Tris-pyrazolyl-borate Dihydrogen Complexes of Ruthenium†

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Reaction of [Ru(PCy$_3$)$_2$(H$_2$)HI] with K(tpb) or Tl(tdmpb) affords the molecular hydrogen complexes [Ru(η^3-L)(PCy$_3$)(H$_2$)H] (L = tpb or tdmpb), *via* the intermediates *trans*-[Ru(η^2-L)(PCy$_3$)$_2$(H$_2$)H]; protonation of [Ru(tpb)(PCy$_3$)(H$_2$)H] with HBF$_4$·Et$_2$O leads to the cationic aquo-dihydrogen complex [Ru(tpb)(PCy$_3$)(OH$_2$)(H$_2$)]BF$_4$.

In contrast to the large number of well characterised polyhydride and dihydrogen complexes containing cyclopentadienyl (Cp) and/or phosphine ligands,[1] and despite the well known binding capabilities of tris-(pyrazolyl)borate ligands,[2] very few polyhydrides supported by tpb or other N-donor ligands have been reported.[3] The rhenium complexes [Re(tpb)H$_6$] and [Re(tpb)(PPh$_3$)H$_4$] were shown to be classical polyhydrides in solution,[3a] as is the corresponding [Re(C$_5$Me$_5$)H$_6$],[4] while in contrast the rhodium species [Rh(tpb)H$_4$] was proposed to adopt the non-classical structure [Rh(tpb)(H$_2$)H$_2$] on the basis of T_1 measurements.[3b] We have previously prepared and studied the chemistry of [Ru(C$_5$Me$_5$)(PCy$_3$)H$_3$],[5] an unusual compound showing quantum mechanical exchange coupling between the hydride ligands by NMR spectroscopy, which we recently proposed to arise from the existence of two interconvertible trihydride and hydrido–dihydrogen isomers.[6] We were therefore interested to examine the spectroscopic properties and reactivity that tris-(pyrazolyl)borato-ruthenium polyhydrides might show. We report herein the syntheses and properties of the complexes [Ru(tpb)(PCy$_3$)H$_3$] and [Ru(tdmpb)(PCy$_3$)H$_3$], and the reactivity of the former complex towards ligand substitution and protonation.

Reaction of [Ru(PCy$_3$)$_2$(H$_2$)HI][7] **1** with 1 equiv. of K(tpb) in THF under H$_2$ at 293 K for 30 min affords a green solution, from which an air-sensitive oily tan product **2** can be isolated in *ca.* 40% yield following chromatography of the crude mixture over alumina in toluene. The IR spectrum of **2** exhibits peaks due to tpb and PCy$_3$ ligands, together with a broad ν(Ru–H) vibration at 2017 cm^{-1}, while ^{1}H NMR spectroscopy shows, in addition to broad peaks from the tpb and PCy$_3$ ligands, a doublet resonance integrating to 3H at δ −10.4 (J 18 Hz) that broadens considerably below 240 K. A series of T_1 determinations for the high-field resonance at varying temperatures yielded a minimum of 16 ms at 245 K (250 MHz). This is similar to the values obtained for other *cis*-hydride–dihydrogen complexes of Ru,[7,8] and is consistent with the formulation of **2** as the octahedral Ru$^{\mathrm{II}}$ species [Ru(tpb)(PCy$_3$)(H$_2$)H].[1c]‡ Désorption chemical ionisation (DCI) mass spectrometry of **2** (NH$_3$ carrier gas) showed

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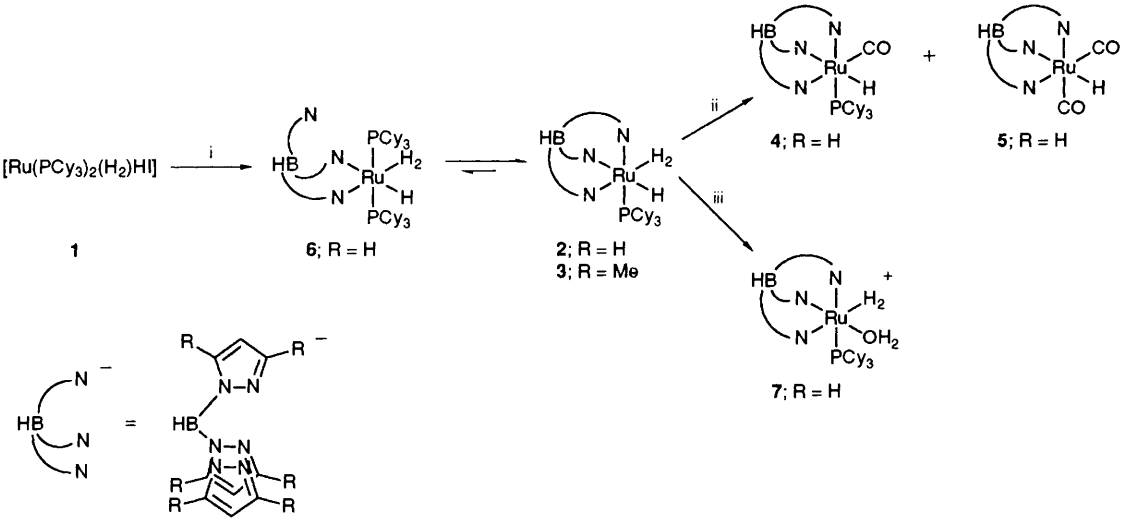
† Abbreviations used: Cy = cyclohexyl; tpb = trispyrazol-1-ylborate; tdmpb = tris-(3,5-dimethylpyrazol-1-yl)borate; THF = tetrahydrofuran.

‡ *Spectroscopic data* for **2**: IR (Nujol): ν(B–H) 2459m cm^{-1}, ν(Ru–H) 2017br cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 7.99 (br, 3H), 7.65 (br, 3H), 6.11 (br, 3H), 1–2 (m, 33H) and −10.44 (d, J 18 Hz, 3H); ^{31}P{^{1}H} NMR (C$_6$D$_6$–C$_6$H$_6$): δ 74.23 (s). T_1 values for the high-field ^{1}H signal (250 MHz): 296 K, 54 ms; 253 K, 19; 233 K, 20; 213 K, 38; 183 K, 124. Estimated T_1 minimum 16 ms at 245 K.

Spectroscopic data for **3**: IR (Nujol): ν(B–H) 2521m cm^{-1}, ν(Ru–H) 2029br cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 5.93 (s, 2H), 5.31 (s, 1H), 2.60 (s, 6H), 2.54 (s, 6H), 2.38 (s, 3H), 2.14 (s, 3H), 1–2 (m, 33H) and −10.71 (d, J 18 Hz, 3H); ^{31}P{^{1}H} NMR (C$_6$D$_6$–C$_6$H$_6$): δ 93.50 (s), T_1 values for the high-field ^{1}H signal (250 MHz): 298 K, 63 ms; 233 K, 25; 218 K, 22; 203 K, 33; 183 K, 86. Estimated T_1 minimum 21 ms at 220 K.



Scheme 1 *Reagents and conditions*: i, K(tpb), THF, H_2, 293 K (yield 40%) or Tl(tdmpb), THF, H_2, 343 K (yield 4%); ii, CO, THF, 293 K (yield 3%); iii, $HBF_4{\cdot}Et_2O$, pentane, 293 K (yield 70%)

approximately equal-intensity peaks at *m/z* 595 and 593, corresponding to M − 3H and M − 5H respectively. These could arise from the expected M + H molecular ion (*m/z* 599, presumably protonated at the terminal hydride ligand, *vide infra*) *via* loss of both resultant H_2 ligands, followed by dehydrogenation of a PCy_3 cyclohexyl group. Such a dehydrogenation reaction has been observed on protonation of $[Ru(C_5Me_5)(PCy_3)H_3]$.[5b][§]

No reaction is observed between **1** and Tl(tdmpb) at 293 K; however, treatment of **1** with Tl(tdmpb) in THF under H_2 at 323 K and purification as above gives a very low but reproducible yield (4%) of complex **3**. The spectroscopic properties of **3** are very similar to those of **2**, *viz*. *m/z* 679 (M − 3H) and 677 (M − 5H), ν(Ru–H) 2029 cm^{-1}, δ(Ru–H) −10.7 (d, *J* 18 Hz, 3H), T_1 (min) 21 ms at 220 K,[‡] and **3** was therefore formulated as the non-classical hydride $[Ru(tdmpb)(PCy_3)(H_2)H]$. The high-field resonance of **3** develops low- and high-frequency shoulders between 233 and 183 K, which may be indicative of partial decoalescence into separate peaks for the hydride and dihydrogen ligands.

The non-classical formulation of **2** and **3** contrasts with the analogous complexes $[Ru(C_5R_5)(PR'_3)H_3]$ (R = H, R′ = Ph; R = Me, R′ = Ph, Pr^i, Cy), which are classical Ru^{IV} trihydrides in the solid state and display exchange couplings in solution,[5,9] particularly since tpb ligands are often considered as analogues of Cp in their complex chemistry. It is noteworthy that EHMO calculations have implied that tpb is a significantly better donor ligand than Cp,[10] which is not consistent with the dihydrogen–hydride structures of **2** and **3**; the observation of non-classical structures for hydride complexes is generally associated with relatively electron-poor metal centres.[1b,d] However, in these systems, Cp* (C_5Me_5) appears to be a better electron donor ligand as deduced from the observation of a CO at 1900 cm^{-1} for $[Ru(C_5Me_5)(PCy_3)(CO)H]$[5] and 1915 cm^{-1} for $[Ru(tpb)(PCy_3)(CO)H]$ (*vide infra*). Furthermore, the strong electronic and steric preference of complexes containing tpb ligands for octahedral coordination is well known,[10] which could preclude the formation of seven-coordinate trihydride structures for **2** and **3**.

Both **2** and **3** are indefinitely stable toward H_2 loss under Ar or *in vacuo*, while no reaction is observed between **2** and N_2, CO_2 or excess of MeCN at 293 K. Treatment of **2** with CO in THF at 293 K for 1 h produces a very low yield (<5%) of a 1 : 1 mixture of $[Ru(tpb)(PCy_3)(CO)H]$ **4** and a dicarbonyl hydride **5** that we propose to be $[Ru(tpb)(CO)_2H]$ [IR (hexane): ν(C–O) 2039, 1971 cm^{-1}; ^{1}H NMR (C_6D_6): δ−9.5 (s)], the remainder of **2** being recovered unchanged. Complex **4** was prepared independently in low yield by reaction of $[RuHCl(CO)(PCy_3)_2]$[11] with K(tpb).[¶]

Freshly prepared samples of **2** were occasionally observed to contain an additional product **6**, characterised by six resonances from the tpb ligand (1 : 2 : 1 : 2 : 1 : 2 integral ratios) and a triplet hydride resonance at δ−11.9 (*J* 15 Hz), by ^{1}H NMR spectroscopy in C_6D_6, and an AB multiplet in the ^{31}P NMR spectrum centred at δ 51.4 (*J* 290 Hz). A 3 : 1 mixture of **2** and **6** can also be generated by dissolution of **2** in the presence of a tenfold excess of PCy_3. A T_1 measurement at 293 K on the hydride resonances of a mixed sample of **2** and **6** afforded an identical value of 56 ms for both species (*cf.* 54 ms for pure **2**), implying that **2** and **6** are in equilibrium under these conditions. These data are consistent with the formulation of *trans*-$[Ru(\eta^2\text{-tpb})(PCy_3)_2(H_2)H]$ for **6**, this being the structure of the putative intermediate in the formation of **2** from **1** (Scheme 1).

The protonation of **2** with 1 mol. equiv. of $HBF_4{\cdot}Et_2O$ in pentane at 223 K leads to the precipitation of a highly air-sensitive off-white solid product **7**. The ^{1}H NMR spectrum of **7** in C_6D_6 at 293 K exhibits a broad hydride resonance at δ−7.24 ($w_{1/2}$ 50 Hz, 2H; T_1 11 ms at 253 K) and a broad singlet at δ 3.43 ($w_{1/2}$ 18 Hz, 2H), together with nine peaks from the tpb pyrazolyl protons and a series of multiplets from a PCy_3 ligand; no ^{1}H resonances assignable to a protonated pyrazole moiety are observed, while ^{13}C NMR spectroscopy rules out

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[§] An M −5 ion was also observed in the DCI (NH_3) mass spectrum of $[Ru(C_5Me_5)(PCy_3)H_3]$. M. A. Halcrow and B. Chaudret, unpublished result.

[¶] *Spectroscopic data* for **4**: IR (Nujol): ν(B–H) 2482m cm^{-1}, ν(Ru–H) 1950m cm^{-1}, ν(C–O) 1915s cm^{-1}; IR (hexane): ν(C–O) 1928 cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ 8.14 (d, *J* 2 Hz, 1H), 7.93 (d, *J* 2 Hz, 1H), 7.86 (d, *J* 2 Hz, 1H), 7.69 (d, *J* 2 Hz, 1H), 7.59 (d, *J* 2 Hz, 1H), 7.48 (d, *J* 2 Hz, 1H), 6.17 (t, *J* 2 Hz, 1H), 6.00 (t, *J* 2 Hz, 1H), 5.90 (t, *J* 2 Hz, 1H), 1–2 (m, 33H) and −12.74 (d, *J* 27 Hz, 1H); ^{31}P{^{1}H} NMR (C_6D_6–C_6H_6): δ 65.16 (s).

Spectroscopic data for **7**: IR (Nujol): ν(O–H) 3408br cm^{-1}, ν(B–H) 2493m cm^{-1}, ν(B–F) 1060br cm^{-1}; ^{1}H NMR (C_6H_6, 200 MHz): δ 8.88 (d, *J* 2 Hz, 1H), 8.10 (d, *J* 2 Hz, 1H), 7.61 (d, *J* 2 Hz, 1H), 7.58 (d, *J* 2 Hz, 1H), 7.47 (d, *J* 2 Hz, 1 H), 6.76 (d, *J* 2 Hz, 1H), 6.16 (t, *J* 2 Hz, 1H), 6.00 (t, *J* 2 Hz, 1H), 5.72 (t, *J* 2 Hz, 1H), 3.43 (br, 2H), 1–2 (m, 33H) and −7.24 (br, 2H); ^{13}C{^{1}H} NMR (C_6D_6): δ 147.89 (1C), 142.74 (1C), 138.10 (1C), 135.12 (2C), 132.18 (1C), 107.14 (br, 3C), 32.25 (d, *J* 16 Hz, 3C), 29.84 (6C), 28.30 (s, 6C) and 25.77 (3C); ^{31}P{^{1}H} NMR (C_6D_6–C_6H_6): δ 38.98 (s); T_1 values for the high-field ^{1}H signal (200 MHz): 294 K, 14 ms; 253 K, 11.

an agostic C–H interaction from or dehydrogenation of, a phosphine cyclohexyl group.[5b] IR spectroscopy (Nujol) shows broad ν(O–H) and δ(H–O–H) absorptions at 3408 and 1634 cm^{-1} respectively but no terminal ν(Ru–H) vibration. We therefore formulate **7** as the cationic molecular hydrogen complex $[Ru(tpb)(PCy_3)(H_2)(OH_2)]BF_4$.¶

Protonation of **2** probably occurs at the terminal hydride ligand, which would afford a highly reactive bis-dihydrogen species $[Ru(tpb)(PCy_3)(H_2)_2]^+$. The subsequent substitution of a dihydrogen ligand by an aquo ligand would afford **7**; such adventitious water probably derives from the acid used, since freshly distilled solvents were employed throughout this study. It is noteworthy that treatment of **2** *in situ* with $HBF_4 \cdot Et_2O$ or CF_3SO_3H in CD_2Cl_2 or C_7D_8 also affords **7**, with observable evolution of H_2; in this case, weaker ^1H resonances at δ −4 to −12 with T_1 values of 10–20 ms at 294 K are also observed, with corresponding ^{31}P singlet resonances at δ 33–46 (*cf.* δ 39.0 for **7**). These additional peaks may arise from other species of type $[Ru(tpb)(PCy_3)(H_2)(L)]^{n+}$ (L = coordinated solvent, anion *etc.*). It is remarkable that only one H_2 ligand is substituted under these conditions; the fine balance between H_2 and OH_2 binding at a metal centre has been noted previously.[12] Complex **7** readily loses H_2 on mild heating, *in vacuo* or in coordinating solvents such as acetone.

In conclusion, we have prepared the first ruthenium polyhydrides containing tpb ligands, and shown that these complexes have very different spectroscopic properties from their C_5Me_5 analogues. Furthermore, whereas protonation of $[Ru(C_5Me_5)(PCy_3)H_3]$ leads to extensive hydrogen evolution and dehydrogenation of the phosphine ligand,[5b] the protonation of $[Ru(tpb)(PCy_3)(H_2)H]$ allows the isolation of a cationic molecular hydrogen complex. This presumably reflects the increased electron richness of the $[Ru(tpb)]^+$ centre over $[Ru(C_5Me_5)]^+$, allowing improved back-donation into the H–H σ*-orbital and hence stabilising the protonated product.

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