Å.<sup>12–14</sup> We have been able to generate in solution the dihydrogen-bonded complex  $[\text{TpRu}(\text{H}\cdots\text{HOOCPh})(R,R\text{-dippach})]$  (**7a**) by reaction of **2a** with 1 equiv of benzoic acid in toluene- $d_8$ . The value of  $(T_1)_{\text{min}}$  for the hydride resonance changes from  $397$  ms in **2a** to  $170$  ms in the dihydrogen-bonded complex. By application of eq 1, we find a  $(T_1)_{\text{min}}$  value due exclusively to a  $\text{RuH}\cdots\text{HOOCPh}$  dipole–dipole interaction of  $297$  ms. This value leads to a H–H separation of  $1.75$  Å, fully consistent with the formation of a dihydrogen bond between the benzoic acid proton and the hydride.

An analogous consideration using the values of  $(T_1)_{\text{min}}$  obtained for the protonation of **2a** and **2b** with  $\text{HBF}_4$  at low temperature leads to H–H bond distances of  $1.2$  Å in both cases, an exceedingly short value for a dihydrogen bond. Very recently, a similar case has been found in which the formation of an extremely short dihydrogen bond of  $1.43$  Å was invoked in order to account for the short  $(T_1)_{\text{min}}$  value of  $49$  ms at  $300$  MHz

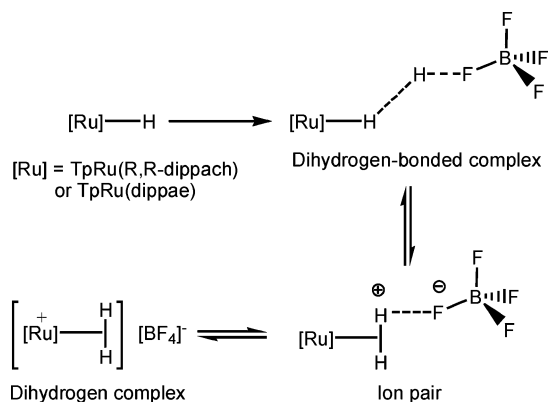


**Figure 6.** VT  $^1\text{H}$  NMR (left, hydride region, 400 MHz) and VT  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.89 MHz) monitoring of a sample made up by addition of an excess  $\text{HBF}_4$  to a frozen  $\text{CD}_2\text{Cl}_2$  solution of **2a** below  $-90^\circ\text{C}$  followed by subsequent warming to the indicated temperatures.





found for the species  $[\text{CpRu}(\text{H}\cdots\text{HOCCF}_3)(\text{PP}^{\text{Ph}}\text{PF})]$  ( $\text{PP}^{\text{Ph}}\text{PF} = 1$ -(diphenylphosphino)-2,1'-(1-(diphenylphosphino)propanediyl)ferrocene).<sup>4</sup> However, since fast proton-hydride exchange occurs within this complex, the short value of  $(T_1)_{\text{min}}$  has been interpreted by Bakhtmutov<sup>1</sup> in terms of averaging of  $T_1$  with the dihydrogen complex  $[\text{CpRu}(\text{H}_2)(\text{PP}^{\text{Ph}}\text{PF})][\text{CF}_3\text{COO}]$ . The latter complex was not observed in the mixture, but it is a feasible intermediate in the fast proton-hydride exchange process. A similar averaging of the  $T_1$  value with the dihydrogen complexes **3a** and **3b** seems unlikely in our case: first, the dihydrogen complexes **3a** and **3b** are stable species which can be clearly seen on the spectra of the protonated mixture, and second, the reduction of  $T_1$  only affects the signals at higher field, whereas the observed  $(T_1)_{\text{min}}$  values for the dihydrogen resonances which appear close to  $-9.5$  ppm remain unchanged with respect to the values measured for **3a** or **3b** alone. Rather, we consider that the anomalous shortening of the  $(T_1)_{\text{min}}$  value might come from the contribution to the overall relaxation of the fluorine atoms in a hydride-interacting  $[\text{BF}_4]^-$  ion. Given the values of the magnetic ratio, nuclear spin, and natural abundance for the  $^{19}\text{F}$  nucleus in comparison with  $^1\text{H}$ , we conclude that whenever short hydrogen-fluorine separations are involved, an important contribution to dipole-dipole relaxation is expected, of the same order of magnitude of H-H dipole-dipole interactions. If we assume that the proton-transfer reactions in our systems follow a pathway analogous to that reported for the related system  $[\text{CpRuH}(\text{CO})(\text{PCy}_3)]$ ,<sup>5,16</sup> both the dihydrogen-bonded complex and the ion pair must be considered as intermediate species in the process.

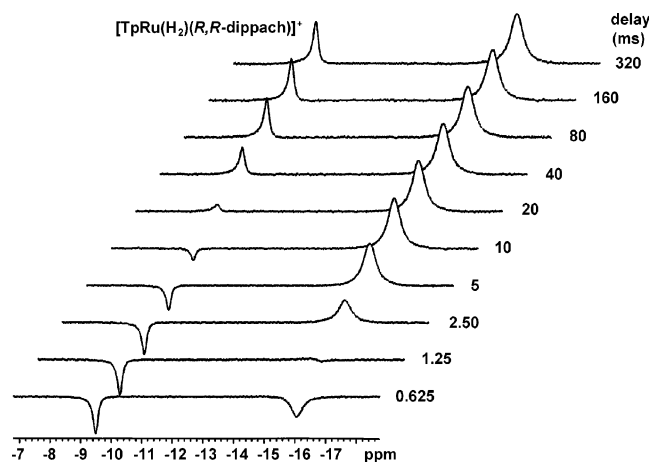


A significant contribution to the relaxation of protons is expected from the  $[\text{BF}_4]^-$  ion interacting with the hydride and the dihydrogen moieties both in the dihydrogen-bonded complex and in the tight ion pair. By application of the method of Halpern and co-workers,<sup>36</sup>

we find that our short  $(T_1)_{\text{min}}$  values for the protonation of **2a** and **2b** at low temperature (29 and 27 ms, respectively) are consistent with two possible situations: one involving  $\text{H}\cdots\text{H}$  separations between 1.03 and 2.2 Å and  $\text{H}\cdots\text{F}$  distances between 1.03 and 1.05 Å, or another situation involving shorter  $\text{H}\cdots\text{H}$  separations between 1.1 and 1.2 Å and longer  $\text{H}\cdots\text{F}$  contacts of ca. 2 Å. These two situations respectively correspond to a dihydrogen-bonded  $\text{RuH}\cdots\text{HBF}_4$  moiety and to a contact ion pair of the type  $\text{Ru}(\text{H}_2)^+\cdots\text{BF}_4^-$  or, more likely, to a situation of equilibrium between these two possibilities. Therefore, the signals observed at high field in the  $^1\text{H}$  NMR spectra having short  $(T_1)_{\text{min}}$  values are hereby attributed to the intermediates in the proton-transfer process of the type  $[\text{TpRu}(\text{H}\cdots\text{HBF}_4)(\text{L})]$  ( $\text{L} = \text{R},\text{R}$ -dippach, dippae). Although with the current data we cannot discern between the dihydrogen-bonded species and the contact ion pair, it seems reasonable to consider a fast equilibrium between these two situations prior to the complete proton transfer and subsequent formation of the free dihydrogen complexes **3a** and **3b**.

The protonation reactions of **2a** and **2b** with less than 1 equiv of acid were also studied. Addition of 0.5 equiv of  $\text{HBF}_4$  to a  $\text{CD}_2\text{Cl}_2$  solution of **2b** at  $-80$  °C yielded equimolar amounts of the dihydrogen complex **3b** and the starting monohydride complex **2b**, just as expected from an immediate and quantitative proton transfer taking place under these conditions. However, an analogous experiment performed on a  $\text{CD}_2\text{Cl}_2$  solution of **2a** turned out to be different. In this case, a broad resonance ( $\Delta\nu_{1/2} \approx 100$  Hz) was observed in the  $^1\text{H}$  NMR spectrum at  $-16.05$  ppm along with the resonance of the dihydrogen ligand in **3a** at  $-9.4$  ppm, whereas the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at  $-88$  °C showed the pattern for the dihydrogen complex plus two broad signals (ca. 250 Hz half-width) centered at 115 and 118.7 ppm, respectively, consistent with the expected pattern of an unresolved AM spin system. These signals become much broader as the temperature is raised. The broad signal at  $-16.05$  ppm in the  $^1\text{H}$  NMR spectrum also gets much broader at higher temperatures, and the process is fully reversible with temperature. Whereas the resonance for the dihydrogen complex has the expected  $(T_1)_{\text{min}}$  value of 19 ms, the broad signal at higher field exhibits an extremely short  $(T_1)_{\text{min}}$  value of 0.5 ms at  $-62$  °C. Figure 7 shows an inversion-recovery experiment in which the fast relaxation of the resonance at  $-16.05$  ppm can be clearly seen (null intensity at 1.25 ms pulse delay) in comparison with the also short but standard relaxation for the dihydrogen signal of complex **3a** (null intensity between the 10 and 20 ms pulse delays).

The intensity ratio of the signals corresponding to the dihydrogen complex and the other hydride species is approximately 1:2.3 at  $-88$  °C. If we perform the experiment using 0.25 equiv of acid, the result is almost identical, including the extremely short  $(T_1)_{\text{min}}$  value for the resonance at higher field, the only noticeable difference being the modification of the ratio in which the hydride species are present from 1:2.3 to 1:3.8. If 0.75 equiv of  $\text{HBF}_4$  is added, this ratio is reduced to 1:1.7, whereas the value of  $(T_1)_{\text{min}}$  for the resonance at higher field increases to 9.3 ms. If the stoichiometric amount or an excess of  $\text{HBF}_4$  is used, then the only hydride signal observed in the  $^1\text{H}$  NMR spectrum corresponds



**Figure 7.**  $^1\text{H}$  NMR (hydride region,  $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $-88^\circ\text{C}$ ) profile of **2a** + 0.5  $\text{HBF}_4$  recorded at variable delay times in a typical inversion–recovery experiment for  $T_1$  determination, showing the very fast relaxation of the resonance at higher field compared to that for the dihydrogen complex at  $-9.4$  ppm.

to the dihydrogen complex **3a**. Hence, the increase in the amount of  $\text{HBF}_4$  added to  $\text{CD}_2\text{Cl}_2$  solutions of **2a** at  $-80^\circ\text{C}$  involves the quantitative increase in the intensity of the dihydrogen signal of **3a** with respect to that of the broad resonance at  $-16.05$  ppm and the increase of the measured  $(T_1)_{\text{min}}$  value of the latter until this signal is not observed any longer once the 1:1 monohydride to  $\text{HBF}_4$  ratio is reached.

Changing from using 0.5 equiv of  $\text{HBF}_4$  to 0.5 equiv of  $\text{CF}_3\text{COOH}$  instead causes some changes in the spectra. The observed amount of dihydrogen complex **3a** is almost negligible in this case, possibly due to the weaker acidity of  $\text{CF}_3\text{COOH}$  in comparison to  $\text{HBF}_4$ , and the minimum relaxation time measured for the broad signal at  $-16.05$  ppm is now 8.5 ms. This is in any case much shorter than the value of  $(T_1)_{\text{min}}$  expected for a dihydrogen-bonded species or even for a dihydrogen complex. Using  $\text{CF}_3\text{COOD}$  instead of  $\text{CF}_3\text{COOH}$  causes a very significant sharpening of the high-field resonance from ca. 100 Hz to only 10 Hz at  $-80^\circ\text{C}$ . Hence, the splitting of the signal due to coupling to the phosphorus atoms can be clearly observed, although no H–D splitting was detected. Also, the value of  $(T_1)_{\text{min}}$  for the resonance at  $-16.05$  ppm increases from 8.5 to 30 ms.

The short  $(T_1)_{\text{min}}$  observed under these conditions cannot be explained by taking into account dipole–dipole interactions only. Interactions with fluorine atoms can be ruled out, since similar results are obtained with  $\text{CF}_3\text{COOH}$ , and in any case the contacts with fluorine atoms would never account for such a dramatic increase in the relaxation rate. The involvement of the NH groups of the phosphinoamine ligand is unclear, since this phenomenon has not been observed in the case of compound **2b**. Another analogous experiment performed with  $[\text{TpRuH}(\text{PPh}_3)_2]$  failed to exhibit such extremely short  $T_1$  values.

There are a couple of cases in the literature where very short relaxation times, similar to ours, have been reported. The complex  $[\{\eta^5\text{-C}_5\text{H}_4\text{CH}(\text{CH}_2\text{CH}_2)_2\text{NHMe}\}\text{-RuH}(\text{PPh}_3)_2][\text{BF}_4]$  exhibits a  $T_1$  value at 400 MHz which ranges from 1.4 ms at 233 K to 4.8 ms at 223 K 400 MHz.<sup>20</sup> The Cp protons also have short  $(T_1)_{\text{min}}$  values

of 10 ms. The authors pointed out, after ruling out the possibility of external paramagnetic impurities as a cause for the shortening in  $T_1$ , that the exact origin of this phenomenon was unknown. A related problem affecting  $T_1$ , exchange and anomalous broadening in metal dihydrogen complexes had been previously reported by Faller, Crabtree, and co-workers.<sup>40</sup> On the other hand, a very short  $T_1$  of 0.67 ms at 400 MHz and 240 K was reported recently for one of the products derived from the reaction of  $[\text{Cp}^*\text{FeH}(\text{dppe})]$  with trifluoroethanol in the alcohol-to-complex ratio of 3:1.<sup>41</sup> In this particular case, this was attributed to the presence of small amounts of the known 17-electron paramagnetic hydride  $[\text{Cp}^*\text{FeH}(\text{dppe})]^+$ .<sup>42</sup> Even small amounts of this material might participate in a fast spin exchange with the isostructural  $[\text{Cp}^*\text{FeH}(\text{dppe})]$  complex, decreasing the value of  $T_1$  for the hydride. In fact, when the experiments were performed using pure, recrystallized samples of the monohydride under rigorous conditions, the  $^1\text{H}$  NMR resonances for the hydride were sharp and well-resolved, with much longer values of  $T_1$ .<sup>43</sup> In our case, for an analogous explanation we should assume that the 17-electron species  $[\text{TpRuH}(\text{R},\text{R}\text{-dippach})]^+$  must be present somehow in the reaction mixture. This species would give fast spin exchange with isostructural **2a**, but a slow exchange with **3a**, which seems not to be affected. We have so far failed to oxidize **2a** using  $[\text{FeCp}_2][\text{PF}_6]$  in an attempt to prepare  $[\text{TpRuH}(\text{R},\text{R}\text{-dippach})][\text{PF}_6]$ . Furthermore, the related half-sandwich  $\text{Ru}^{\text{III}}$  hydride complexes are rather elusive species, which have been detected by cyclic voltammetry or identified by ESR spectroscopy but only in very few cases have shown to be amenable to isolation.<sup>44</sup> Besides, only the hydride resonance near  $-16$  ppm is affected by the fast relaxation, whereas all the signals of Tp and phosphinoamine protons exhibit long  $T_1$  values. This fact, along with the reproducibility of our measurements even using pure, recrystallized samples of the monohydride **2a**, and the nonobservation of similar behavior in the case of **2b**, make us think that we have another example of a rare relaxation phenomenon of so far unknown origin, rather than an artifact resulting from fast spin exchange with traces of a isostructural  $\text{Ru}^{\text{III}}$  hydride complex. Further experiments are being performed in an attempt to clarify this most unusual behavior.

## Conclusions

A series of TpRu hydride, dihydrogen, and related complexes bearing chelating chiral as well as nonchiral phosphinoamine ligands have been prepared and characterized. The dihydrogen complexes are stable species which do not undergo rearrangement to the correspond-

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ing dihydride isomers. No significant interactions between the hydrogen atoms bound to the metal and the NH groups of the phosphinoamine ligands have been detected. Protonation of the monohydride complexes **2a** and **2b** with an excess of  $\text{HBF}_4$  leads to the dicationic dihydrogen complexes **5a** and **5b** resulting from protonation at the hydride and at one of the NH groups of the phosphinoamine ligand. The same species are generated by reaction of the dihydrogen complexes **3a** and **3b** with an excess of  $\text{HBF}_4$ . These dihydrogen complexes undergo slow rearrangement to their isomeric dicationic monohydrides **6a** and **6b**. A remarkable shortening in the  $(T_1)_{\text{min}}$  value of the hydride signal of the monohydrides **2a** and **2b** has been observed upon addition of excess  $\text{HBF}_4$  at temperatures near  $-90^\circ\text{C}$ , prior to the proton transfer to yield the dihydrogen derivatives **3a** and **3b**. This shortening is attributed to the formation of dihydrogen-bonded intermediates between the monohydride and the proton donor, possibly in equilibrium with the corresponding contact ion pairs. Both H–H and H–F dipole–dipole contributions to relaxation are expected in these species, accounting for the efficient relaxation. **2a** also forms a dihydrogen-bonded complex with benzoic acid in toluene- $d_8$ , for which a H···H separation of 1.75 Å has been estimated.

Extremely fast relaxation ( $(T_1)_{\text{min}} = 0.5$  ms) has been observed for the broadened hydride resonance of **2a** when it reacts with  $\text{HBF}_4$  in  $\text{CD}_2\text{Cl}_2$  at  $-80^\circ\text{C}$  in a 2:1 or 4:1 molar ratio. A similar process occurs when less acidic  $\text{CF}_3\text{COOH}$  is used ( $(T_1)_{\text{min}} = 8.5$  ms) as proton donor. Paramagnetic contributions to relaxation have been ruled out. The origins of this fast relaxation phenomenon remain unknown.

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**Supporting Information Available:** CIF files giving X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles for complexes **3b** and **4b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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