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Hydride, dihydrogen, dinitrogen and related complexes of ruthenium containing the ligand hydrotris(pyrazolyl)borate. X-ray crystal structure of $[\{HB(pz)_3\}Ru(\eta^2\text{-}H_2)(dippe)][BPh_4]$ (dippe = 1,2-bis(diisopropylphosphino)ethane)

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Abstract

The complex $[\{HB(pz)_3\}RuCl(PPh_3)_2]$ reacts with one equivalent of dippe in toluene to yield $[\{HB(pz)_3\}RuCl(dippe)]$. This compound reacts with $NaBH_4$ in MeOH furnishing the monohydride $[\{HB(pz)_3\}RuH(dippe)]$, whereas $[\{HB(pz)_3\}RuH(PPh_3)_2]$ was obtained by reaction of $[RuHCl(PPh_3)_3]$ with $K[HB(pz)_3]$. Both monohydride complexes are protonated by $HBF_4 \cdot OEt_2$ at −80°C to give the corresponding dihydrogen adducts $[\{HB(pz)_3\}Ru(H_2)(dippe)]^+$ and $[\{HB(pz)_3\}Ru(H_2)(PPh_3)_2]^+$, as inferred from longitudinal relaxation time (T_1) and $^1J(H,D)$ measurements. The latter complex is unstable and decomposes at room temperature, but the former is a stable species which does not rearrange to the dihydride form when the temperature is raised. The X-ray crystal structure of $[\{HB(pz)_3\}Ru(H_2)(dippe)][BPh_4]$ has been determined. The dihydrogen ligand in this compound is labile, and readily replaced by a range of neutral donor molecules, yielding the corresponding complexes $[\{HB(pz)_3\}Ru(L)(dippe)][BPh_4]$ ($L = CO$, $CNBu^t$, Me_2CO, thf, N_2). There is also supporting evidence for the formation of a paramagnetic Ru^{III} methoxide complex, namely $[\{HB(pz)_3\}Ru(OMe)(dippe)][BPh_4]$. All compounds were characterized by IR, NMR and microanalysis.

Keywords: Crystal structures; Ruthenium complexes; Hydride complexes; Dihydrogen complexes; Dinitrogen complexes

1. Introduction

The use of the hydrotris(pyrazolyl)borate(1−) anion and its substituted derivatives as ligands in metal complexes was initially described by Trofimenko [1], who pointed out the analogies existing among these species and the η^5-cyclopentadienyl (Cp) or η^5-pentamethylcyclopentadienyl (Cp*) ligands [2]. All these are anionic, formally tridentate, six-electron donors which furnish complexes with analogue stoichiometries and structurally related [3]. However, there are also notable differences which condition the chemical properties of their respective complexes. In general, complexes of the type $[\{HB(pz)_3\}ML_n]$ are more stable than their analogues containing Cp or Cp*, derivatives existing with the hydrotris(pyrazolyl)borate ligand which have no known counterpart with Cp or Cp* [2,3]. In this sense, the extensive chemistry developed for half-sandwich ruthenium complexes of the type $[CpRuClP_2]$ (P_2 = two monodentate phosphines or one bidentate phosphine) [4] contrasts sharply with the scarcity of similar complexes containing hydrotris(pyrazolyl)borate. In fact, the chemistry of ruthenium complexes with poly(pyrazolyl)borate ligands is rather underdeveloped, and only recently has it started to attract increasing attention [5–8]. Complexes such as $[\{HB(pz)_3\}RuCl(PPh_3)_2]$ [6] and $[\{HB(pz)_3\}RuX(PPh_3)(CO)]$ (X = H, Cl) [8], formal homologues of $[CpRuCl(PPh_3)_2]$ and $[CpRuX(PPh_3)(CO)]$ (X = H, Cl), respectively [4], have been prepared by reaction of $[RuCl_2(PPh_3)_3]$ or $[RuHCl(CO)(PPh_3)_3]$ with $K[HB(pz)_3]$. We have recently prepared the complexes $[CpRuCl(dippe)]$ and $[Cp^*RuCl(dippe)]$ (dippe = 1,2-bis(diisopropylphosphino)ethane) [9], and studied their abilities to bind and activate a range of small molecules which include dihydrogen, dinitrogen and alkynes, among others [10,11]. We wanted to prepare related complexes having hydrotris(pyrazolyl)borate instead of Cp or Cp*, in order to estab-

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lish the effects on the chemical reactivity of the metal site towards small molecules, especially towards dihydrogen and dinitrogen. Here we present some of the results of our research on the chemistry of these hydrotris(pyrazolyl)-borate ruthenium derivatives, which parallels the studies made on the Cp and Cp* systems.

2. Experimental

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. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane [12], $K[HB(pz)_3]$ [13], $[\{HB(pz)_3\}RuCl(PPh_3)_2]$ [6] and $[RuHCl(PPh_3)_3]$ [14] were prepared according to the literature. IR spectra were recorded in Nujol mulls on a Perkin-Elmer Spectrum 1000 FTIR spectrophotometer. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz equipments. Chemical shifts are given in ppm from $SiMe_4$ (^1H and $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$). The phosphine protons for all the compounds appeared in the corresponding ^1H NMR spectra as a series of overlapping multiplets in the range 0.5–3 ppm, and were not assigned. Magnetic moment measurements were made at room temperature in solution by the Evans' method [15], and in the solid state using an Oxford Instruments Faraday balance with magnetic field spans up to 0.7 Tesla. Microanalyses were by the Servicios Científico-Técnicos, Universidad de Barcelona.

2.1. *$[\{HB(pz)_3\}RuCl(dippe)]$ (1)*

To $[\{HB(pz)_3\}RuCl(PPh_3)_2]$ (0.4 g, ~0.5 mmol) in toluene (20 ml), dippe (0.15 ml, 0.5 mmol) was added via syringe. The mixture was heated at 100°C for 45 min. During this time, a yellow, crystalline precipitate was formed gradually. The reaction mixture was cooled to room temperature, and then petroleum ether was added. The pale yellow precipitate was filtered off, washed with two portions of petroleum ether and dried in vacuo. Yield: 0.17 g, 55%. *Anal.* Found: C, 45.4; H, 7.18; N, 13.2. Calc. for $C_{23}H_{42}N_6BClP_2Ru$: C, 45.1; H, 6.91; N, 13.7%. IR: $\nu(BH)$ 2465 cm^{-1}. NMR ($CDCl_3$): ^1H δ 5.995 (t, 1H), 6.151 (t, 2H), 7.096 (d, 1H), 7.650 (d, 2H), 7.680 (d, 1H), 8.100 (d, 2H). $^{31}P\{^1H\}$ 79.1 s; $^{13}C\{^1H\}$ 18.4, 19.2, 19.7, 19.8 (s, $P(CH(CH_3)_2)$); 21.6 (t, $J(C,P)$ = 18.0 Hz, PCH_2); 25.7 (t, $J(C,P)$ = 8.5 Hz, $P(CH(CH_3)_2)$); 26.2 (t, $J(C,P)$ = 10.5 Hz, $P(CH(CH_3)_2)$); 104.8, 105.0, 134.4, 136.4, 144.5, 146.4 (s, $HB(C_3H_3N_2)_3$).

2.2. *$[\{HB(pz)_3\}RuH(dippe)]$ (2)*

A slurry of **1** (0.3 g, ~0.5 mmol) in MeOH (15 ml) was treated with an excess of solid $NaBH_4$. The mixture was heated smoothly using a water bath, until effervescence ceased and a pale yellow solution was obtained. This solution was taken to dryness, and the residue extracted with petroleum ether and centrifuged. Removal of the solvent afforded a pale yellow–green microcystalline product, which was recrystallized from petroleum ether. Yield: 0.25 g, 86%. *Anal.* Found: C, 47.5; H, 7.36; N, 14.5. Calc. for $C_{23}H_{43}N_6BP_2Ru$: C, 47.8; H, 7.45; N, 14.6. IR: $\nu(BH)$ 2463, $\nu(RuH)$ 1946 cm^{-1}. NMR (C_6D_6): ^1H δ −15.840 (t, $J(H,P)$ = 28.4 Hz, Ru*H*); 5.930 (t, 2H), 6.040 (t, 1H), 7.401 (d, 1H), 7.590 (d, 2H), 7.704 (d, 1H), 7.882 (d, 2H); $^{31}P\{^1H\}$ 98.0 s; $^{13}C\{^1H\}$ 18.9, 19.0, 19.7, 21.8 (s, $P(CH(CH_3)_2)$); 23.4 (t, $J(C,P)$ = Hz, PCH_2); 26.6 (m, $P(CH(CH_3)_2)$); 27.6 (m, $P(CH(CH_3)_2)$); 104.2, 104.4, 134.4, 134.6, 144.5, 145.8 (s, $HB(C_3H_3N_2)_3$).

2.3. *$[\{HB(pz)_3\}RuH(PPh_3)_2]$ (3)*

To a suspension of $[RuHCl(PPh_3)_3]$ (0.52 g, 0.56 mmol) in MeOH (20 ml), solid $K[HB(pz)_3]$ (0.14 g, 0.56 mmol) was added. The mixture was stirred for 30 min at 40–50°C (warm water bath). During this time, the initial purple color of the mixture changed to yellow. The yellow precipitate was filtered off, washed with ethanol and dried in vacuo. Yield: essentially quantitative. *Anal.* Found: C, 64.1; H, 5.02; N, 9.6. Calc. for $C_{45}H_{41}N_6BP_2Ru$: C, 64.4; H, 4.89; N, 10.0%. IR: $\nu(BH)$ 2473, $\nu(RuH)$ 1936 cm^{-1}. NMR (C_6D_6): ^1H δ −13.613 (t, $J(H,P)$ = 27.2 Hz, Ru*H*); 5.159 (t, 2H), 5.646 (t, 1H), 6.806 (d, 2H), 6.857 (d, 1H), 7.095 (d, 2H), 7.488 (d, 1H); 6.594, 7.198 (m, $P(C_6H_5)_3$); $^{31}P\{^1H\}$ 68.6 s; $^{13}C\{^1H\}$ 104.5, 105.0, 128.4, 134.9, 142.5, 146.9 (s, $HB(C_3H_3N_2)_3$); 127.5, 128.4, 139.6 (s, $P(C_6H_5)$).

2.4. *$[\{HB(pz)_3\}Ru(H_2)(dippe)][BPh_4]$ (4)*

To a solution of **2** (0.2 g, ~0.35 mmol) in diethyl ether at −80°C, an excess of $HBF_4\cdot OEt_2$ was added. A white precipitate was formed almost immediately, which became sticky and oily when the mixture was warmed at room temperature. Then, the solvent was removed using reduced pressure, and the residue was dissolved in MeOH at −80°C. Addition of an excess of solid $NaBPh_4$ to the mixture afforded a white precipitate. The suspension was warmed to room temperature with continuous stirring. Then the product was filtered off, washed with ethanol and petroleum ether and dried in vacuo. It was recrystallized from an H_2-saturated mixture CH_2Cl_2/EtOH. The isotopomer $[\{HB(pz)_3\}Ru(HD)(dippe)][BPh_4]$ was obtained in a similar fashion, using $HBF_4\cdot OEt_2/D_2O$. Yield: 0.28 g, 88%. *Anal.* Found: C, 62.9; H, 7.22; N, 9.4. Calc. for $C_{47}H_{64}N_6BP_2Ru$: C, 62.9; H, 7.14; N, 9.37%. IR: $\nu(BH)$ 2506 cm^{-1}. NMR (CD_2Cl_2, 223 K): ^1H δ −10.250 (s br, T_1(223 K) = 14 ms, $Ru(H_2)$); 6.240 (t, 2H), 6.340 (t, 1H), 7.481 (d, 1H), 7.742 (d, 2H), 7.770 (d, 2H), 7.861 (d, 2H); $^{31}P\{^1H\}$ 82.2 s; $^{13}C\{^1H\}$ 18.0, 18.6, 19.8, 21.3 (s, $P(CH(CH_3)_2)$); 23.3 (t, $J(C,P)$ = 10.5 Hz, PCH_2); 26.2 (m, $P(CH(CH_3)_2)$); 26.3 (m,

$P(\mathit{C}H(CH_3)_2)$); 106.7, 107.1, 136.7, 137.7, 145.8, 146.3 (s, $HB(\mathit{C}_3H_3N_2)_3$).

2.5. $[\{HB(pz)_3\}Ru(H_2)(PPh_3)_2][BF_4]$ (5)

This compound was obtained and characterized in solution by protonation of the monohydride **3** in acetone-d_6 or CD_2Cl_2 at −80°C using a slight excess of $HBF_4 \cdot OEt_2$. The isotopomer $[\{HB(pz)_3\}Ru(HD)(PPh_3)_2][BF_4]$ was obtained in a similar fashion, using $HBF_4 \cdot OEt_2/D_2O$. Yield: quantitative. NMR (acetone-d_6, 223 K): ^1H δ −8.38 (s, br, $Ru(\mathit{H}_2)$, T_1 (400 MHz, 223 K): 19 ms); 5.526 (t, 1H), 5.729 (t, 2H), 5.935 (d, 1H), 6.286 (d, 2H), 7.630 (d, 2H), 7.763 (d, 1H); $^{31}P\{^1H\}$ 45.0 s.

2.6. $[\{HB(pz)_3\}Ru(CO)(dippe)][BPh_4]$ (6)

CO was bubbled through a solution of **5** in dichloromethane, to yield an orange solution. Addition of EtOH, concentration and cooling to −20°C afforded mauve microcrystals, which were filtered off, washed with petroleum ether, and dried in vacuo. Yield: quantitative. *Anal.* Found: C, 62.3; H, 6.84; N, 9.0. Calc. for $C_{48}H_{62}N_6BOP_2Ru$: C, 62.3; H, 6.76; N, 9.1%. IR: ν(BH) 2507, $\nu(C{\equiv}O)$ 1973, 1929(sh) cm^{-1}. NMR ($CDCl_3$): ^1H δ 6.235 (t, 2H), 6.349 (t, 1H), 7.343 (d, 1H), 7.683 (d, 2H), 7.748 (d, 2H), 7.792 (d, 1H); $^{31}P\{^1H\}$ 73.1 s; $^{13}C\{^1H\}$ 18.0, 18.3, 19.3, 19.9 (s, $P(CH(\mathit{C}H_3)_2)$); 21.4 (m, $P\mathit{C}H_2$); 26.4 (m, $P(\mathit{C}H(CH_3)_2)$); 28.8 (m, $P(\mathit{C}H(CH_3)_2)$); 106.7, 136.5, 137.4, 145.0, 145.2 (s, $HB(\mathit{C}_3H_3N_2)_3$); 203.1 (t, $J(C,P) = 14.5$ Hz, $\mathit{C}O$).

2.7. $[\{HB(pz)_3\}Ru(CNBu^t)(dippe)][BPh_4]$ (7)

To a dichloromethane solution of **5**, an excess of $CNBu^t$ was added, yielding an orange–brown solution. Addition of EtOH, concentration and cooling to −20°C afforded pale pink microcrystals, wich were filtered off, washed with petroleum ether, and dried. Yield: quantitative. *Anal.* Found: C, 63.4; H, 7.30; N, 10.0. Calc. for $C_{52}H_{71}N_7BP_2Ru$: C, 63.7; H, 7.31; N, 10.0%. IR: ν(BH) 2465; $\nu(C{\equiv}N)$ 2126 cm^{-1}. NMR ($CDCl_3$): ^1H δ 1.362 (s, $CNC(C\mathit{H}_3)_3$); 6.203 (t, 2H), 6.249 (t, 1H), 7.320 (d, 1H), 7.677 (d, 2H), 7.723 (d, 2H), 7.764 (d, 1H); $^{31}P\{^1H\}$ 77.6 s; $^{13}C\{^1H\}$ 18.1, 18.6, 19.5, 20.0 (s, $P(CH(\mathit{C}H_3)_2)$); 21.5 (m, $P\mathit{C}H_2$); 26.3 (m, $P(\mathit{C}H(CH_3)_2)$); 28.9 (m, $P(\mathit{C}H(CH_3)_2)$); 106.1, 125.5, 135.9, 137.0, 144.3, 144.9 (s, $HB(\mathit{C}_3H_3N_2)_3$); 30.8 (s, $CNC(\mathit{C}H_3)_3$); 58.0 (s, $CN\mathit{C}(CH_3)_3$); $\mathit{C}NC(CH_3)_3$) not observed.

2.8. $[\{HB(pz)_3\}Ru(Me_2CO)(dippe)][BPh_4]$ (8)

An acetone solution of **1** (0.1 g, ~0.16 mmol) under Ar, was treated with the stoichiometric amount of $AgBF_4$. The mixture was stirred for 10 min at room temperature. Then it was centrifuged and the solvent removed in vacuo. The residue was extracted with EtOH, and an excess of solid $NaBPh_4$ was then added to the solution. A reddish precipitate was obtained, which was filtered, washed with EtOH and petroleum ether, and dried in vacuo. Yield: 0.1 g, 66%. *Anal.* Found: C, 62.8; H, 7.06; N, 8.5. Calc. for $C_{50}H_{68}N_6BOP_2Ru$: C, 63.0; H, 7.14; N, 8.8%. IR: ν(BH) 2498, $\nu(C{=}O)$ 1650 cm^{-1}. NMR (CD_3COCD_3): ^1H δ 6.269 (t, 1H), 6.363 (t, 2H), 7.228 (d, 1H), 7.352 (d, 2H), 7.842 (d, 1H), 7.891 (d, 2H); signals for coordinated $(CH_3)_2CO$ not observed; $^{31}P\{^1H\}$ 78.5 s.

2.9. $[\{HB(pz)_3\}Ru(thf)(dippe)][BPh_4]$ (9)

This compound was formed when compound **4** was dissolved in thf under argon, yielding an orange solution. It appears mixed in a 1:1 ratio with the dihydrogen complex at room temperature, but it can be converted quantitatively by refluxing under Ar. This material was characterized only in solution. NMR (thf-d_8): ^1H δ 6.043 (t, 1H), 6.328 (t, 2H), 7.105 (d, 1H), 7.795 (d, 1H), 7.885 (d, 2H), 7.948 (d, 2H); signals for coordinated thf not observed; $^{31}P\{^1H\}$: 80.9 s.

2.10. $[\{HB(pz)_3\}Ru(OMe)(dippe)][BPh_4]$ (10)

A solution of **4** (0.1 g, 0.11 mmol) in thf was refluxed under argon for some minutes. Then the solvent was removed in vacuo and the residue treated with MeOH. A deep red solid, together with a red solution, was obtained. The mixture was heated until all the solid was dissolved. Slow cooling at room temperature afforded nice red crystals. Yield: 0.07 g, 69%. *Anal.* Found: C, 62.2; H, 7.15; N, 9.1. Calc. for $C_{48}H_{65}N_6B_2OP_2Ru$: C, 62.2; H, 7.02; N, 9.1%. IR: ν(BH) 2499 cm^{-1}. $\mu_{eff} = 2.1\ \mu_B$ (CH_2Cl_2 solution at 298 K, Evans' method); $\mu_{eff} = 1.7\ \mu_B$ (solid at 298 K, Faraday balance).

2.11. $[\{HB(pz)_3\}Ru(N_2)(dippe)][BPh_4]$ (11)

A solution of **1** (0.1 g, ~0.16 mmol) in thf under dinitrogen was treated with $AgBF_4$ (~0.16 mmol). A color change from yellow to red, and then to orange was observed, together with the concomitant formation of a precipitate of AgCl. The mixture was stirred for 10 min. Then it was centrifuged and the solvent removed in vacuo. The residue was dissolved in EtOH, and a red solution was obtained. Addition of an excess of solid $NaBPh_4$ yielded a red precipitate, which was filtered off, washed with EtOH and petroleum ether, and dried in vacuo. Yield: 0.1 g, 68%. *Anal.* Found: C, 60.9; H, 6.69; N, 11.3. Calc. for $C_{47}H_{62}N_8B_2P_2Ru$: C, 61.1; H, 6.72; N, 12.1%. IR: ν(BH) 2507, $\nu(N{\equiv}N)$ 2165 cm^{-1}. NMR (CD_2Cl_2): ^1H δ 6.269 (t, 1H), 6.363 (t, 2H), 7.228 (d, 1H), 7.352 (d, 2H), 7.842 (d, 1H), 7.891 (d, 2H); $^{31}P\{^1H\}$ 74.0 s; $^{13}C\{^1H\}$ 18.4, 19.3, 19.8, 19.9 (s, $P(CH(\mathit{C}H_3)_2)$); 21.7 (t, $J(C,P) = 18.8$ Hz, $P\mathit{C}H_2$); 26.16 (m, $P(\mathit{C}H(CH_3)_2)$); 27.6 (m, $P(\mathit{C}H(CH_3)_2)$); 105.1, 122.1, 126.0, 136.5, 144.8, 147.0 (s, $HB(\mathit{C}_3H_3N_2)_3$).

2.12. Experimental data for the X-ray crystal structure determination of **4**

A summary of crystallographic data for compound **4** is given in Table 1. X-ray measurements were made on a colorless crystal of dimensions 0.24×0.14×0.35 mm, which was mounted onto a glass fiber, and transferred to an AFC6S-Rigaku automatic diffractometer, using Mo Kα graphite-monochromated radiation. Cell parameters were determined from the settings of 25 high-angle reflections. Data were collected by the ω scan method. Lorentz, polarization, and absorption (ψ-scan method) corrections were applied. The transmission factors ranged from 0.80 to 1.00. Three standard reflections were intensity controlled, in order to establish a decay correction, which was found to be negligible. 7464 reflections were collected, 7120 being unique ($R_{int}=0.092$). 4055 reflections having $I>2\sigma(I)$ were used for structure resolution. All calculations for data reduction, structure solution and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN [16] software system and ORTEP [17] for plotting. The structure was solved by the Patterson method, and anisotropically refined by full-matrix least-squares methods for all non-hydrogen atoms. The hydrogen atoms H(1) and H(2) of the dihydrogen ligand were localized in a successive difference Fourier map using low-angle reflections (upper limit $2\theta=28°$, 1213 reflections with $I>2\sigma(I)$). The peak heights were 0.87 and 0.53 e Å^{-3}. Their positions were allowed to refine with fixed isotropic thermal parameters except in the last cycle. The boron-attached hydrogen atom H(3) was located in a regular difference Fourier map and not refined. All other hydrogen atoms were included at idealized positions and not refined. Maximum and minimum peaks in the final difference Fourier maps were +1.06 and −0.61 e Å^{-3}. Atomic coordinates and B_{eq} values, and selected bond lengths and angles are listed in Tables 2 and 3, respectively.

Table 1
Summary of data for the crystal structure analysis of **4**

Compound	**4**
Formula	$C_{47}H_{64}N_6B_2P_2Ru$
Formula weight	897.70
Crystal size (mm)	0.24×0.14×0.35
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Cell parameters	
a (Å)	10.592(6)
b (Å)	27.323(5)
c (Å)	16.238(4)
β (°)	97.72(3)
Volume (Å^3)	4657(5)
Z	4
ρ_{calc} (g cm^{-3})	1.280
T (K)	290
λ (Å)	0.71069 (Mo Kα)
μ (cm^{-1})	4.34 (Mo Kα)
Absorption correction	ψ-method
Transmision factors	0.80–1.00
F(000)	1888
Scan speed (ω) (° min^{-1})	8
2θ Interval (°)	$5<2\theta<50$
Collected reflections	7464
Unique reflections	7120 ($R_{int}=0.092$)
Observed reflections ($I>2\sigma(I)$)	4055
No. parameters	523
Reflection/parameter ratio	7.75
R [a]	0.057
R_w ($w=\sigma_F^{-2}$) [b]	0.067
Maximum Δ/σ in final cycle	0.28
GOF	1.74

[a] $R=\Sigma\|F_o\|-\|F_c\|/\Sigma\|F_o\|$.
[b] $R_w=(\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

Table 2
Atomic fractional coordinates and B_{eq} values for [{HB(pz)$_3$}Ru(H$_2$)(dippe)][BPh$_4$]

Atom	x	y	z	B_{eq}
Ru(1)	0.65461(6)	0.82830(3)	0.76563(4)	2.65(3)
P(1)	0.6702(2)	0.89962(9)	0.8438(1)	3.4(1)
P(2)	0.7986(2)	0.86560(9)	0.6900(1)	3.2(1)
N(11)	0.4980(7)	0.7436(3)	0.6773(4)	3.8(4)
N(12)	0.6213(7)	0.7598(2)	0.6964(4)	3.4(3)
N(21)	0.4093(6)	0.7791(3)	0.7982(4)	3.5(3)
N(22)	0.5214(6)	0.7954(3)	0.8377(4)	3.6(4)
N(31)	0.3946(6)	0.8259(3)	0.6657(4)	3.4(3)
N(32)	0.4988(6)	0.8546(3)	0.6843(4)	3.2(3)
C(1)	0.5198(8)	0.9349(3)	0.8333(6)	4.0(4)
C(2)	0.528(1)	0.9904(4)	0.837(1)	8.6(8)
C(3)	0.428(1)	0.9158(5)	0.8887(8)	7.8(7)
C(4)	0.7172(9)	0.8948(4)	0.9576(6)	5.2(5)
C(5)	0.830(1)	0.8629(5)	0.9831(6)	6.4(6)
C(6)	0.741(1)	0.9444(5)	1.0003(8)	9.5(8)
C(7)	0.793(1)	0.9382(4)	0.8098(7)	5.7(6)
C(8)	0.8100(8)	0.9305(3)	0.7201(6)	4.2(5)
C(9)	0.755(1)	0.8707(4)	0.5764(6)	4.8(5)
C(10)	0.696(1)	0.8262(4)	0.5328(6)	5.5(5)
C(11)	0.498(1)	0.6983(4)	0.6490(6)	4.5(5)
C(12)	0.621(1)	0.6835(4)	0.6473(6)	5.1(5)
C(13)	0.6942(9)	0.7230(4)	0.6761(6)	4.2(5)
C(14)	0.858(1)	0.8931(4)	0.5309(6)	5.9(6)
C(15)	0.9664(8)	0.8455(3)	0.7059(6)	3.9(4)
C(16)	0.9848(9)	0.7934(4)	0.6768(7)	6.1(6)
C(17)	1.0328(8)	0.8520(4)	0.7919(7)	5.4(5)
C(18)	0.0615(8)	0.8571(3)	0.3366(5)	3.0(4)
C(19)	0.1349(8)	0.8316(3)	0.3987(5)	3.6(4)
C(20)	0.085(1)	0.7913(3)	0.4387(5)	4.1(5)
C(21)	0.344(1)	0.7574(4)	0.8548(7)	5.1(5)
C(22)	0.412(1)	0.7613(4)	0.9303(6)	5.2(5)
C(23)	0.523(1)	0.7862(4)	0.9184(6)	4.6(5)
C(24)	−0.039(1)	0.7793(3)	0.4207(6)	4.2(5)
C(25)	−0.1157(9)	0.8044(4)	0.3610(6)	4.4(5)
C(26)	−0.0655(9)	0.8434(3)	0.3195(5)	3.8(4)
C(27)	0.1326(8)	0.8823(3)	0.1900(5)	3.1(4)
C(28)	0.189(1)	0.9116(4)	0.1348(6)	5.2(5)
C(29)	0.208(1)	0.8970(5)	0.0562(7)	6.2(6)
C(30)	0.175(1)	0.8506(4)	0.0297(6)	4.9(5)
C(31)	0.3096(9)	0.8478(4)	0.6086(6)	4.8(5)
C(32)	0.357(1)	0.8921(4)	0.5888(6)	4.6(5)
C(33)	0.4727(8)	0.8949(3)	0.6377(6)	3.6(4)
C(34)	0.120(1)	0.8204(4)	0.0807(6)	5.1(5)

(*continued*)

Table 2 (*continued*)

Atom	x	y	z	B_{eq}
C(35)	0.0987(8)	0.8361(3)	0.1588(5)	3.9(4)
C(36)	0.2621(8)	0.9173(4)	0.3269(5)	3.9(4)
C(37)	0.286(1)	0.9596(3)	0.3372(6)	4.2(5)
C(38)	0.409(1)	0.9727(4)	0.4070(7)	6.8(7)
C(39)	0.511(1)	0.9460(5)	0.3938(8)	7.4(8)
C(40)	0.492(1)	0.9042(6)	0.3436(8)	7.4(8)
C(41)	0.368(1)	0.8919(4)	0.3130(7)	5.8(6)
C(42)	0.0171(8)	0.9469(3)	0.2810(6)	3.4(4)
C(43)	−0.022(1)	0.9642(3)	0.3546(6)	4.8(5)
C(44)	−0.110(1)	1.0015(4)	0.3557(8)	5.7(6)
C(45)	−0.161(1)	1.0241(4)	0.2829(9)	5.7(6)
C(46)	−0.124(1)	1.0085(4)	0.2115(7)	5.2(6)
C(47)	−0.0388(9)	0.9700(3)	0.2111(6)	4.1(5)
B(1)	0.388(1)	0.7742(4)	0.7032(7)	3.6(5)
B(2)	0.119(1)	0.9012(4)	0.2844(6)	3.1(4)
H(1)	0.7717	0.8189	0.7946	3.2
H(2)	0.7447	0.8075	0.8275	3.2
H(3)	0.2842	0.7684	0.6966	4.3
H(4)	0.4801	0.9279	0.7787	4.9
H(5)	0.5876	1.0013	0.8010	10.3
H(6)	0.5567	1.0008	0.8917	10.3
H(7)	0.4473	1.0043	0.8182	10.3
H(8)	0.3455	0.9287	0.8711	9.5
H(9)	0.4553	0.9253	0.9444	9.5
H(10)	0.4248	0.8810	0.8854	9.5
H(11)	0.6474	0.8803	0.9797	6.2
H(12)	0.8166	0.8318	0.9572	7.6
H(13)	0.8415	0.8589	1.0417	7.6
H(14)	0.9039	0.8776	0.9664	7.6
H(15)	0.8153	0.9587	0.9839	11.4
H(16)	0.7524	0.9399	1.0588	11.4
H(17)	0.6699	0.9651	0.9847	11.4
H(18)	0.8714	0.9312	0.8434	6.9
H(19)	0.7707	0.9714	0.8172	6.9
H(20)	0.7457	0.9483	0.6863	5.0
H(21)	0.8914	0.9425	0.7117	5.0
H(22)	0.6888	0.8943	0.5701	5.7
H(23)	0.6580	0.8350	0.4783	6.6
H(24)	0.6320	0.8135	0.5628	6.6
H(25)	0.7592	0.8021	0.5292	6.6
H(26)	0.4243	0.6792	0.6320	5.4
H(27)	0.6497	0.6525	0.6302	6.1
H(28)	0.7845	0.7240	0.6810	5.1
H(29)	0.9234	0.8696	0.5269	7.2
H(30)	0.8939	0.9209	0.5609	7.2
H(31)	0.8220	0.9029	0.4767	7.2
H(32)	1.0097	0.8661	0.6717	4.6
H(33)	0.9418	0.7896	0.6219	7.4
H(34)	0.9509	0.7711	0.7128	7.4
H(35)	1.0731	0.7872	0.6771	7.4
H(36)	1.1213	0.8458	0.7927	6.5
H(37)	0.9987	0.8298	0.8281	6.5
H(38)	1.0211	0.8846	0.8098	6.5

Table 3
Selected bond distances (Å) and angles (°) for [{HB(pz)$_3$}Ru(H$_2$)(dippe)][BPh$_4$]

Intramolecular distances			
Ru(1)–P(1)	2.320(3)	Ru(1)–H(1)	1.29
Ru(1)–P(2)	2.319(2)	Ru(1)–H(2)	1.41
Ru(1)–N(12)	2.187(7)	H(1)–H(2)	0.71
Ru(1)–N(22)	2.147(7)		
Ru(1)–N(32)	2.098(7)		
Intramolecular bond angles			
P(1)–Ru(1)–P(2)	85.26(9)	P(2)–Ru(1)–N(12)	100.1(2)
P(1)–Ru(1)–N(12)	174.2(2)	P(2)–Ru(1)–N(22)	178.5(2)
P(1)–Ru(1)–N(22)	93.3(2)	P(2)–Ru(1)–N(32)	91.9(2)
P(1)–Ru(1)–N(32)	92.8(2)	P(2)–Ru(1)–H(1)	67.22
P(1)–Ru(1)–H(1)	88.47	P(2)–Ru(1)–H(2)	97.16
P(1)–Ru(1)–H(2)	87.53		

E.s.d.s in the least significant figure are given in parentheses.

3. Results and discussion

The complex [{HB(pz)$_3$}RuCl(dippe)] (1) has been obtained by thermal displacement of PPh$_3$ by dippe in toluene, a synthetic procedure which has been widely used for the preparation of half-sandwich ruthenium derivatives of the type [CpRuCl(diphos)] starting from [CpRuCl(PPh$_3$)$_2$] [4,9]. 1 is an air stable, pale yellow crystalline material which precipitates from the reaction mixture upon addition of petroleum ether and cooling. It can be easily separated from the free PPh$_3$ formed during the reaction by direct filtration and washing with petroleum ether, the use of column chromatography being not necessary for achieving separation, at variance with the synthetic procedure for the preparation of the related derivative [CpRuCl(dippe)] [9]. The IR spectrum of 1 displays one characteristic medium intensity band at 2465 cm^{-1} attributable to the ν(BH) stretching of the HB(pz)$_3$ ligand. This band is present in the IR spectrum of all compounds prepared in this work. The ^{1}H NMR spectrum of 1 consists of a series of multiplets in the range 0.5–3.0 ppm, which correspond to the protons of the dippe ligand, these being not assigned. Apart from these, six separate resonances are observed between 6.0 and 8.1 ppm, attributable to the protons of the pyrazol rings of the HB(pz)$_3$ ligand. Each of the protons of a pyrazol ring in an HB(pz)$_3$ group has a different chemical environment, being therefore nonequivalent to each other. Consistent with this, coupling among these protons is observed in the ^{1}H NMR spectrum, but the coupling constants J(H,H) are usually small, so this coupling is not always resolved. The presence in the spectrum of two sets of three signals each, one of the sets being of double integrated intensity than the other, suggests the presence of two equivalent pyrazol rings, plus another one which is non-equivalent. This pattern has been previously observed for other hydrotris(pyrazolyl)borato complexes of ruthenium such as [{HB(pz)$_3$}RuCl(COD)] (COD = 1,5-cyclooctadiene) [5b,18], [{HB(pz)$_3$}RuCl(tht)$_2$] (tht = tetrahydrothiophene) [18] or [{HB(pz)$_3$}RuCl(PPh$_3$)$_2$] [6], being consistent with an octahedral structure, analogous to that found by X-ray crystallography for the parent complex [{HB(pz)$_3$}RuCl(PPh$_3$)$_2$] [6], in which two of the pyrazol rings are *trans* to the phosphorus atoms of the bidentate dippe ligand, the other being *trans* to the chloride. The equivalence of the phospsorus atoms in this structure is supported by the presence of one singlet in the ^{31}P{^{1}H} NMR spectrum. The

$^{13}C\{^1H\}$ NMR spectrum of **1** shows seven resonances for the carbon atoms of the dippe ligand, a pattern identical to that shown by half-sandwich complexes containing dippe such as [CpMCl(dippe)] or [Cp*MCl(dippe)] (M = Fe [19], Ru [9]), plus six signals in the range 104.0–147.0 ppm corresponding to the carbon atoms of the pyrazol rings. The connectivity between these and their corresponding proton resonances was determined by a 2D-HETCOR NMR experiment. The spectral features of the $HB(pz)_3$ and the dippe ligands in **1** are common to most compounds described in this work, and these will not be discussed in detail again.

1 reacts with $NaBH_4$ in MeOH furnishing the neutral monohydride complex $[\{HB(pz)_3\}RuH(dippe)]$ (**2**) as a pale yellow, air-sensitive material, soluble in non-polar solvents, which reacts slowly with chlorinated solvents to yield **1**. The IR spectrum of **2** displays one broad band at 1946 cm^{-1} assigned to $\nu(RuH)$, whereas the hydride resonance appears in the ^1H NMR spectrum as a high field triplet at −15.84 ppm, due to coupling to two equivalent phosphorus atoms. These data, together with $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy, are in support of an octahedral structure, analogous to that proposed for compound **1**, in which the chloride ligand has been replaced by one hydride. We have also prepared the related monohydride complex $[\{HB(pz)_3\}RuH(PPh_3)_2]$ (**3**) by direct reaction of $[RuHCl(PPh_3)_3]$ with $K[HB(pz)_3]$ in MeOH, a procedure equivalent to that used for the preparation of the hydride $[\{HB(pz)_3\}RuH(CO)(PPh_3)]$ [8]. The spectral properties of **3** are very similar to those of **2**, including the presence of a broad $\nu(RuH)$ band in the IR spectrum, and of one high-field triplet signal in the ^1H NMR spectrum, corresponding to the hydride. Again, an octahedral structure is assumed for this derivative.

Protonation of neutral hydrides of the type $[CpRuHP_2]$ or $[Cp^*RuHP_2]$ has proven to be an effective procedure for the preparation of cationic Ru^{II} dihydrogen complexes, as well as for Ru^{IV} dihydrides [20,21]. In analogous fashion, the monohydrides **3** and **4** are protonated by $HBF_4 \cdot OEt_2$ at −80°C to yield the cationic dihydrogen complexes $[\{HB(pz)_3\}Ru(H_2)(dippe)]^+$ and $[\{HB(pz)_3\}Ru(H_2)(PPh_3)_2]^+$, respectively. The dippe complex was isolated as the tetraphenylborate salt $[\{HB(pz)_3\}Ru(H_2)(dippe)][BPh_4]$ (**4**). This compound can be deprotonated using a strong base such as $KOBu^t$, to yield the monohydride **3** in essentially quantitative yields. $[\{HB(pz)_3\}Ru(H_2)(PPh_3)_2][BF_4]$ (**5**) was only obtained and characterized in solution at low temperature. The formulation of **4** and **5** as 'non-classical' hydrides was established based upon longitudinal relaxation time (T_1) measurements for the dihydrogen resonance in the ^1H NMR spectra, and by the values of the $^1J(H,D)$ coupling constants in the isotopomers $[\{HB(pz)_3\}Ru(HD)(dippe)]^+$ and $[\{HB(pz)_3\}Ru(HD)(PPh_3)_2]^+$. Thus, both **4** and **5** exhibit one broad high-field resonance attributable to the coordinated dihydrogen molecule, these having short T_1 values, 14 ms for **4** at −50°C, and 19 ms for **5** at −40°C (CD_2Cl_2, 400 MHz), typical for dihydrogen complexes according to the literature [22,23]. The $^1J(H,D)$ coupling constants are close to 30 Hz for both isotopomers of **4** and **5**, being also in the range expected for molecular hydrogen complexes.

It has been possible to determine the X-ray crystal structure of compound **4**. A view of the cation $[\{HB(pz)_3\}Ru(H_2)(dippe)]^+$ is shown in Fig. 1. Fractional atomic coordinates and B_{eq}, and selected bond lengths and angles are listed in Tables 2 and 3, respectively. The coordination around the Ru atom is distorted octahedral, very similar to that found in $[\{HB(pz)_3\}RuCl(PPh_3)_2]$ [6]. The pyrazolyl rings are planar, with mean deviations of 0.007 Å, but the dihedral angles between these planes are irregular, having the values 98.2, 125.5 and 136.0°, respectively, instead of the ideal 120°. The dihydrogen ligand was located in a low-angle sucessive difference Fourier map. It appears attached to the metal in the side-on manner, as expected, although the dimensions obtained for this ligand may be subject to considerable inaccuracy and, therefore, they must be regarded with caution, given the uncertainty in the position of hydrogen atoms determined by X-ray crystallography. Bearing this in mind, the H(1) and H(2) atoms appear at 1.29 and 1.41 Å, respectively, from the Ru atom, and 0.71 Å apart. Whereas the Ru–H(2) bond distance is reasonable, and similar to that found by X-ray crystallography in the ruthenium–dihydrogen complex $[Ru(H_2)(C{\equiv}CPh)(dippe)_2][BPh_4]$ (1.5 Å) [24], the Ru–H(1) and H(1)–H(2) separations are rather short. In fact, the H(1)–H(2) bond length is essentially identical to that in the free H_2 molecule (0.74 Å), and consistent with the NMR data which point to a dihydrogen rather than a dihydride complex. Very short H–H distances have been also found for other dihydrogen complexes by X-ray crystallography, i.e. 0.75(16) Å in the complex $[W(H_2)(CO)_3(P^iPr_3)_2]$ [25], although this separation has shown to be larger (0.84 Å) by more accurate neutron diffraction studies

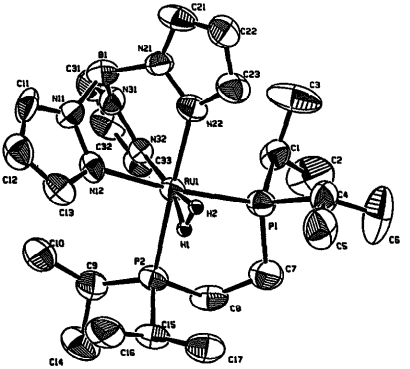

Fig. 1. ORTEP drawing of the cation $[\{HB(pz)_3\}Ru(H_2)(dippe)]^+$ with 50% probability thermal ellipsoids. Hydrogen atoms, except hydrides, are omitted.

[26]. Most dihydrogen complexes examined by neutron diffraction have H–H bond distances in the range 0.8–1.0 Å [22]. The remaining dimensions in the [{HB(pz)$_3$}]$^-$ and dippe ligands, as well as in the tetraphenylborate anion, are in the expected range, being unexceptional. This is the first structural report of a tris(pyrazolyl)borate ruthenium–dihydrogen complex. In fact, tris(pyrazolyl)borate ruthenium–dihydrogen complexes, such as [{HB(pz)$_3$}RuH(H$_2$)(PCy$_3$)] [7] or [{HB(3,5-Me$_2$pz)$_3$}RuH(H$_2$)$_2$] [27], have been prepared only recently. At variance with the complexes [CpRu(H$_2$)(dippe)]$^+$ and [Cp*Ru(H$_2$)(dippe)]$^+$, which are stable only at low temperature and rearrange to their dihydride tautomers when the temperature is raised, complex **4** is stable up to 55°C in thf-d$_8$ under H$_2$, and its dihydride tautomer, namely [{HB(pz)$_3$}RuH$_2$(dippe)]$^+$, has not been detected so far. This could be attributed to the fact that the ligand [{HB(pz)$_3$}]$^-$ favors six-coordinate complexes [2,3], such as **4**, over seven-coordinate species, such as the dihydride isomer. However, it could also happen that the metal center in complex **4** was not electron-rich enough to achieve homolytic dihydrogen splitting, at difference with the {[CpRu(dippe)]$^+$} or {[Cp*Ru(dippe)]$^+$} moieties. In contrast with compound **4**, the dihydrogen complex **5** decomposes when the temperature is raised, yielding an uncharacterized mixture of hydride-containing species, as inferred from NMR spectroscopy. All attempts to isolate **5** as a solid were unsuccessful.

The dihydrogen ligand in **4** is very labile, being replaced by a range of neutral donors. Thus, reaction with CO or CNBu^t affords [{HB(pz)$_3$}Ru(CO)(dippe)][BPh$_4$] (**6**) and [{HB(pz)$_3$}Ru(CNBu^t)(dippe)][BPh$_4$] (**7**), respectively. These crystalline, air-stable complexes have octahedral structures, as inferred from NMR data, and display one strong ν(CO) or ν(CN) band in their respective IR spectra. The value of ν(CO) in **6** is a qualitative measure of the electron density at the metal, and it can be used as reference for comparing with the related derivatives [CpRu(CO)(dippe)][BPh$_4$] and [Cp*Ru(CO)(dippe)][BPh$_4$]. The value of 1973 cm^{-1} for ν(CO) in **6** is greater than for the Cp and Cp* complexes (1959 and 1926 cm^{-1}, respectively), but it remains of the same order, suggesting that back-bonding from the metal occurs to a similar extent in all these complexes, especially in **6** and in its Cp analogue. CNBu^t is known to act mainly as a σ-donor, the value for ν(CN) in **7** being similar to that found for other tris(pyrazolyl)borate ruthenium–isocyanide complexes [8].

When **4** is dissolved in acetone-d$_6$ under Ar, the signal corresponding to the dihydrogen complex disappears from the ^{31}P{^{1}H} NMR spectrum, being replaced by a new signal at 78.5 ppm. Something similar takes place when the solvent is thf-d$_8$. These changes in the spectra have been interpreted in terms of substitution of coordinated dihydrogen by a solvent molecule, to yield the corresponding adducts [{HB(pz)$_3$}Ru(L)(dippe)][BPh$_4$] (L = Me$_2$CO (**8**) or thf (**9**)). No signals attributable to coordinated acetone or thf are observed in the ^{1}H NMR spectra, due possibly to rapid exchange with the solvent. The thf adduct **9** is extremely labile, and it has only been characterized in solution. However, it has been possible to isolate **8** as a microcrystalline solid, by reaction of **1** with AgBF$_4$ in acetone under Ar, followed by NaBPh$_4$/EtOH. This compound displays one medium ν(C=O) band at 1650 cm^{-1} in the IR spectrum, due to the acetone ligand, similar to the band observed for the related complex [CpRu(O=CMe$_2$)(dippe)][BPh$_4$] [10]. Attempts made to isolate **9** as a solid, by precipitation with MeOH, led to a red, crystalline material, which was shown to be paramagnetic. This prevented the use of NMR spectroscopy for structural studies in solution. Thus, the characterization of this compound was made based upon microanalysis, magnetic moment measurements and chemical behavior, since no single crystals of this material could be obtained. Microanalysis data are consistent with the formula [{HB(pz)$_3$Ru(OMe)(dippe)][BPh$_4$] (**10**). This compound has room temperature magnetic moments of 2.1 μ_B in CH$_2$Cl$_2$ solution (Evans' method), and 1.7 μ_B in the solid state (Faraday balance), which suggest the presence of one unpaired electron and hence a low spin Ru^{III} metal center. **10** is reduced by CO, CNBu^t or acetone yielding the corresponding Ru^{II} diamagnetic complexes **6**, **7** and **8**, respectively, whereas treatment with KOBu^t in thf affords the monohydride complex **2**. This latter compound is presumably formed by a β-elimination reaction from an unstable alkoxide complex, namely [{HB(pz)}Ru(OMe)(dippe)]. The related Ru^{III} methoxy derivative, [{HB(pz)}Ru(OMe)Cl(PCy$_3$)], has been recently prepared and structucturally characterized [28].

At difference with other tris(pyrazolyl)borate ruthenium–dihydrogen complexes [7,27], **4** reacts slowly with N$_2$ yielding the dinitrogen complex [{HB(pz)$_3$}Ru(N$_2$)(dippe)][BPh$_4$] (**11**). This compound together with [{HB(pz)$_3$}Ru(N$_2$)(Ph$_2$PCH$_2$CH$_2$NMe$_2$)][BPh$_4$] [28] constitute the first known examples of tris(pyrazolyl)borate ruthenium–dinitrogen derivatives, although tris(pyrazolyl)borate–dinitrogen complexes of Co [29] and Ir [30] are known. Compound **11** has been better prepared by reaction of **1** with AgBF$_4$, which acts as halide scavenger, under dinitrogen in a non-coordinating solvent, such as dichloromethane, followed by addition of NaBPh$_4$/EtOH. **11** displays one strong ν(N≡N) band at 2165 cm^{-1} in its IR spectrum. This value falls in the range observed for other Ru–N$_2$ complexes [31], being greater than that found for the complexes [CpRu(N$_2$)(dippe)]$^+$ and [Cp*Ru(N$_2$)(dippe)]$^+$, 2145 and 2120 cm^{-1}, respectively [10], suggesting that, compared to these, the Ru–N$_2$ interaction in **11** is slightly weaker, but stronger than in [{HB(pz)$_3$}Ru(N$_2$)(Ph$_2$PCH$_2$CH$_2$NMe$_2$)]$^+$ (ν(N≡N) 2182 cm^{-1}) [28]. The value of ν(N≡N) in **11** is essentially consistent with the observation that the dihydrogen complex **4** is a stable species, according to the criterion proposed by Morris for the stability of the metal–dihydrogen bond based upon the value of ν(N≡N) for the associated dinitrogen complex [32]. NMR data for **11** support an octahedral structure. All attempts made to obtain crystals of this compound suitable for X-ray crystal structure analysis have been so far unsuccessful.

4. Conclusions

The system [{HB(pz)$_3$}RuCl(dippe)] exhibits a chemical reactivity towards small molecules which is similar in many aspects to that of the related complexes [CpRuCl(dippe)] and [Cp*RuCl(dippe)]. However, significant differences have also been found, i.e. the fact that compounds involving seven-coordinate Ru^{IV}, such as the dihydride [{HB(pz)$_3$}RuH$_2$(dippe)]$^+$, are not favored. Our results suggest that the tris(pyrazolyl)ruthenium bis(phosphine) system may be as effective as their counterparts having Cp or Cp* for the binding and activation of small molecules.

5. Supplementary material

Tables of X-ray crystallographic data, including atomic coordinates and anisotropic thermal parameters, interatomic distances and angles, and listings of observed and calculated structure factors (55 pages) are available from the authors on request.

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References

[1] S. Trofimenko, *J. Am. Chem. Soc., 88* (1966) 1842.
[2] S. Trofimenko, *J. Am. Chem. Soc., 89* (1967) 3904; *Chem. Rev., 72* (1972) 497.
[3] S. Trofimenko, *Chem. Rev., 93* (1993) 943.
[4] S.G. Davies, J.P. McNally and A. Smallridge, *Adv. Organomet. Chem., 30* (1990) 1, and Refs. therein.
[5] (a) M. Onishi, K. Ikemoto and K. Hiraki, *Inorg. Chim. Acta, 190* (1991) 157; (b) M.M. de V. Steyn, E. Singleton, S. Hietkamp and D.C. Liles, *J. Chem. Soc., Dalton Trans.*, (1990) 2991; (c) A.F. Hill, *J. Organomet. Chem., 395* (1990) C35.
[6] N.W. Alcock, I.D. Burns, K.S. Claire and A.F. Hill, *Inorg. Chem., 31* (1992) 2906.
[7] M.A. Halcrow, B. Chaudret and S. Trofimenko, *J. Chem. Soc., Chem. Commun.*, (1993) 465.
[8] N.-Y. Sun and S.J. Simpson, *J. Organomet. Chem., 434* (1992) 341.
[9] I. de los Ríos, M. Jiménez Tenorio, J. Padilla, M.C. Puerta and P. Valerga, *J. Chem. Soc., Dalton Trans.*, (1996) 377.
[10] I. de los Ríos, M. Jiménez Tenorio, J. Padilla, M.C. Puerta and P. Valerga, *Organometallics, 15* (1996) 4565.
[11] I. de los Ríos, M. Jiménez Tenorio, M.C. Puerta and P. Valerga, *J. Chem. Soc., Chem. Commun.*, (1995) 1757.
[12] M.D. Fryzuk, M.D. Jones and F.W.B. Einstein, *Organometallics, 3* (1984) 185; T.A. Burt, J. Chatt, W. Hussain and G.J. Leigh, *J. Organomet. Chem., 182* (1979) 203.
[13] S. Trofimenko, *Inorg. Synth., 12* (1970) 99.
[14] M. Jiménez Tenorio, M.C. Puerta and P. Valerga, *Inorg. Chem., 33* (1994) 3515.
[15] D.F. Evans, *J. Chem. Soc.*, (1959) 2003; T.H. Crawford and J. Swanson, *J. Chem. Educ., 48* (1971) 382.
[16] Molecular Structure Corporation, *TEXSAN*, single-crystal structure analysis software, Version 5.0, The Woodlands, TX, 1989.
[17] C.K. Johnson, *ORTEP*, a thermal ellipsoid plotting program, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
[18] F.A. Jalón, A. Otero and A. Rodríguez, *J. Chem. Soc., Dalton Trans.*, (1995) 1629.
[19] M. Jiménez Tenorio, M.C. Puerta and P. Valerga, *Organometallics, 13* (1994).
[20] M.S. Chinn and D.M. Heinekey, *J. Am. Chem. Soc., 113* (1990) 5166.
[21] F.R. Lemke and L. Brummer, *Organometallics, 14* (1995) 3980.
[22] P.G. Jessop and R.H. Morris, *Coord. Chem. Rev., 121* (1992) 155.
[23] R.H. Crabtree and D.G. Hamilton, *J. Am. Chem. Soc., 108* (1986) 3124; *110* (1988) 4126.
[24] M. Jiménez Tenorio, M.C. Puerta and P. Valerga, *J. Chem. Soc., Chem. Commun.*, (1993) 1750.
[25] G.J. Kubas, R.R. Ryan, B.I. Swanson, P.J. Vergamini and H.J. Wasserman, *J. Am. Chem. Soc., 106* (1984) 61.
[26] G.J. Kubas, C.J. Unkefer, B.I. Swanson and E. Fukushima, *J. Am. Chem. Soc., 108* (1986) 7000.
[27] B. Moreno, S. Sabo-Etienne, B. Chaudret, A. Rodríguez-Fernández, F.A. Jalón and S. Trofimenko, *J. Am. Chem. Soc., 116* (1994) 2635.
[28] K. Kirchner, personal communication.
[29] O.M. Reinaud and K.H. Theopold, *J. Am. Chem. Soc., 116* (1994) 6979.
[30] O. Boutry, E. Gutiérrez, A. Monge, M.C. Nicasio, P.J. Pérez and E. Carmona, *J. Am. Chem. Soc., 116* (1994) 791.
[31] C. Bianchini, P.J. Pérez, M. Peruzzini, F. Zanobini and A. Vacca, *Inorg. Chem., 30* (1991) 279; M.T. Bautista, E.P. Cappellani, S.D. Drouin, R.H. Morris, C.T. Schweitzer, A. Sella and J. Zubkowski, *J. Am. Chem. Soc., 113* (1991) 4876.
[32] R.H. Morris, *Inorg. Chem., 31* (1992) 1471.