

# Synthesis and reactivity of hydride and dihydrogen complexes of ruthenium with tris(pyrazolyl)borate and phosphite ligands

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## Abstract

Chloro phosphite complexes  $\text{RuClTpL}(\text{PPh}_3)$  (**1a**, **1b**) [ $\text{L} = \text{P}(\text{OEt})_3$ ,  $\text{PPh}(\text{OEt})_2$ ] and  $\text{RuClTp}[\text{P}(\text{OEt})_3]_2$  (**1c**) [ $\text{Tp} = \text{hydrido-tris}(\text{pyrazolyl})\text{borate}$ ] were prepared by allowing  $\text{RuClTp}(\text{PPh}_3)_2$  to react with an excess of phosphite. Treatment of the chloro complexes **1** with  $\text{NaBH}_4$  in ethanol yielded the hydride  $\text{RuHTpL}(\text{PPh}_3)$  (**2a**, **2b**) and  $\text{RuHTp}[\text{P}(\text{OEt})_3]_2$  (**2c**) derivatives. Protonation reaction of **2** with Brønsted acids was studied and led to thermally unstable (above 10 °C) dihydrogen  $[\text{Ru}(\eta^2\text{-H}_2)\text{TpL}(\text{PPh}_3)]^+$  (**3a**, **3b**) and  $[\text{Ru}(\eta^2\text{-H}_2)\text{Tp}\{\text{P}(\text{OEt})_3\}_2]^+$  (**3c**) complexes. The presence of the  $\eta^2\text{-H}_2$  ligand is indicated by short  $T_{1\text{min}}$  values and  $J_{\text{HD}}$  measurements of the partially deuterated derivatives. Aquo  $[\text{RuTp}(\text{H}_2\text{O})\text{L}(\text{PPh}_3)]\text{BPh}_4$  (**4**), carbonyl  $[\text{RuTp}(\text{CO})\text{L}(\text{PPh}_3)]\text{BPh}_4$  (**5**), and nitrile  $[\text{RuTp}(\text{CH}_3\text{CN})\text{L}(\text{PPh}_3)]\text{BPh}_4$  (**6**) derivatives [ $\text{L} = \text{P}(\text{OEt})_3$ ] were prepared by substituting  $\text{H}_2$  in the  $\eta^2\text{-H}_2$  derivatives **3**. Vinylidene  $[\text{RuTp}\{\text{C}=\text{C}(\text{H})\text{R}\}\text{L}(\text{PPh}_3)]\text{BPh}_4$  (**7**, **8**) ( $\text{R} = \text{Ph}$ ,  $t\text{Bu}$ ) and allenylidene  $[\text{RuTp}(\text{C}=\text{C}=\text{CR}1\text{R}2)\text{L}(\text{PPh}_3)]\text{BPh}_4$  (**9–11**) complexes ( $\text{R}1 = \text{R}2 = \text{Ph}$ ,  $\text{R}1 = \text{Ph}$ ,  $\text{R}2 = \text{Me}$ ) were also prepared by allowing dihydrogen complexes **3** to react with the appropriate  $\text{HC}=\text{CR}$  and  $\text{HC}=\text{CC}(\text{OH})\text{R}1\text{R}2$  alkynes. Deprotonation of vinylidene complexes **7**, **8** with  $\text{NEt}_3$  was studied and led to acetylides  $\text{Ru}(\text{C}=\text{CR})\text{TpL}(\text{PPh}_3)$  (**12**, **13**) derivatives. The trichlorostannyl  $\text{Ru}(\text{SnCl}_3)\text{TpL}(\text{PPh}_3)$  (**14**) compound was also prepared by allowing the chloro complex  $\text{RuClTpL}(\text{PPh}_3)$  to react with  $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$ .

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## 1. Introduction

Since Kubas' initial discovery [1] of the first dihydrogen complexes of transition metals, a large number of  $\eta^2\text{-H}_2$  derivatives have been prepared and their properties extensively studied [2,3]. The ancillary ligands used in this chemistry involve mainly  $\pi$ -acceptors such as tertiary phosphine, carbon monoxide and cyclopentadienyl and only recently hydridotris(pyrazolyl)borate (Tp) has been introduced as a supporting ligand in the chemistry of classical and non-classical transition metal hydrides [4,5]. The related complexes include metals of Groups

8 and 9 and for the ruthenium [4] are of the  $[\text{RuTp}(\eta^2\text{-H}_2)\text{P}_2]^+$ ,  $[\text{RuTp}(\eta^2\text{-H}_2)\text{PL}]^+$  and  $\text{RuTp}^*\text{H}(\eta^2\text{-H}_2)\text{P}$  [ $\text{P} = \text{PPh}_3$ ,  $\text{P}^i\text{Pr}_3$  and  $\text{P}2 = 1,2\text{-bis}(\text{diisopropylphosphine})$ ;  $\text{L} = \text{CO}$ ,  $\text{CH}_3\text{CN}$ ;  $\text{Tp}^* = \text{hydridotris}(3\text{-isopropyl-4-bromopyrazolyl})\text{borate}$ ] type with the ligand associated to the Tp ligand being tertiary phosphine, carbonyl and acetonitrile. No dihydrogen complexes with Tp and the phosphite  $\text{P}(\text{OR})_3$  or  $\text{PPh}(\text{OR})_2$ , however, have been prepared although phosphites have shown interesting properties in both the stabilization and the reactivity of dihydrogen derivatives [6,7].

We are interested in the chemistry of classical and non-classical transition metal hydrides and have reported on the synthesis and reactivity of  $\eta^2\text{-H}_2$  complexes of manganese [7] and iron [6] triads of the  $[\text{M}(\eta^2\text{-H}_2)(\text{CO})_n\text{P}_{5-n}]^+$  ( $\text{M} = \text{Mn}$ ,  $\text{Re}$ ;  $n = 1, 2, 3, 4$ ) and

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$[\text{MX}(\eta^2\text{-H}_2)\text{P}_4]^+$  (M = Fe, Ru, Os; X = H, Cl, Br) types stabilized by phosphite ligands. Recently, the use of nitrogen donor ligands such as 1,2-bipyridine (bpy) and 1,10-phenanthroline (phen) in the hydride chemistry have allowed the synthesis of mixed-ligands  $[\text{MH}(\text{N}-\text{N})\text{P}_3]^+$  and  $[\text{M}(\eta^2\text{-H}_2)(\text{N}-\text{N})\text{P}_3]^{2+}$  (M = Fe, Ru, Os; N–N = bpy, phen; P = phosphite) complexes with phosphites and polypyridyls [8]. Now we have extended these studies with the aim of introducing phosphite ligands into the chemistry of tris(pyrazolyl)borate hydride complexes and the results of these studies on the ruthenium, which involve the synthesis and the reactivity of new classical and non-classical hydride complexes, are reported here.

## 2. Experimental

### 2.1. General considerations

All synthetic work was carried out in an appropriate atmosphere (Ar, N<sub>2</sub>) using standard Schlenk techniques or a vacuum atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored in an inert atmosphere at –25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. RuCl<sub>3</sub>·3H<sub>2</sub>O salt was a ChemPur (USA) product, used as received. Potassium hydrido-tris(pyrazolyl)borate (KTp) was prepared according to a published procedure [9]. Phosphite PPh(OEt)<sub>2</sub> was prepared by the method of Rabinowitz and Pellon [10], while P(OEt)<sub>3</sub> was an Aldrich product purified by distillation under nitrogen. Alkynes RC≡CH (R = Ph, <sup>t</sup>Bu) and HC≡CC(OH)R<sub>1</sub>R<sub>2</sub> (R<sub>1</sub> = R<sub>2</sub> = Ph; R<sub>1</sub> = Ph, R<sub>2</sub> = Me) were Aldrich products used without any further purification. Lithium acetylide Li<sup>+</sup>[PhC≡C]<sup>–</sup> was prepared by reacting a slight excess of 1-alkyne (PhC≡CH, 2.42 mL, 22 mmol) with lithium (20 mmol, 0.14 g) in 10 mL of thf. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra (<sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C, <sup>119</sup>Sn) were obtained on AC200 or AVANCE 300 Bruker spectrometers at temperatures between –90 and +30 °C, unless otherwise noted. <sup>1</sup>H and <sup>13</sup>C spectra are referred to internal tetramethylsilane; <sup>31</sup>P{<sup>1</sup>H} chemical shifts are reported with respect to 85% H<sub>3</sub>PO<sub>4</sub>, while <sup>119</sup>Sn with respect to SnMe<sub>4</sub>, in both cases with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed using their standard programs. The Swan-MR software package [11] was used to treat NMR data. The conductivity of 10<sup>–3</sup> mol dm<sup>–3</sup> solutions of the complexes in CH<sub>3</sub>NO<sub>2</sub> at 25 °C were measured with a Radiometer CDM 83.

### 2.2. Synthesis of complexes

The RuClTp(PPh<sub>3</sub>)<sub>2</sub> was prepared following the method previously reported [12].

#### 2.2.1. RuClTpL(PPh<sub>3</sub>) (1) [L = P(OEt)<sub>3</sub> (a), PPh(OEt)<sub>2</sub> (b)]

An excess of the appropriate phosphite (2.76 mmol) was added to a solution of RuClTp(PPh<sub>3</sub>)<sub>2</sub> (0.4 g, 0.46 mmol) in 15 mL of benzene and the reaction mixture was refluxed for 3 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 mL). A yellow–brown solid separated out by slow cooling of the solution, which was filtered and dried under vacuum; yield: **1a** 0.30 g (85%), **1b** 0.32 g (86%). **1a**: C<sub>33</sub>H<sub>40</sub>BClN<sub>6</sub>O<sub>3</sub>P<sub>2</sub>Ru (778.15): Calcd. C, 50.95; H, 5.18; N, 10.80; Cl, 4.56. Found: C, 50.82; H, 5.24; N, 10.67; Cl, 4.71%. **1b**: C<sub>37</sub>H<sub>40</sub>BClN<sub>6</sub>O<sub>2</sub>P<sub>2</sub>Ru (810.04): Calcd. C, 54.86; H, 4.98; N, 10.37; Cl, 4.38. Found: C, 54.97; H, 5.05; N, 10.26; Cl, 4.51%.

#### 2.2.2. RuClTp[P(OEt)<sub>3</sub>]<sub>2</sub> (1c)

An excess of P(OEt)<sub>3</sub> (4.6 mmol, 0.76 mL) was added to a solution of RuClTp(PPh<sub>3</sub>)<sub>2</sub> (0.4 g, 0.46 mmol) in 15 mL of toluene and the reaction mixture was refluxed for 4 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL). By slow cooling to –25 °C of the resulting solution, yellow microcrystals slowly separated out, which were collected and dried under vacuum; yield: 0.25 g (78%). C<sub>21</sub>H<sub>40</sub>BClN<sub>6</sub>O<sub>6</sub>P<sub>2</sub>Ru (681.86): Calcd. C, 36.99; H, 5.91; N, 12.33; Cl, 5.20. Found: C, 37.14; H, 5.86; N, 12.19; Cl, 5.08%.

#### 2.2.3. RuHTpL(PPh<sub>3</sub>) (2) [L = P(OEt)<sub>3</sub> (a), PPh(OEt)<sub>2</sub> (b)] and RuHTp[P(OEt)<sub>3</sub>]<sub>2</sub> (2c)

To a solution of the appropriate chloro-complex RuClTpL(PPh<sub>3</sub>) or RuClTp[P(OEt)<sub>3</sub>]<sub>2</sub> (0.3 mmol) in 10 mL of ethanol was added an excess of NaBH<sub>4</sub> (8 mmol, 0.30 g) in 10 mL of ethanol and the reaction mixture refluxed for 1 h. The solvent was removed under reduced pressure to give an oil from which the hydride was extracted first with three 5-mL portions of CH<sub>2</sub>Cl<sub>2</sub> and then with three 5-mL portions of benzene:petroleum ether (40–60 °C) 1:1 mixture. The extracts were evaporated to dryness and the obtained oil triturated with ethanol (2 mL). By slow cooling of the resulting solution, a pale-yellow solid separated out, which was filtered and crystallized from ethanol; yield: **2a** 0.14 g (64%), **2b** 0.15 g (66%), **2c** 0.13 g (68%). **2a**: C<sub>33</sub>H<sub>41</sub>BN<sub>6</sub>O<sub>3</sub>P<sub>2</sub>Ru (743.55): Calcd. C, 53.31; H, 5.56; N, 11.30. Found: C, 53.20; H, 5.43; N, 11.18%. **2b**: C<sub>37</sub>H<sub>41</sub>BN<sub>6</sub>O<sub>2</sub>P<sub>2</sub>Ru (775.60): Calcd. C, 57.30; H, 5.33; N, 10.84. Found: C, 57.46; H, 5.24; N, 10.97%. **2c**: C<sub>21</sub>H<sub>41</sub>BN<sub>6</sub>O<sub>6</sub>P<sub>2</sub>Ru (647.42): Calcd. C, 38.96; H, 6.38; N, 12.98. Found: C, 38.77; H, 6.28; N, 12.85%.

2.2.4.  $[RuTp(\eta^2-H_2)L(PPh_3)]^+BF_4^-$  (**3**) [ $L=P(OEt)_3$  (**a**),  $PPh(OEt)_2$  (**b**)] and  $[RuTp(\eta^2-H_2)\{P(OEt)_3\}_2]^+BF_4^-$  (**3c**)

These complexes were prepared in solution in a NMR tube at temperature below 10 °C. A typical experiment involves the preparation of a solution of the appropriate hydride (0.03 mmol) in  $CD_2Cl_2$  (0.5 mL) in a NMR tube, which was cooled to –80 °C. A slight excess of  $HBf_4 \cdot Et_2O$  (0.033 mmol, 4.7  $\mu$ L) was added and the tube transferred into the probe of the NMR instrument, pre-cooled to –80 °C. The progress of the reaction was monitored by  $^1H$  and  $^{31}P\{^1H\}$  spectra in the temperature range from –80 to 20 °C.

2.2.5.  $[RuTp(H_2O)\{P(OEt)_3\}(PPh_3)]BF_4$  (**4**)

This complex was obtained in an attempt to isolate the dihydrogen complex  $[RuTp(\eta^2-H_2)\{P(OEt)_3\}(PPh_3)]BF_4$ . To a solution of  $RuHTp\{P(OEt)_3\}(PPh_3)$  (100 mg, 0.13 mmol) in 10 mL of diethylether cooled to –196 °C was added a slight excess of  $HBf_4 \cdot Et_2O$  (20  $\mu$ L, 0.14 mmol). The reaction mixture was brought to –10 °C and stirred for about 30 min. A gummy product separated out from the solution which, by addition of ethanol (2–3 mL) slowly gave a yellow solid which was filtered and crystallized from ethanol and diethylether; yield 60 mg (55%).  $C_{33}H_{42}B_2F_4N_6O_4P_2Ru$  (847.36): Calcd. C, 46.78; H, 5.00; N, 9.92. Found: C, 46.63; H, 4.91; N, 10.04%.

2.2.6.  $[RuTp(CO)\{P(OEt)_3\}(PPh_3)]BPh_4$  (**5**)

An equimolar amount of  $HBf_4 \cdot Et_2O$  (0.13 mmol, 19  $\mu$ L) was added to a solution of  $RuHTp\{P(OEt)_3\}(PPh_3)$  (100 mg, 0.13 mmol) in 10 mL of  $CH_2Cl_2$  cooled to –196 °C. The reaction mixture was allowed to stand under a CO atmosphere (1 atm) and slowly left to reach the room temperature. After 3 h of stirring, the solvent was removed under reduced pressure to give an oil which was treated with ethanol (2 mL) containing an excess of  $NaBPh_4$  (0.26 mmol, 89 mg). A yellow solid slowly separated out from the resulting solution which was filtered and crystallized from  $CH_2Cl_2$  and ethanol; yield 102 mg (72%).  $C_{58}H_{60}B_2N_6O_4P_2Ru$  (1089.79): Calcd. C, 63.92; H, 5.55; N, 7.71. Found: C, 64.06; H, 5.49; N, 7.66%.

2.2.7.  $[RuTp(CH_3CN)\{P(OEt)_3\}(PPh_3)]BPh_4$  (**6**)

An equimolar amount of  $HBf_4 \cdot Et_2O$  (0.13 mmol, 19  $\mu$ L) was added to a solution of  $RuHTp\{P(OEt)_3\}(PPh_3)$  (100 mg, 0.13 mmol) in 5 mL of  $CH_2Cl_2$  cooled to –196 °C. The reaction mixture was brought to –10 °C, stirred for 10 min and then an excess of  $CH_3CN$  (1 mmol, 52  $\mu$ L) added. The resulting solution was left to reach the room temperature and stirred for 3 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol containing an excess of  $NaBPh_4$  (0.26 mmol, 89 mg). A pale yellow solid slowly separated out from the resulting solution,

which was filtered and crystallized from  $CH_2Cl_2$  and ethanol; yield 90 mg (62%).  $C_{59}H_{63}B_2N_7O_3P_2Ru$  (1102.83): Calcd. C, 64.26; H, 5.76; N, 8.89. Found: C, 64.11; H, 5.81; N, 8.77%.

2.2.8.  $[RuTp\{C=C(H)R\}\{P(OEt)_3\}(PPh_3)]BPh_4$  (**7**, **8**) [ $R=Ph$  (**7**),  $t-Bu$  (**8**)]

An equimolar amount of  $HBf_4 \cdot Et_2O$  (0.27 mmol, 39  $\mu$ L) was added to a solution of  $RuHTp\{P(OEt)_3\}(PPh_3)$  (200 mg, 0.27 mmol) in 10 mL of  $CH_2Cl_2$  cooled to –196 °C. The reaction mixture was brought to –10 °C, stirred for 10 min and then an excess of the appropriate alkyne  $HC\equiv CR$  (0.54 mmol) was added. The resulting solution was left to reach the room temperature and stirred for about 2 h. The solvent was removed under reduced pressure to give a brown oil which was treated with ethanol (3 mL) containing an excess of  $NaBPh_4$  (0.54 mmol, 0.185 g). A pink solid separated out from the resulting solution which was filtered and crystallized from  $CH_2Cl_2$  and ethanol; yield: **7** 188 mg (60%), **8** 195 mg (63%). **7**:  $C_{65}H_{66}B_2N_6O_3P_2Ru$  (1163.91): Calcd. C, 67.08; H, 5.72; N, 7.22. Found: C, 66.95; H, 5.78; N, 7.15%. **8**:  $C_{63}H_{70}B_2N_6O_3P_2Ru$  (1143.92): Calcd. C, 66.15; H, 6.17; N, 7.35. Found: C, 66.28; H, 6.10; N, 7.23%.

2.2.9.  $[RuTp\{C=C=C(Ph)R\}\{P(OEt)_3\}(PPh_3)]BPh_4$  (**9**, **10**) [ $R=Ph$  (**9**),  $Me$  (**10**)] and  $[RuTp\{C=C=C(Ph)_2\}\{P(OEt)_3\}_2]BPh_4$  (**11**)

An equimolar amount of  $HBf_4 \cdot Et_2O$  (0.13 mmol, 19  $\mu$ L) was added to a solution of  $RuHTp\{P(OEt)_3\}(PPh_3)$  (100 mg, 0.13 mmol) in 5 mL of  $CH_2Cl_2$  cooled to –196 °C. The reaction mixture was brought to –20 °C, stirred for 10 min and then an excess of the appropriate propargylic alcohol  $HC\equiv CC(OH)(Ph)R$  (0.26 mmol) in 5 mL of  $CH_2Cl_2$  was added. The resulting solution was left to reach the room temperature, stirred for 4 h and then the solvent removed under reduced pressure. The oil obtained was triturated with ethanol (3 mL) containing an excess of  $NaBPh_4$  (0.26 mmol, 89 mg). A purple solid slowly separated out from the resulting solution which was filtered and crystallized from  $CH_2Cl_2$  and ethanol; yield: **9** 94 mg (58%), **10** 94 mg (61%), **11** 97 mg (64%). **9**:  $C_{72}H_{70}B_2N_6O_3P_2Ru$  (1252.02): Calcd. C, 69.07; H, 5.64; N, 6.71. Found: C, 68.91; H, 5.60; N, 6.63%. **10**:  $C_{67}H_{68}B_2N_6O_3P_2Ru$  (1189.95): Calcd. C, 67.63; H, 5.76; N, 7.06. Found: C, 67.82; H, 5.69; N, 6.94%. **11**:  $C_{60}H_{70}B_2N_6O_6P_2Ru$  (1155.89): Calcd. C, 62.35; H, 6.10; N, 7.27. Found: C, 62.20; H, 6.34; N, 7.17%.

2.2.10.  $Ru(C\equiv CR)Tp\{P(OEt)_3\}(PPh_3)$  (**12**, **13**) [ $R=Ph$  (**12**),  $t-Bu$  (**13**)]

An excess of triethylamine (0.3 mmol, 42  $\mu$ L) was added to a solution of the appropriate vinylidene  $[RuTp\{C=C(H)R\}\{P(OEt)_3\}(PPh_3)]BPh_4$  (**7**, **8**) (0.10

mmol) in 5 mL of  $\text{CH}_2\text{Cl}_2$  and the reaction mixture was stirred for 3 h. A white solid ( $[\text{NHEt}_3]\text{BPh}_4$ ) separated out from the solution which was filtered and rejected. The solution was evaporated to dryness under reduced pressure to give an oil which was triturated with ethanol (2 mL). By cooling of the resulting solution to  $-25^\circ\text{C}$  a yellow solid separated out, which was filtered and dried under vacuum; yield: **12** 72 mg (85%), **13** 67 mg (82%).  
**12**:  $\text{C}_{41}\text{H}_{45}\text{BN}_6\text{O}_3\text{P}_2\text{Ru}$  (843.67): Calcd. C, 58.37; H, 5.38; N, 9.96. Found: C, 58.19; H, 5.33; N, 10.04%.  
**13**:  $\text{C}_{39}\text{H}_{49}\text{BN}_6\text{O}_3\text{P}_2\text{Ru}$  (823.68): Calcd. C, 56.87; H, 6.00; N, 10.20. Found: C, 57.00; H, 5.88; N, 10.32%.

#### 2.2.11. $\text{Ru}(\text{SnCl}_3)\text{Tp}\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)$ (**14**)

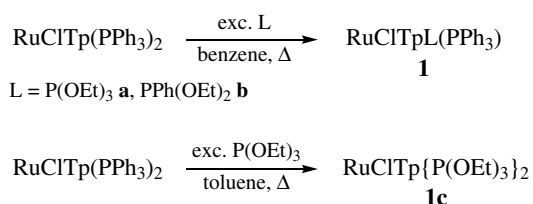
An excess of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (0.26 mmol, 59 mg) was added to a solution of  $[\text{RuClTp}\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$  (**1a**) (100 mg, 0.13 mmol) in 20 mL of  $\text{CH}_2\text{Cl}_2$  and the resulting suspension was stirred for 10 h. The volume of the solvent was reduced to about 5 mL by evaporation under reduced pressure and the solid formed was filtered, washed with ethanol and dried under vacuum. The complex was extracted from the solid obtained with five 5-mL portions of  $\text{CH}_2\text{Cl}_2$  and the extracts were concentrated to about 3–4 mL. A yellow solid separated out whose precipitation was completed by addition of ethanol. The solid was filtered and dried under vacuum; yield: 69 mg (55%).  $\text{C}_{33}\text{H}_{40}\text{BCl}_3\text{N}_6\text{O}_3\text{P}_2\text{RuSn}$  (967.59): Calcd. C, 40.96; H, 4.17; N, 8.69; Cl, 10.99. Found: C, 40.79; H, 4.11; N, 8.82; Cl, 11.07%.

### 3. Results and discussion

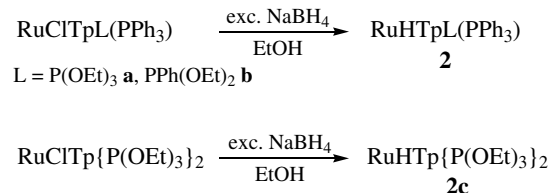
When using benzene as a solvent, the chloro complex [12]  $\text{RuClTp}(\text{PPh}_3)_2$  reacts with phosphites to give the mixed-ligands  $\text{RuClTpL}(\text{PPh}_3)$  (**1a**, **1b**) derivatives, while using toluene the reaction gives the  $\text{RuClTp}\{\text{P}(\text{OEt})_3\}_2$  (**1c**) complex in a good yield, as shown in Scheme 1.

The related  $\text{RuClTp}\{\text{PPh}(\text{OEt})_2\}_2$  (**1d**) compound, however, was obtained under all conditions, as a mixture of products which were not separated.

Treatment of the chloro complexes **1a**, **1b**, **1c** with  $\text{NaBH}_4$  in refluxing ethanol gave the corresponding hydride  $\text{RuHTpL}(\text{PPh}_3)$  (**2a**, **2b**) and  $\text{RuHTp}\{\text{P}(\text{OEt})_3\}_2$  (**2c**), which were isolated in good yields and characterized (Scheme 2).



Scheme 1.



Scheme 2.

Good analytical data were obtained of all the compounds **1–2**, which are white or pale yellow solids stable in air and in solution of all the common organic solvents, where they behave as non electrolytes [13]. The IR and NMR spectra (Table 1) support the proposed formulation.

The infrared of both chloro and hydrido complexes show the characteristic  $\nu_{\text{BH}}$  band of the Tp ligand at  $2484\text{--}2461\text{ cm}^{-1}$ , while a medium-intensity absorption at  $1994\text{--}1948\text{ cm}^{-1}$  attributed to  $\nu_{\text{RuH}}$  was observed in the spectra of the hydride derivatives **2**. The  $^1\text{H}$  NMR spectra confirm the presence of the hydridotris(pyrazolyl)borate ligand showing, between 8.12 and 5.53 ppm, the characteristic multiplets of the pyrazole hydrogen atoms of the Tp group. The signals due to the phosphites  $\text{P}(\text{OEt})_3$  and  $\text{PPh}(\text{OEt})_2$  are also present in the spectra of compounds **1**, **2**. Furthermore, the  $^1\text{H}$  NMR spectra of the mixed-ligand  $\text{RuHTpL}(\text{PPh}_3)$  (**1a**, **1b**) hydride complexes show a multiplet near  $-14$  ppm attributed to the hydride resonances coupled to the phosphorus nuclei of the phosphine. Taking into account that the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra appear as an AB multiplet, the spectra can be simulated as the X part of an ABX spectrum with the parameters reported in Table 1. Values for the two  $J_{\text{PH}}$  of 24 and of 32 or 34 Hz, respectively, were calculated.

The proton spectrum of the phosphite  $\text{RuHTp}\{\text{P}(\text{OEt})_3\}_2$  (**2c**) complex, instead, appears as a triplet at  $-13.91$  ppm with  $J_{\text{PH}}$  of 33 Hz. The related  $^{31}\text{P}$  spectrum is a sharp singlet at 160.5 ppm. These data support the formulation proposed for the new Tp complexes **1**, **2**, whose geometry should be of the types **I** and **II**, reported in Chart 1.

Hydride  $\text{RuHTpL}(\text{PPh}_3)$  (**2a**, **2b**) and  $\text{RuHTp}\{\text{P}(\text{OEt})_3\}_2$  (**2c**) complexes react with the Brønsted acids  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  or  $\text{CF}_3\text{SO}_3\text{H}$  to give the dihydrogen  $[\text{Ru}(\eta^2\text{-H}_2)\text{TpL}(\text{PPh}_3)]^+$  (**3a**, **3b**) and  $[\text{Ru}(\eta^2\text{-H}_2)\text{Tp}\{\text{P}(\text{OEt})_3\}_2]^+$  (**3c**) derivatives (Scheme 3), which are stable below  $5\text{--}10^\circ\text{C}$ . At higher temperatures the loss of  $\text{H}_2$  takes place, thus preventing the separation of the dihydrogen complexes in the solid state. Spectroscopic data (Table 2), however, strongly support the formation of the dihydrogen derivatives **3**.

The protonation reaction was carried out at variable temperatures and was monitored by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra. The addition of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  or  $\text{CF}_3\text{SO}_3\text{H}$  to **2**

Table 1  
Selected IR and NMR spectroscopic data for ruthenium complexes

Compound	IR <sup>a</sup> $\nu$ (cm <sup>-1</sup> )	Assgnt	<sup>1</sup> H NMR <sup>b</sup> $\delta$ (J, Hz)	Assgnt	Spin system	<sup>31</sup> P{ <sup>1</sup> H} NMR <sup>b,c</sup> $\delta$ (J, Hz)
<b>1a</b> RuCl(Tp){P(OEt) <sub>3</sub> }(PPh <sub>3</sub> )	2480 m	$\nu_{\text{BH}}$	8.02–7.60 m 3.51 m 0.98 t	Ph + Tp CH <sub>2</sub> CH <sub>3</sub>	AB	$\delta_{\text{A}}$ 140.9 $\delta_{\text{B}}$ 45.6 $J_{\text{AB}} = 55$
<b>1b</b> RuCl(Tp){PPh(OEt) <sub>2</sub> }(PPh <sub>3</sub> )	2478 m	$\nu_{\text{BH}}$	7.85–5.66 m 3.83 m 3.43 m 1.11 t 0.88 t	Ph + Tp CH <sub>2</sub> CH <sub>3</sub>	AB	$\delta_{\text{A}}$ 167.2 $\delta_{\text{B}}$ 42.5 $J_{\text{AB}} = 45$
<b>1c</b> RuCl(Tp){P(OEt) <sub>3</sub> } <sub>2</sub>	2484 m	$\nu_{\text{BH}}$	8.01–6.04 m 3.70 m 1.16 s	Tp CH <sub>2</sub> CH <sub>3</sub>	A <sub>2</sub>	141.8 s
<b>2a</b> RuH(Tp){P(OEt) <sub>3</sub> }(PPh <sub>3</sub> )	2473 m 1994 m	$\nu_{\text{BH}}$ $\nu_{\text{RuH}}$	7.84–5.53 m 3.65 m 3.35 m 0.87 t ABX spin syst $\delta_{\text{X}} -14.14$ $J_{\text{AX}} = 24$ $J_{\text{BX}} = 34$	Ph + Tp CH <sub>2</sub> CH <sub>3</sub> H	AB	$\delta_{\text{A}}$ 161.6 $\delta_{\text{B}}$ 73.0 $J_{\text{AB}} = 63$
<b>2b</b> RuH(Tp){PPh(OEt) <sub>2</sub> }(PPh <sub>3</sub> )	2482 m	$\nu_{\text{BH}}$	7.89–5.54 m 3.95 m 3.34 m 1.01 t 0.76 t ABX spin syst $\delta_{\text{X}} -14.04$ $J_{\text{AX}} = 24$ $J_{\text{BX}} = 32$	Ph + Tp CH <sub>2</sub> CH <sub>3</sub> H	AB	$\delta_{\text{A}}$ 181.7 $\delta_{\text{B}}$ 71.6 $J_{\text{AB}} = 53$
<b>2c</b> RuH(Tp){P(OEt) <sub>3</sub> } <sub>2</sub>	2461 m 1948 m	$\nu_{\text{BH}}$ $\nu_{\text{RuH}}$	8.12–6.12 m 3.71 m 1.18 t –13.91 t $J_{\text{PH}} = 33$	Tp CH <sub>2</sub> CH <sub>3</sub> H	A <sub>2</sub>	160.5 s
<b>3a</b> [Ru( $\eta^2$ -H <sub>2</sub> )(Tp){P(OEt) <sub>3</sub> }(PPh <sub>3</sub> )] <sup>+</sup> BF <sub>4</sub> <sup>-</sup>			7.98–5.81 m <sup>d</sup> 3.49 m 3.19 m 1.05 t –8.97 br	Ph + Tp CH <sub>2</sub> CH <sub>3</sub> H <sub>2</sub>	AB	$\delta_{\text{A}}$ 128.6 $\delta_{\text{B}}$ 42.1 $J_{\text{AB}} = 51$
<b>3b</b> [Ru( $\eta^2$ -H <sub>2</sub> )(Tp){PPh(OEt) <sub>2</sub> }(PPh <sub>3</sub> )] <sup>+</sup> BF <sub>4</sub> <sup>-</sup>			8.00–5.84 m <sup>e</sup> 3.60 m 3.30 m 1.14 t 0.93 t –8.90 br	Ph + Tp CH <sub>2</sub> CH <sub>3</sub> H <sub>2</sub>	AB	$\delta_{\text{A}}$ 157.2 $\delta_{\text{B}}$ 43.4 $J_{\text{AB}} = 43.5$

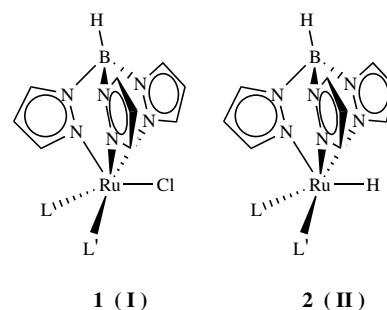
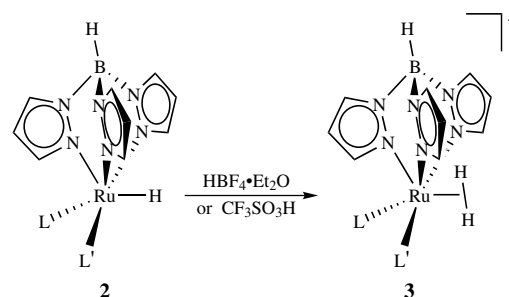
3c	$[\text{Ru}(\eta^2\text{-H}_2)(\text{Tp})\{\text{P}(\text{OEt})_3\}_2]^+\text{BF}_4^-$			7.98–6.25 m <sup>e</sup> 3.60 m 1.18 t –9.21 br	Tp CH <sub>2</sub> CH <sub>3</sub> H <sub>2</sub>	A <sub>2</sub>	131.7 s
4	$[\text{RuTp}(\text{H}_2\text{O})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BF}_4$	2484 w	$\nu_{\text{BH}}$	7.88–6.00 m 3.66 m 3.29 m 2.13 s,br 1.08 t	Ph + Tp CH <sub>2</sub>  H <sub>2</sub> O CH <sub>3</sub>	AB	$\delta_{\text{A}}$ 133.1 $\delta_{\text{B}}$ 47.8 $J_{\text{AB}} = 45$
5	$[\text{RuTp}(\text{CO})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	2494 w 1998 s	$\nu_{\text{BH}}$ $\nu_{\text{CO}}$	7.83–5.92 m 3.58 m 3.35 m 1.05 t	Ph + Tp CH <sub>2</sub>  CH <sub>3</sub>	AB	$\delta_{\text{A}}$ 121.7 $\delta_{\text{B}}$ 38.6 $J_{\text{AB}} = 49$
6	$[\text{RuTp}(\text{CH}_3\text{CN})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	2484 w 2287 w	$\nu_{\text{BH}}$ $\nu_{\text{CN}}$	7.90–6.00 m 3.56 m 3.25 m 1.69 s 1.00 t	Ph + Tp CH <sub>2</sub>  CH <sub>3</sub> CN CH <sub>3</sub> phos	AB	$\delta_{\text{A}}$ 131.8 $\delta_{\text{B}}$ 44.8 $J_{\text{AB}} = 53$
7	$[\text{RuTp}\{\text{=C=C}(\text{H})\text{Ph}\}\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	2486 w 1653 m 1636 m	$\nu_{\text{BH}}$ $\nu_{\text{C=C}}$	7.98–5.63 m 5.68 q $J_{\text{PH}} = J_{\text{PH}} = 4$ 3.43 m 1.04 t	Ph + Tp =CH  CH <sub>2</sub> CH <sub>3</sub>	AB	$\delta_{\text{A}}$ 116.6 $\delta_{\text{B}}$ 37.1 $J_{\text{AB}} = 49$
8	$[\text{RuTp}\{\text{=C=C}(\text{H})\text{-}i\text{-Bu}\}\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	2482 w 1672 m 1653 m	$\nu_{\text{BH}}$ $\nu_{\text{C=C}}$	8.12–5.93 m 4.59 t $J_{\text{PH}} = 3$ 3.60 m 3.39 m 1.07 t 1.03 s	Ph + Tp =CH  CH <sub>2</sub>  CH <sub>3</sub> phos <i>t</i> -Bu	AB	$\delta_{\text{A}}$ 120.4 $\delta_{\text{B}}$ 39.9 $J_{\text{AB}} = 49$
9	$[\text{RuTp}\{\text{=C=C=CPh}_2\}\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	2486 w 1948 s	$\nu_{\text{BH}}$ $\nu_{\text{C=C=C}}$	8.02–5.91 m 3.75 m 3.55 m 1.08 t	Ph + Tp CH <sub>2</sub>  CH <sub>3</sub>	AB	$\delta_{\text{A}}$ 123.9 $\delta_{\text{B}}$ 42.5 $J_{\text{AB}} = 55$
10	$[\text{RuTp}\{\text{=C=C=C}(\text{Me})\text{Ph}\}\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	2484 w 1956 s	$\nu_{\text{BH}}$ $\nu_{\text{C=C=C}}$	8.03–5.89 m 3.66 m 3.50 m 2.28 s 1.06 t	Ph + Tp CH <sub>2</sub>  =CCH <sub>3</sub> CH <sub>3</sub> phos	AB	$\delta_{\text{A}}$ 122.9 $\delta_{\text{B}}$ 41.1 $J_{\text{AB}} = 53$
11	$[\text{RuTp}\{\text{=C=C=CPh}_2\}\{\text{P}(\text{OEt})_3\}_2]\text{BPh}_4$	2482 w 1952 s	$\nu_{\text{BH}}$ $\nu_{\text{C=C=C}}$	8.40–5.83 m 3.65 m 1.20 t	Ph + Tp CH <sub>2</sub> CH <sub>3</sub>	A <sub>2</sub>	127.0 s

(continued on next page)



Table 1 (continued)

Compound	IR <sup>a</sup> $\nu$ (cm <sup>-1</sup> )	Assgnt	<sup>1</sup> H NMR <sup>b</sup> $\delta$ (J, Hz)	Assgnt	Spin system	<sup>31</sup> P{ <sup>1</sup> H} NMR <sup>b,c</sup> $\delta$ (J, Hz)
<b>12</b> Ru(C≡CPh)Tp{P(OEt) <sub>3</sub> }(PPh <sub>3</sub> )	2471 w	$\nu_{\text{BH}}$	8.15–5.77 m	Ph + Tp	AB	$\delta_{\text{A}}$ 144.8
	2081 m	$\nu_{\text{C}\equiv\text{C}}$	3.63 m 1.00 t	CH <sub>2</sub> CH <sub>3</sub>		$\delta_{\text{B}}$ 52.6 $J_{\text{AB}}$ = 55
<b>13</b> Ru(C≡C <i>t</i> -Bu)Tp{P(OEt) <sub>3</sub> }(PPh <sub>3</sub> )	2461 w	$\nu_{\text{BH}}$	8.17–5.70 m	Ph + Tp	AB	$\delta_{\text{A}}$ 145.1
	2091 m	$\nu_{\text{C}\equiv\text{C}}$	3.62 m 1.35 s 1.00 t	CH <sub>2</sub> <i>t</i> -Bu CH <sub>3</sub> phos		$\delta_{\text{B}}$ 52.6 $J_{\text{AB}}$ = 57
<b>14</b> Ru(SnCl <sub>3</sub> )Tp{P(OEt) <sub>3</sub> }(PPh <sub>3</sub> ) <sup>f</sup>	2488 w	$\nu_{\text{BH}}$	8.51–5.49 m	Ph + Tp	AB(M, N) M = <sup>119</sup> Sn N = <sup>117</sup> Sn	$\delta_{\text{A}}$ 134.2
			3.61 m 3.36 m 1.05 t	CH <sub>2</sub> CH <sub>3</sub>		$\delta_{\text{B}}$ 49.2 $J_{\text{AB}}$ = 49 ( $J_{\text{AM}}$ = 513) ( $J_{\text{BN}}$ = 351) ( $J_{\text{AN}}$ = 480) ( $J_{\text{BN}}$ = 336)

<sup>a</sup> In KBr pellets.<sup>b</sup> In CD<sub>2</sub>Cl<sub>2</sub> at 25 °C, unless otherwise noted.<sup>c</sup> Positive shift downfield from 85% H<sub>3</sub>PO<sub>4</sub>.<sup>d</sup> At –15 °C.<sup>e</sup> At 0 °C.<sup>f</sup> <sup>119</sup>SnNMR (from SnMe<sub>4</sub>): ABM spin system,  $\delta_{\text{M}}$  –218 ppm,  $J_{\text{AM}}$  = 513,  $J_{\text{BM}}$  = 351 Hz.Chart 1. L = P(OEt)<sub>3</sub> or PPh(OEt)<sub>2</sub>, L' = PPh<sub>3</sub>; L = L' = P(OEt)<sub>3</sub>.Scheme 3. L' = PPh<sub>3</sub>, L = P(OEt)<sub>3</sub> (a), PPh(OEt)<sub>2</sub> (b); L = L' = P(OEt)<sub>3</sub> (c).

caused the disappearance of the hydride multiplet near –14 ppm and the appearance of a broad signal near –9.0 ppm attributed to the  $\eta^2$ -H<sub>2</sub> ligand. Measurements of  $T_1$  on these signals gave  $T_{1\text{min}}$  values of 8.0–7.1 ms (Table 2) in agreement with the presence of a dihydrogen derivative [14].

Further support for the presence of the  $\eta^2$ -H<sub>2</sub> ligand came from the measurement of the  $J_{\text{HD}}$  values of the isotopomer [Ru( $\eta^2$ -HD)TpLL']<sup>+</sup> derivatives. These HD complexes were prepared by addition of deuterated triflic acid, CF<sub>3</sub>SO<sub>3</sub>D, to the hydrides **2** in CD<sub>2</sub>Cl<sub>2</sub>. In the hydride region, the <sup>1</sup>H NMR spectra show a relatively sharp triplet of multiplets of 1:1.4:1 intensity. The increased intensity of the center peak of the triplet of the HD resonances is due to the presence of a small amount of H<sub>2</sub> species resulting from the incomplete deuteration of the triflic acid, while the splitting of each signal of the triplet is attributable to the coupling with the phosphorus of the phosphines, with <sup>2</sup>J<sub>PH(HD)</sub> of 9 Hz for **3c** and with values of about 7–8 Hz for **3a** and **3b**. From this triplet values of 31.5 and 32.0 Hz for  $J_{\text{HD}}$  were measured, which confirm the formation of dihydrogen derivatives. From the  $J_{\text{HD}}$  values the H–H distances were calculated [15], which are reported in Table 2. Values between 0.90 and 0.91 Å were observed for our  $\eta^2$ -H<sub>2</sub> complexes **3**, which are strictly comparable with those reported for related tris(pyrazolyl)borate ruthenium dihydrogen complexes containing tertiary phosphine of the [Ru( $\eta^2$ -H<sub>2</sub>)Tp(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>, [Ru( $\eta^2$ -H<sub>2</sub>)Tp(dppe)]-BF<sub>4</sub>, [Ru( $\eta^2$ -H<sub>2</sub>)TpL(PPh<sub>3</sub>)]BF<sub>4</sub> (L = CO, CH<sub>3</sub>CN) type

Table 2  
 $T_{1\text{min}}$  (200 MHz) and  $J_{\text{HD}}$  NMR data for some dihydrogen and hydride complexes and calculated H–H distances

Compound	$T$ (K)	$\delta$ (ppm)	$T_{1\text{min}}$ (ms)	$J_{\text{HD}}$ (Hz)	$r_{\text{H-H}}$ (Å)		
<b>3a</b> $[\text{Ru}(\eta^2\text{-H}_2)(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]^+$	208	−8.95	7.1	32.0	1.05 <sup>a</sup>	0.83 <sup>b</sup>	0.90 <sup>c</sup>
<b>3b</b> $[\text{Ru}(\eta^2\text{-H}_2)(\text{Tp})\{\text{PPh}(\text{OEt})_2\}(\text{PPh}_3)]^+$	211	−9.1	8.0	31.5	1.07	0.85	0.91
<b>3c</b> $[\text{Ru}(\eta^2\text{-H}_2)(\text{Tp})\{\text{P}(\text{OEt})_3\}_2]^+$	204	−9.2	7.2	31.5	1.06	0.84	0.91
<b>2a</b> $\text{RuH}(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)$	203	−14.04	225				

<sup>a</sup> The H–H distances were calculated [16] from  $T_{1\text{min}}$  values for static regimes of the  $\text{H}_2$  ligand.

<sup>b</sup> The H–H distances were calculated [16] from  $T_{1\text{min}}$  values for fast rotation of the  $\text{H}_2$  ligand.

<sup>c</sup> H–H distances were calculated from the  $J_{\text{HD}}$  values for the HD complexes using the equation [15]:  $r_{\text{H-H}} = 1.44 - 0.0168 (J_{\text{HD}})$ .

[4d,4e]. In tris(pyrazolyl)borate Ru (II) dihydrogen complexes, therefore, the nature of the supporting ligands does not seem to have a strong influence on the H–H distance of the  $\eta^2\text{-H}_2$  group.

The H–H bond length in the  $\text{H}_2$  ligand can also be calculated from  $T_{1\text{min}}$  values [16]. The results for complexes **3** are reported in Table 2 for both a fast and a slow rotation model and are not comparable with those calculated from the  $J_{\text{HD}}$  values. The H–H distance of 0.90–0.91 Å calculated from  $J_{\text{HD}}$ , in fact, are just intermediate between the two possible values of 1.05–1.07 Å (slow rotation) and 0.83–0.85 Å (fast rotation), calculated from the  $T_{1\text{min}}$  values. Similar results were found in other dihydrogen ruthenium (II) derivatives [8b].

In the temperature range between +20 and −80 °C the  $^3\text{P}\{^1\text{H}\}$  NMR spectra of the dihydrogen complexes appear as an AB quartet for  $[\text{RuTp}(\eta^2\text{-H}_2)\text{L}(\text{PPh}_3)]^+$  (**3a**, **3b**) while a sharp singlet is observed for  $[\text{RuTp}(\eta^2\text{-H}_2)\{\text{P}(\text{OEt})_3\}_2]^+$  (**3c**) derivative, in agreement with the geometry proposed in Scheme 3.

The preparation of complexes **2**, **3** highlights that also phosphite ligands can be used to stabilize classical and non-classical tris(pyrazolyl)borate Ru hydride complexes. A comparison with the related carbonyl or phosphine  $[\text{Ru}(\eta^2\text{-H}_2)\text{TpLP}]^+$  derivatives [4] shows, however, that the introduction of phosphite ligands into Tp complexes decreases the thermal stability of the  $\eta^2\text{-H}_2$  derivatives like **3**. This is somewhat unexpected in light of our previous results on the ability of phosphite to stabilize  $\eta^2\text{-H}_2$  complexes. Probably, in Tp-hydride chemistry the influence of the supporting ligands on the properties and the stabilization of  $\eta^2\text{-H}_2$  ligand is rather restricted.

### 3.1. Reactivity of $\eta^2\text{-H}_2$ complexes

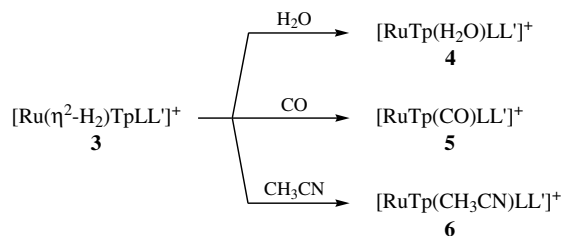
The  $\eta^2\text{-H}_2$  ligand is labile in the  $[\text{RuTp}(\eta^2\text{-H}_2)\text{LL}]^+$  (**3**) cations and can be easily substituted by several ligands allowing new RuTp complexes to be prepared. Some examples have been reported in Schemes 4 and 5.

At first, the aquo complex **4** was obtained in an attempt to isolate the  $\eta^2\text{-H}_2$  complex in the solid state, due to the presence of traces of  $\text{H}_2\text{O}$  in the solvent. It was also obtained as a pale-yellow solid by adding an excess of  $\text{H}_2\text{O}$  to a solution of  $\eta^2\text{-H}_2$  complex **3a** in

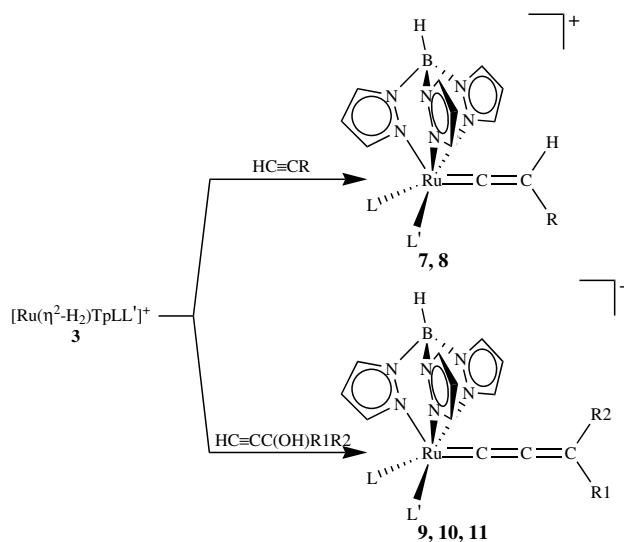
$\text{CH}_2\text{Cl}_2$ . Carbonyl **5** and acetonitrile **6** complexes were also obtained by substituting the  $\eta^2\text{-H}_2$  ligand in **3a** and were isolated as yellow solids.

Interesting is the reaction of the dihydrogen complexes with terminal alkyne  $\text{RC}\equiv\text{CH}$  (Scheme 5), which gives the vinylidene [17]  $[\text{RuTp}\{\text{C}=\text{C}(\text{H})\text{R}\}\text{LL}]^+$  (**7**, **8**) cations, isolated as pale-pink  $\text{BPh}_4$  salts. The substitution of the  $\eta^2\text{-H}_2$  ligand by the alkyne probably give a  $[\text{Ru}(\eta^2\text{-RC}\equiv\text{CH})]$  intermediate complex, which tautomerises [18] to yield the final vinylidene derivatives **7**, **8**.

Propargyl alcohol  $\text{HC}\equiv\text{CC}(\text{OH})\text{R}_1\text{R}_2$  also reacts with dihydrogen complex **3a** giving a deep-purple



Scheme 4. L = P(OEt)<sub>3</sub>, L' = PPh<sub>3</sub>.



Scheme 5. L = P(OEt)<sub>3</sub>, L' = PPh<sub>3</sub>, R = Ph (**7**), <sup>t</sup>Bu (**8**), R<sub>1</sub> = R<sub>2</sub> = Ph (**9**), R<sub>1</sub> = Ph, R<sub>2</sub> = Me (**10**); L = L' = P(OEt)<sub>3</sub>, R<sub>1</sub> = R<sub>2</sub> = Ph (**11**).



Table 3  
 $^{13}\text{C}\{^1\text{H}\}$  NMR data for selected ruthenium complexes

	Compound <sup>a</sup>	$^{13}\text{C}\{^1\text{H}\}$ NMR $\delta$ (J, Hz)	Assgmt
6	$[\text{RuTp}(\text{CH}_3\text{CN})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	165–106 m ABX spin syst $\delta_{\text{X}}$ 142.9 $J_{\text{AX}} = 4.2$ $J_{\text{BX}} = 1.4$ 62.0 d 16.1 d 3.67 s	Ph + Tp CH <sub>3</sub> CN  CH <sub>2</sub> CH <sub>3</sub> phos CH <sub>3</sub> CN
7	$[\text{RuTp}\{\text{C}=\text{C}(\text{H})\text{Ph}\}\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	ABX spin syst $\delta_{\text{X}}$ 376.4 $J_{\text{AX}} = 17.8$ $J_{\text{BX}} = 21.7$ 165–106 m 114.1 s 64.2 d 15.9 d	C $\alpha$  Ph + Tp C $\beta$ CH <sub>2</sub> CH <sub>3</sub>
8	$[\text{RuTp}\{\text{C}=\text{C}(\text{H})\text{-Bu}\}\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	ABX spin syst $\delta_{\text{X}}$ 373.3 $J_{\text{AX}} = 22.0$ $J_{\text{BX}} = 17.5$ 165–106 m 121.2s 63.8d 33.2s 32.2s 15.9d	C $\alpha$  Ph + Tp C $\beta$ CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub> C(CH <sub>3</sub> ) <sub>3</sub> CH <sub>3</sub> phos
9	$[\text{RuTp}\{\text{C}=\text{C}=\text{CPh}_2\}\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	ABX spin syst $\delta_{\text{X}}$ 319.0 $J_{\text{AX}} = 25.6$ $J_{\text{BX}} = 17.8$ 204.4 s 163.0 s 163–106 m 63.0 d 15.9 d	C $\alpha$  C $\beta$ C $\gamma$ Ph + Tp CH <sub>2</sub> CH <sub>3</sub>
10	$[\text{RuTp}\{\text{C}=\text{C}=\text{C}(\text{Me})\text{Ph}\}\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	ABX spin syst $\delta_{\text{X}}$ 321.6 $J_{\text{AX}} = 17.5$ $J_{\text{BX}} = 25.7$ 200.5 s 164.4 s 164–106 m 63.1 d 31.6 s 16.0 d	C $\alpha$  C $\beta$ C $\gamma$ Ph + Tp CH <sub>2</sub> =CCH <sub>3</sub> CH <sub>3</sub> phos
11	$[\text{RuTp}\{\text{C}=\text{C}=\text{CPh}_2\}\{\text{P}(\text{OEt})_3\}_2]\text{BPh}_4$	319.2 t $J_{\text{PC}} = 7$ 201.9 s 163.8 s 165–122 m 62.3 d 16.1 d	C $\alpha$  C $\beta$ C $\gamma$ Ph + Tp CH <sub>2</sub> CH <sub>3</sub>
12	$\text{Ru}(\text{C}\equiv\text{CPh})\text{Tp}\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)$	144–104 m 110.4 m 60.5 d 16.1 d	Ph + Tp C $\alpha$ CH <sub>2</sub> CH <sub>3</sub>

Table 3 (continued)

Compound <sup>a</sup>	<sup>13</sup> C{ <sup>1</sup> H} NMR $\delta$ (J, Hz)	Assgmt
13 Ru(C≡C <i>t</i> -Bu)Tp{P(OEt) <sub>3</sub> }(PPh <sub>3</sub> )	145–104 m	Ph + Tp
	116.0 s	C $\beta$
	ABX spin syst	C $\alpha$
	$\delta_X$ 99.6	
	$J_{AX}$ = 23	
	$J_{BX}$ = 21.5	
	60.2 d	CH <sub>2</sub>
	33.4 s	C(CH <sub>3</sub> ) <sub>3</sub>
	29.9 s	C(CH <sub>3</sub> ) <sub>3</sub>
16.1 d	CH <sub>3</sub> phos	

<sup>a</sup> In CD<sub>2</sub>Cl<sub>2</sub> at 25 °C.

solution from which the allenylidene [RuTp(=C=C=CR1R2)LL']<sup>+</sup> (**9–11**) cations were isolated as BPh<sub>4</sub> salts and characterized. The reaction probably gives hydroxovinylidene [RuTp{=C=C(H)CR1R2OH}LL']<sup>+</sup> intermediate by tautomerization of the alkyne on the metal center. The loss of water from this intermediate allows the formation of the final allenylidene species **9–11**.

Despite the large number of reported vinylidene [17–19] and allenylidene [20,21] complexes of ruthenium, relatively few contain tris(pyrazolyl)borate as supporting ligand [22]. The use of the dihydrogen complexes **3** as precursors allows the facile synthesis of the new mixed-ligand derivatives **9–11** with phosphite and tris(pyrazolyl)borate.

The new complexes are yellow (**4–6**), pink (**7, 8**), and deep-purple (**9–11**) solids stable in air and in a solution of polar organic solvents, where they behave as 1:1 electrolytes [13]. Analytical and spectroscopic data (Tables 1 and 3) support the proposed formulation. The IR spectra show the medium-intensity  $\nu_{BH}$  band at 2494–2482 cm<sup>-1</sup> of the Tp ligand, whose presence in all the complexes **4–11** is confirmed by the <sup>1</sup>H NMR spectra, which show the characteristic signals of the pyrazole protons between 8.40 and 5.63 ppm.

The <sup>1</sup>H NMR spectrum of the aquo-complex **4** shows a slightly broad signal at 2.13 ppm, attributed [23] to the protons of the coordinated H<sub>2</sub>O. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum appears as an AB multiplet, in agreement with the proposed formulation.

The infrared spectrum of the [RuTp(CO)LL']BPh<sub>4</sub> (**5**) complex shows a strong band at 1998 cm<sup>-1</sup>, attributed to the  $\nu_{CO}$  of the carbonyl ligand, while the <sup>1</sup>H NMR spectrum shows, as expected, the signals of the Tp and the phosphine ligands. An AB multiplet, finally, is observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum.

The presence of the nitrile ligand in [RuTp(CH<sub>3</sub>CN)LL']BPh<sub>4</sub> (**6**) is confirmed by the IR spectrum, which shows a weak band at 2287 cm<sup>-1</sup> due to the  $\nu_{CN}$  of the CH<sub>3</sub>CN group. Further support comes from the <sup>13</sup>C spectra, which show a singlet at 3.67 ppm and a multiplet at 142.9 ppm, attributed to the methyl and the CN carbon resonances, respectively, of the CH<sub>3</sub>CN ligand.

The multiplicity of the signal at 142.9 ppm is due to the coupling of the carbon with the phosphorus nuclei and can be easily simulated using an ABX model, with the parameters reported in Table 3. Values of 4.2 and 1.4 Hz were observed for <sup>3</sup>J<sub>CP</sub>, in agreement with the N-coordination of the nitrile.

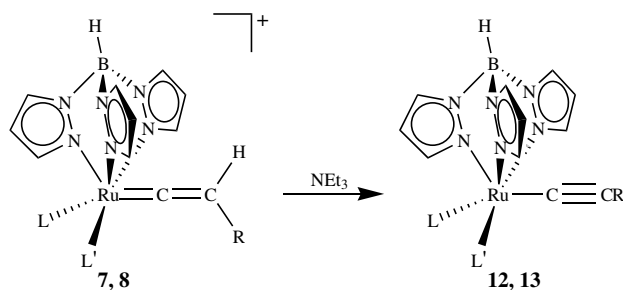
The IR spectra of the vinylidene [RuTp{=C=C(H)R}LL']BPh<sub>4</sub> (**7, 8**) complexes show two medium-intensity bands at 1672–1636 cm<sup>-1</sup>, which are characteristic [17,18] of the vinylidene ligands. The presence of this ligand, however, is confirmed by both the <sup>1</sup>H and <sup>13</sup>C NMR spectra, which show the characteristic signals of the =C=C(H)R group. A quartet at 5.68 ppm for **7** and a triplet at 4.59 ppm for **8**, attributed to the vinylidene =C(H)R proton, are observed in the <sup>1</sup>H NMR spectra of the complexes. In the spectra of [RuTp{=C=C(H)C(CH<sub>3</sub>)<sub>3</sub>}LL']BPh<sub>4</sub> (**8**) a singlet at 1.03 ppm is also present due to the methyl resonance of the <sup>t</sup>Bu substituent. Furthermore, a multiplet at 376.4 ppm for **7** and at 373.3 ppm for **8** are present in the <sup>13</sup>C NMR spectra, which are attributed to the C $\alpha$  resonances of the vinylidene ligands. In the spectra a singlet at 114.1 ppm for **7** and at 121.2 ppm for **8** are also present, attributed to the C $\beta$  carbon resonance of the Ru=C=C(H)R vinylidene ligand. The HMQC and the HMBC experiments confirms these attributions showing the correlation between the <sup>13</sup>C signal at 114–121 ppm with the multiplet of the CH resonances at 5.68–4.59 ppm in the proton spectra. In the temperature range between +20 and –80 °C the <sup>31</sup>P{<sup>1</sup>H} NMR spectra appear as a AB multiplet, in agreement with the presence of two different phosphine ligands. On the basis of the spectroscopic data, a geometry of the type of Scheme 5 can be reasonably proposed for the vinylidene derivatives.

The IR spectra of the allenylidene [RuTp(=C=C=CR1R2)LL']BPh<sub>4</sub> (**9–11**) complexes show a strong band at 1956–1948 cm<sup>-1</sup> attributed to  $\nu_{C=C=C}$  of the propadienylidene [20,21] ligand. Strong support for the presence of the =C=C=CR1R2 group comes from the <sup>13</sup>C NMR spectra (Table 3), which show the characteristic resonance at 321–319 ppm for C $\alpha$ , at 204–200 ppm for C $\beta$ ,

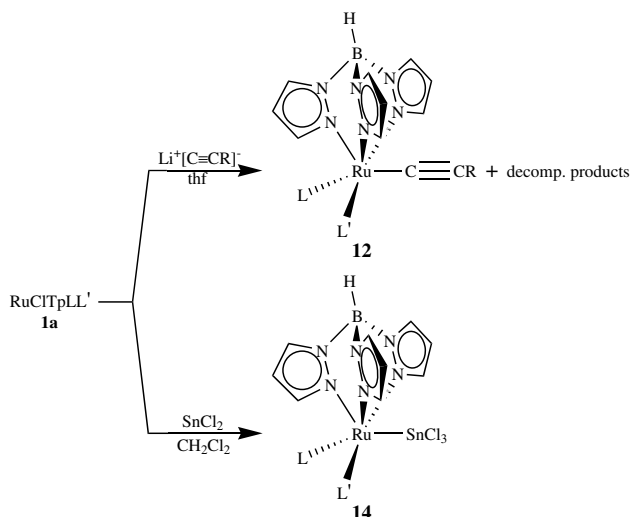
and at 164–163 ppm for  $C_\gamma$  of the coordinate allenylidene ligand. Furthermore, the  $C_\alpha$  carbon resonances appear as a triplet (**11**) or as a multiplet (**9**, **10**) due to the coupling with the phosphorus nuclei. The multiplet can also be simulated using an ABX model with the parameters reported in Table 3. Finally, the  $^{31}\text{P}$  spectra are AB multiplets for **9** and **10**, while a singlet is observed for **11**, so confirming the geometry proposed in Scheme 5 for the allenylidene derivatives.

Vinylidene  $[\text{RuTp}\{\text{C}=\text{C}(\text{H})\text{R}\}\text{LL}'\text{BPh}_4$  (**7**, **8**) complexes can be easily deprotonated with base ( $\text{NEt}_3$ ) to give the related acetylide  $\text{RuTp}(\text{C}\equiv\text{CR})\text{LL}'$  (**12**, **13**) derivatives, which were isolated in the solid state and characterized (Scheme 6).

Acetylide complexes can also be formed by reacting the chloro-complex **1a** with an excess of  $\text{Li}^+\text{C}\equiv\text{CR}^-$  in thf (Scheme 7), but in this case the yield is low due to the formation of byproducts. The chloro-complex also reacts with  $\text{SnCl}_2$  in  $\text{CH}_2\text{Cl}_2$  to give the trichlorostannyl  $[\text{Ru}(\text{SnCl}_3)\text{TpLL}']$  (**14**) complex, which was isolated as a yellow solid and characterized (Scheme 7).



Scheme 6.  $\text{L} = \text{P}(\text{OEt})_3$ ,  $\text{L}' = \text{PPh}_3$ ;  $\text{R} = \text{Ph}$  (**12**),  $\text{tBu}$  (**13**).



Scheme 7.  $\text{L} = \text{P}(\text{OEt})_3$ ,  $\text{L}' = \text{PPh}_3$ ;  $\text{R} = \text{Ph}$ .

Compound **14** is generated by insertion of  $\text{SnCl}_2$  into the  $\text{Ru}-\text{Cl}$  bond of the precursor **1a**. Such a process is well known and has been thoroughly studied due to the ability of the trichlorostannyl ligand to promote or modify the catalytic activity of transition metal complexes [24,25].

Good analytical data were obtained for complexes **12–14**, which are yellow solids stable in air and in a solution of common organic solvents, where they behave as non-electrolytes [13]. Infrared and NMR data (Tables 1 and 3) support the proposed formulation. In particular, the presence of the acetylide ligand in **12**, **13** is indicated by the medium-intensity  $\nu_{\text{C}\equiv\text{C}}$  band at  $2081\text{ cm}^{-1}$  (**12**) and at  $2091\text{ cm}^{-1}$  (**13**) observed in the IR spectra. Further support comes from the  $^{13}\text{C}$  spectra, which show the signals of the  $C_\alpha$  carbon atom of the acetylide as a multiplet at 110.4 ppm for **12** and at 99.6 ppm for **13**. In the latter complex, the singlet at 116.0 ppm is attributed to the  $C_\beta$  carbon resonance, while the signals at 33.4 and 29.9 ppm are due to the carbons of the  $\text{tBu}$  substituent. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra appear as a AB multiplet, in agreement with the geometry proposed in Scheme 5.

The presence of the  $\text{SnCl}_3$  ligand in the  $[\text{Ru}(\text{SnCl}_3)\text{TpLL}']$  (**14**) complex is confirmed by the  $^{119}\text{Sn}$  NMR spectra, which show a multiplet at  $-218$  ppm (from  $\text{SnMe}_4$ ) due to the coupling with the phosphorus nuclei of the phosphines. Taking into account that the  $^{31}\text{P}$  spectrum is a AB multiplet with the satellites due to the coupling of the phosphorus atoms with the NMR-active  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  nuclei, the multiplet of the  $^{119}\text{Sn}$  spectrum can be simulated using a ABM ( $M = ^{119}\text{Sn}$ ) model with the parameters reported in Table 1. On the basis of these data, a geometry of the type of Scheme 7 can reasonably be proposed for the trichlorostannyl derivative.

#### 4. Conclusions

An easy route for the introduction of phosphite ligands in the chemistry of classical and non-classical tris(pyrazolyl)borate ruthenium (II) hydride complexes has been achieved using  $\text{RuClTp}(\text{PPh}_3)_2$  as a precursor. Mixed-ligand  $\text{RuHTpLL}'$  hydrides and  $[\text{Ru}(\eta^2\text{-H}_2)\text{TpLL}']^+$  dihydrogen derivatives were prepared and information on the H–H distances of  $\eta^2\text{-H}_2$  complexes were obtained from  $T_1$  measurements and  $J_{\text{HD}}$  values. New tris(pyrazolyl)borate complexes containing vinylidene and allenylidene ligands of the  $[\text{RuTp}\{\text{C}=\text{C}(\text{H})\text{R}\}\text{LL}'\text{BPh}_4$  and  $[\text{RuTp}(\text{C}\equiv\text{C}(\text{R})\text{R}_2)\text{LL}']\text{BPh}_4$  type, as well as acetylide  $\text{Ru}(\text{C}\equiv\text{CR})\text{TpLL}'$  and trichlorostannyl  $\text{Ru}(\text{SnCl}_3)\text{TpLL}'$  derivatives, were also obtained using the dihydrogen complexes as a precursor.

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