

# Synthesis of the acidic dihydrogen complexes $trans\text{-}[M(H_2)\text{-}(CN)L_2]^+$ and $trans\text{-}[M(H_2)(CNH)L_2]^{2+}$ where $M = Fe, Ru, Os$ and $L = dpmm, dppe, dppp, depe$ , and dihydrogen substitution by the trifluoromethanesulfonate anion to give $trans\text{-}[Ru(OTf)(CN)L_2]$ or $trans\text{-}[Ru(OTf)(CNH)L_2]OTf^\dagger$

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Very acidic complexes  $trans\text{-}[M(\eta^2\text{-}H_2)(CN)L_2]^+$  and  $trans\text{-}[M(\eta^2\text{-}H_2)(CNH)L_2]^{2+}$ , with the dihydrogen ligand *trans* to the cyanide or to the hydrogen isocyanide ligand, are generated by reaction of trifluoromethanesulfonic acid (HOTf) with hydrido(cyano) complexes of Fe(II), Ru(II) and Os(II). The use of the different metals and phosphines (dpmm = [bis(diphenylphosphino)methane], dppe = [1,2-bis(diphenylphosphino)ethane], dppp = [1,3-bis(diphenylphosphino)propane], and depe = [1,2-bis(diethylphosphino)ethane]) as ancillary ligands influences the stability and the reactivity of these complexes. The iron and osmium complexes are more stable than the ruthenium complexes that lose the dihydrogen ligand and coordinate the trifluoromethanesulfonate anion. The crystal structure of  $trans\text{-}[Ru(OTf)(CN)\text{-}(dppe)_2]$  is reported. The Ru–OTf bond is weak and so the triflate ligand can be displaced by  $H_2(g)$  to give  $trans\text{-}[Ru(\eta^2\text{-}H_2)(CN)L_2]OTf$ . There is a delicate balance of stability between the complexes  $trans\text{-}[M(\eta^2\text{-}H_2)(CN)L_2]^+$  and  $trans\text{-}[M(H)(CNH)L_2]^+$ ,  $M = Fe, Ru$ , determined by electronics and hydrogen bonding, both classical ( $CNH \cdots OTf^-$ ,  $TfOH \cdots OTf^-$ ) and non-classical ( $MH_2 \cdots OTf^-$ ). Therefore isomerisation reactions between these forms are observed for the first time. In order to determine where the protonation occurs it is useful to use a cyanide group labeled as  $C^{15}N$  or  $^{13}CN$ . It is significant that the very acidic dihydrogen complex  $trans\text{-}[Ru(\eta^2\text{-}H_2)\text{-}(CNH)L_2]OTf$  is observed to form from the reaction of the weak Brønsted acids  $H_2$  and  $trans\text{-}[Ru(OTf)(CNH)L_2]\text{-}OTf$  in  $CH_2Cl_2$ ; the dihydrogen complex releases HOTf. The chemistry is of possible relevance to the action of iron-containing hydrogenases.

## Introduction

There is an interest in determining how acidic dihydrogen can become when coordinated as an  $\eta^2\text{-}H_2$  ligand. Cationic and especially dicationic  $\eta^2$ -dihydrogen complexes can be more acidic than strong acids like protonated diethyl ether or triflic acid ( $CF_3SO_3H$ , HOTf) in  $CH_2Cl_2$ , particularly when  $\pi$ -acid ligands like CO or CNH are present in the complex. Examples from our groups that are as acidic or more acidic than triflic acid in  $CH_2Cl_2$  include  $trans\text{-}[Fe(\eta^2\text{-}H_2)(CO)(dppe)_2]^{2+}$ ,<sup>1</sup>  $trans\text{-}[M(CO)(\eta^2\text{-}H_2)(dppp)_2]^{2+}$  ( $M = Ru, Os$ )<sup>2</sup> and  $trans\text{-}[Ru(\eta^2\text{-}H_2)(CNH)(dppe)_2]^{2+}$ .<sup>3</sup> These complexes are surprisingly stable with respect to the loss of  $H_2(g)$ .<sup>1</sup> This was rationalised in terms of an increase in importance of the metal– $H_2$   $\sigma$  bond to compensate for the lack of  $\pi$ -backdonating ability of these electrophilic metal centres. Other highly acidic dihydrogen complexes included  $[Os(\eta^2\text{-}H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ ,<sup>4</sup> *cis*- $[Re(CO)_4(\eta^2\text{-}H_2)(PR_3)]^+$ ,<sup>5</sup>  $[Ru(C_5Me_5)(\eta^2\text{-}H_2)(CO)_2]BF_4$ ,<sup>6</sup>  $[Ru(\eta^2\text{-}H_2)(PPh_3)(CO)(tacn)]^{2+}$  (tacn = 1,4,7-triazacyclononane),<sup>7</sup>  $trans\text{-}[Os(\eta^2\text{-}H_2)(CH_3CN)(dppe)_2]^{2+}$ ,<sup>8</sup>  $[Cp^*Os(CO)_2\text{-}$

$(\eta^2\text{-}H_2)]OTf^9$  and  $[(\text{triphos})Ir(\eta^2\text{-}H_2)(H)_2]BPh_4$  (triphos =  $MeC(CH_2PPh_2)_3$ ).<sup>10</sup>

In this paper we give the complete details of our studies of dihydrogen complexes **3Mj** or **4Mj** derived from protonating complexes  $trans\text{-}[MH(CN)L_2]$ , **1Mj**, where the numbering scheme is explained in Table 1. Protonation can take place at three different sites in these complexes (Scheme 1): (i) at the cyanide to give a hydrogen isocyanide ligand; (ii) at the metal–hydride bond to produce a dihydrogen complex; (iii) at the metal to give a dihydride complex. An interesting complication is the fact that the  $pK_a$  of coordinated hydrogen isocyanide might be in a similar range to that of monocationic dihydrogen complexes. At least one  $pK_a$  determination of a CNH ligand has been reported: the  $pK_a$  of  $[Fe(CNH)(CN)_5]^{3-}$  in water is 4.2.<sup>11</sup> Several dihydrogen complexes in  $CH_2Cl_2$  or THF have similar acidities to acids that have  $pK_a$  in the range 0–10 in water.<sup>12</sup> Therefore there is the possibility of tautomers forming and indeed this is observed in the current work for the first time for cyanide ligands. There are only a few examples of tautomeric equilibria between dihydrogen complexes and hydride complexes with a protonated ligand. These include  $[Os(H_2)\text{-}(quinS)(CO)(PPh_3)_2]^+$  (quinS = quinoline-8-thiolate)<sup>13,14</sup> and  $[\{\eta^5\text{-}C_5H_4(CH_2)_3NMe_2H^+\}RuH(dpmm)]BF_4$ .<sup>15</sup> Some of us have already reported the important effect of the ancillary ligand on the protonation of hydridocyano complexes.<sup>16</sup> With the basic depe ligand, protonation at the Fe–H bond in  $trans\text{-}[FeH(CN)(depe)_2]$  **1Fe4** is thermodynamically favored to give

<sup>†</sup> Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/1999/4475/>

Also available: additional experimental and spectroscopic data. For direct electronic access see <http://www.rsc.org/suppdata/dt/1999/4475/>, otherwise available from BLDSC (No. SUP 57672, 6 pp.) or the RSC library. See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/dalton>).

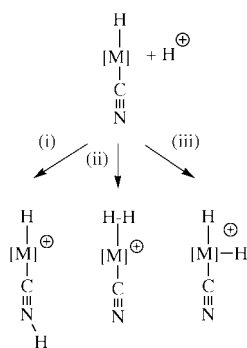
**Table 1** The numbering scheme for the complexes **iMj** as triflate salts and other salts<sup>a</sup>

<b>iMj</b>	<b>i</b>	<b>M</b>	<b>j</b>	<b>L</b>	Abbreviation
[MH(CN)L <sub>2</sub> ]	<b>1</b>	<b>Fe</b>	<b>1</b>	PPh <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub>	dppm
[MH(CNH)L <sub>2</sub> ][OTf]	<b>2</b>	<b>Ru</b>	<b>2</b>	PPh <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub>	dppe
[M(η <sup>2</sup> -H <sub>2</sub> )(CN)L <sub>2</sub> ][OTf]	<b>3</b>	<b>Os</b>	<b>3</b>	PPh <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> PPh <sub>2</sub>	dppp
[M(η <sup>2</sup> -H <sub>2</sub> )(CNH)L <sub>2</sub> ](OTf) <sub>2</sub>	<b>4</b>	<b>4</b>	<b>4</b>	PEt <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> PEt <sub>2</sub>	depe
[M(OTf)(CN)L <sub>2</sub> ]	<b>5</b>				
[M(OTf)(CNH)L <sub>2</sub> ][OTf]	<b>6</b>				

Other salts	<b>i</b>	<b>M</b>	<b>j</b>
[Ru(η <sup>2</sup> -H <sub>2</sub> )(CN)(dppe) <sub>2</sub> ](TfO...HOTf)	<b>3'</b>	<b>Ru</b>	<b>2</b>
[Ru(η <sup>2</sup> -H <sub>2</sub> )(CNH)(dppe) <sub>2</sub> ](TfO...HOTf) <sub>2</sub>	<b>4'</b>	<b>Ru</b>	<b>2</b>
[Os(η <sup>2</sup> -H <sub>2</sub> )(CN)(dppp) <sub>2</sub> ][BF <sub>4</sub> ]	<b>3*</b>	<b>Os</b>	<b>2</b>
[M(η <sup>2</sup> -H <sub>2</sub> )(CN)(depe) <sub>2</sub> ][BF <sub>4</sub> ]	<b>3*</b>	<b>Fe</b>	<b>4</b>
	<b>3*</b>	<b>Ru</b>	<b>4</b>
[Fe(η <sup>2</sup> -H <sub>2</sub> )(CNH)(depe) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	<b>4*</b>	<b>Fe</b>	<b>4</b>

<sup>a</sup> In addition further symbols are used for <sup>13</sup>C labelled complexes (**c**), <sup>2</sup>H labelled complexes (**d**) and <sup>15</sup>N labelled complexes (**n**) e.g. **iMj-c**.



**Scheme 1** Protonation can take place at (i) the cyanide, (ii) the metal-hydride bond, or (iii) the metal.

*trans*-[Fe(η<sup>2</sup>-H<sub>2</sub>)(CN)(depe)<sub>2</sub>][OTf] **3Fe4** while with the analogous dppe complex **1Fe2**, the proton ends up on the nitrogen to give *trans*-[Fe(H)(CNH)(dppe)<sub>2</sub>][OTf] **2Fe2**. Further chemistry of **2Fe2** has recently been reported.<sup>17</sup>

In certain cases, as described in our recent communication,<sup>3</sup> very acidic dihydrogen complexes such as *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CNH)(L)<sub>2</sub>]<sup>2+</sup>X<sup>-2</sup>, L = dppe, X = (TfO...HOTf) **4'Ru2**, L = dppp, X = OTf **4Ru3** can be generated by displacing coordinated triflate in *trans*-[Ru(OTf)(CNH)(L)<sub>2</sub>][OTf] (**6Ru2** or **6Ru3**) with dihydrogen gas. Only a few other highly acidic complexes have been generated by use of dihydrogen gas. These are [(triphos)Ir(η<sup>2</sup>-H<sub>2</sub>)(H)<sub>2</sub>]BPh<sub>4</sub> by hydrogenation of the ethene complex [(triphos)Ir(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)(H)<sub>2</sub>]BPh<sub>4</sub>,<sup>10</sup> and *cis*-[Re(η<sup>2</sup>-H<sub>2</sub>)(PR<sub>3</sub>)(CO)<sub>4</sub>] by displacement of CH<sub>2</sub>Cl<sub>2</sub> from *cis*-[Re(η<sup>1</sup>-CICH<sub>2</sub>Cl)(PR<sub>3</sub>)(CO)<sub>4</sub>]<sup>+5</sup>.

Hydrogen-bonding interactions are expected to be very important for this chemistry in low dielectric solvents. The CNH ligand is an excellent hydrogen bond donor. It is known to donate hydrogen bonds to the fluoride of a PF<sub>6</sub><sup>-</sup> anion and to the oxygen of ethers.<sup>18</sup> Recently, Sapunov *et al.* reported the crystalline structures of [Ru<sub>2</sub>Cp<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>(μ-CNHC)]CF<sub>3</sub>SO<sub>3</sub>, a bridged complex with a short (2.573 Å) N(H)...N bond length, and of [RuCp(PPh<sub>3</sub>)<sub>2</sub>(CNH)]CF<sub>3</sub>SO<sub>3</sub>, where the CNH group forms a strong hydrogen bond to the triflate group, N...O = 2.75 Å.<sup>19</sup> We have also previously published the solid-state structure of *trans*-[Ru(OTf)(CNH)(dppe)<sub>2</sub>][OTf], **6Ru2**, where the N...O distance is found to be 2.62 Å.<sup>3</sup> This complex has a long Ru-OTf bond of 2.299 Å, longer than that of other ruthenium(II)-triflate complexes.<sup>20-22</sup>

In addition there is the possibility that the dihydrogen ligand might act as an unconventional hydrogen bond donor to

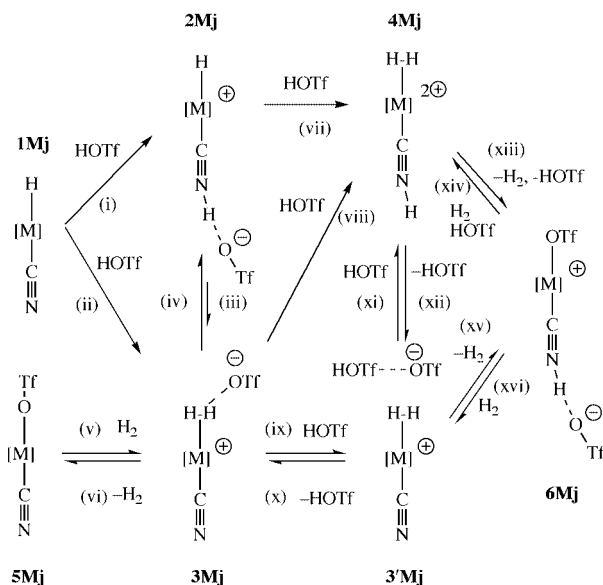
triflate. For example there is a related Os(HH)...F<sub>3</sub>B<sup>-</sup> interaction in *trans*-[Os(η<sup>2</sup>-H<sub>2</sub>)(CH<sub>3</sub>CN)(dppe)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub><sup>8</sup> and IrCl... (HH)Ir hydrogen bonds in Ir(η<sup>2</sup>-H<sub>2</sub>)(Cl)<sub>2</sub>(H)(P<sup>i</sup>Pr)<sub>2</sub>.<sup>23</sup>

Finally this chemistry is relevant to the chemistry of iron-nickel and iron-only hydrogenases which also appear to be low-spin Fe(II) cyanide complexes that activate dihydrogen.<sup>24-27</sup> The iron-nickel active site might have dihydrogen coordinated as (cysteine)<sub>2</sub>Ni(μ-cysteine)<sub>2</sub>Fe(η<sup>2</sup>-H<sub>2</sub>)(CO)(CN)<sub>2</sub><sup>28</sup> before it is released as H<sub>2</sub>(g) while the iron-only active sites might have (cysteine)<sub>3</sub>Fe<sub>4</sub>S<sub>4</sub>(μ-cysteine)Fe<sub>2</sub>(CO)<sub>x</sub>(CN)<sub>y</sub>(η<sup>2</sup>-H<sub>2</sub>) composition before dihydrogen is separated into protons and electrons. The possible formation of a hydrogen isocyanide ligand at these sites has not been discussed.

## Results and discussion

### Observation of the species formed by protonation of *trans*-[MH(CN)L<sub>2</sub>]

Scheme 2 outlines the formation of the important hydride and



**Scheme 2** The preparative routes. [M] refers to the M(diphosphine)<sub>2</sub> fragment. The solvent is CH<sub>2</sub>Cl<sub>2</sub> or CD<sub>2</sub>Cl<sub>2</sub> although parts of the Scheme are valid for other solvents as indicated in the text.

dihydrogen complexes characterised in this work. Only certain of the pathways are followed for each combination of ligands, metal, solvent and acid. The protonation reactions of the dppp complexes **1M3**, M = Ru, Os, are the most straightforward and will be described first. Then the other systems will be described and finally the detailed characterization of the complexes. In general these highly acidic, reactive complexes are difficult to crystallise and characterise by elemental analysis. Most of the characterization is spectroscopic in nature. In particular, important NMR properties of the dihydrogen complexes are listed in Table 2. The properties of complexes **1Mj** and **2Mj** can be found elsewhere.<sup>28</sup>

### Addition of HOTf to *trans*-[RuH(CN)(dppp)<sub>2</sub>] **1Ru3** and related reactions

The stepwise protonation of **1Ru3** in CD<sub>2</sub>Cl<sub>2</sub> with HOTf can be conveniently followed by NMR spectroscopy. <sup>31</sup>P and <sup>1</sup>H NMR measurements confirm that the addition of HOTf to a solution of **1Ru3** results mainly in protonation of the CN ligand to give *trans*-[RuH(CNH)(dppp)<sub>2</sub>][OTf], **2Ru3** (step i, Scheme 2). When less than one equivalent is added, the hydride resonances and the <sup>31</sup>P resonances of **1Ru3** and **2Ru3** are averaged by fast proton transfer. However there is also the immediate formation of a small amount of the dihydrogen complex *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CN)(dppp)<sub>2</sub>][OTf] **3Ru3** (step ii, Scheme 2) as indicated by

**Table 2** Characteristics of dihydrogen complexes observed (in CD<sub>2</sub>Cl<sub>2</sub>)

Complex	<sup>1</sup> H NMR/ $\delta$	<sup>31</sup> P{ <sup>1</sup> H} NMR/ $\delta$	<i>J</i> (HD)/ Hz	<i>d</i> (H–H) from <i>J</i> (HD)/ $\text{\AA}$	<i>T</i> <sub>1</sub> (min)/ms	<i>d</i> (H–H) from <i>T</i> <sub>1</sub> (min)/ $\text{\AA}$ <sup>a</sup>
<b>3Ru1</b>	–4.7 (br)	–6.1 (br s)	32.0	0.89	5.8 <sup>d</sup> (213 K)	0.81, 1.02
<b>4Ru1</b>	–3.7 (br) <sup>b</sup>	–12.2 (br s) <sup>b</sup>	32.2 <sup>b</sup>	0.88 <sup>b</sup>	6.4 <sup>d</sup> (233 K)	0.82, 1.04
<b>3Fe2</b>	–8.7 (br)	72.2 (s)	32.7	0.87	11.7 <sup>e</sup> (234 K)	0.85, 1.07
<b>4Fe2</b>	–9.1 (br)	70.4 (s)	32.5	0.88	21.5 <sup>f</sup> (262 K)	0.87, 1.09
<b>3Ru2</b>	–7.3 (br) <sup>c</sup>	53.7 (s) <sup>c</sup>	32.5	0.88		
<b>3'Ru2<sup>g</sup></b>	–5.5 (br)	54.2 (s)	32.0	0.89	12.4 <sup>e</sup> (240 K)	0.86, 1.08
<b>4'Ru2</b>	–5.9 (br)	52.2 (s)	32.4	0.88	13.6 <sup>e</sup> (247 K)	0.87, 1.10
<b>3*Os2<sup>h</sup></b>	–6.4 (br)	21.7 (s)	28.7	0.94	14.7 <sup>e</sup> (233 K)	0.88, 1.11
<b>4Os2-c</b>	–6.1 (br)	22.0 (d)	29.1	0.93	14 <sup>e</sup> (253 K)	0.88, 1.11
<b>3Ru3</b>	–5.4 (br)	9.7 (br s)	31.6	0.89	5.4 <sup>d</sup> (223 K)	0.80, 1.01
<b>4Ru3</b>	–4.2 (br)	8.9 (br s)	31.8	0.89	5.9 <sup>d</sup> (233 K)	0.81, 1.02
<b>4Os3</b>	–4.6 (br)	–29.4 (br s)	28.8	0.94	7.6 <sup>d</sup> (233 K)	0.85, 1.07
<b>3*Fe4<sup>h</sup></b>	–14.0 (br)	77.7 (s)	31.6	0.89	15.2 <sup>i</sup> (262 K)	0.85, 1.07
<b>4Fe4</b>	–12.1 (br)	72.5 (s)			19.0 <sup>i</sup> (229 K)	0.88, 1.11
<b>3*Ru4<sup>h</sup></b>	–9.1 (br)	54.4 (s)			12.8 <sup>e</sup> (191 K)	0.86, 1.09
<b>3Os4-c</b>	–9.5 (br)	21.7 (d)	25.4	1.00	16 <sup>e</sup> (213 K)	0.90, 1.13
<b>4Os4</b>	–8.1 (br)	17.9 (s)			12 <sup>e</sup> (223 K)	0.86, 1.08

<sup>a</sup> The first value is calculated for the fast spinning while the second is referred to the slow spinning. <sup>b</sup> Values measured at 193 K. <sup>c</sup> NMR spectra recorded at 263 K. <sup>d</sup> *T*<sub>1</sub> measured at 200 MHz. <sup>e</sup> *T*<sub>1</sub> measured at 300 MHz. <sup>f</sup> *T*<sub>1</sub> measured at 500 MHz; see ref. 1. <sup>g</sup> (TfO...HOTf)<sup>–</sup> counter anion. <sup>h</sup> BF<sub>4</sub><sup>–</sup> counter anion. <sup>i</sup> *T*<sub>1</sub> measured at 400 MHz.

the appearance in the <sup>1</sup>H NMR spectrum of a broad signal at  $\delta$  –5.4 due to a dihydrogen ligand. This new complex is also visible in the <sup>31</sup>P NMR spectrum as a broad singlet centered at  $\delta$  9.7. The integration of the <sup>31</sup>P NMR signals indicates that in a 32 mM solution of **1Ru3** the amount of the dihydrogen complex **3Ru3** formed is *ca.* 6% and 10% for the molar ratios HOTf–**1Ru3** of 0.5 and 1, respectively. We do not know why **3Ru3** forms quickly in this reaction when it is only produced slowly when pure **2Ru3** is dissolved in CH<sub>2</sub>Cl<sub>2</sub> (see below).

For HOTf–**1Ru3** > 1 both complexes **2Ru3** and **3Ru3** react with HOTf to give the dihydrogen complex *trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(CNH)(dppp)<sub>2</sub>](OTf)<sub>2</sub>, **4Ru3** (steps vii, viii, Scheme 2). Thus for a molar ratio = 2 the solution contains a mixture of the complexes **2Ru3**, **3Ru3** and **4Ru3**; if the solution is under Ar, the H<sub>2</sub> is slowly lost and an increasing amount of the derivative *trans*-[Ru(OTf)(CNH)(dppp)<sub>2</sub>]OTf **6Ru3** is formed (step xiii, Scheme 2). If the protonation is carried out under H<sub>2</sub> the formation of **6Ru3** is inhibited. When a molar ratio greater than 3 is used the complex **4Ru3** is quantitatively formed.

The stepwise protonation of the <sup>13</sup>CN enriched compound *trans*-[RuH(<sup>13</sup>CN)(dppp)<sub>2</sub>] **1Ru3-c** to give the corresponding complexes **2Ru3-c**, **3Ru3-c** and **4Ru3-c** was also studied in CD<sub>2</sub>Cl<sub>2</sub> by <sup>13</sup>C{<sup>1</sup>H} NMR. The protonation of the <sup>13</sup>CN group to produce <sup>13</sup>CNH results in a broadening of the <sup>13</sup>C resonance which shifts to low field (from  $\delta$  156.7 for **1Ru3-c** to  $\delta$  165.5 for **2Ru3-c**). For HOTf–**1Ru3-c** in a molar ratio less than one, a binomial quintet attributable to **3Ru3-c** is also observed at  $\delta$  142.4. When the molar ratio HOTf–**1Ru3-c** increases, the protonation occurs both at the Ru–H of **2Ru3-c** and at the nitrogen of the <sup>13</sup>CN of **3Ru3-c** with the final formation of **4Ru3-c**, which shows the <sup>13</sup>CNH resonance as a broad quintet at  $\delta$  149.9. In solution the complex **4Ru3-c** slowly loses H<sub>2</sub> to give *trans*-[Ru(OTf)(<sup>13</sup>CNH)(dppp)<sub>2</sub>]OTf **6Ru3-c** which exhibits a <sup>13</sup>C signal at  $\delta$  159.7.

When the protonation of **1Ru3** with HOTf under H<sub>2</sub> is carried out in Cl<sub>2</sub>CDCDCl<sub>2</sub>, a larger ratio of **3Ru3** to **2Ru3** is observed (47:53) compared to the reaction in CD<sub>2</sub>Cl<sub>2</sub> solution. Furthermore, when argon is bubbled into the Cl<sub>2</sub>CDCDCl<sub>2</sub> solution, the hydrogen is easily displaced with the quantitative formation of a red solution containing **5Ru3** *via* steps iii, vi, Scheme 2.

The complex **2Ru3**, which can be obtained as a pure solid,<sup>28</sup> appears to be stable in solution under H<sub>2</sub> in oxygenated solvents such as acetone or THF, but converts slowly in chlorinated solvents to an equilibrium mixture with the dihydrogen complex **3Ru3** (step iii, Scheme 2). In CD<sub>2</sub>Cl<sub>2</sub> (after 12 hours) the

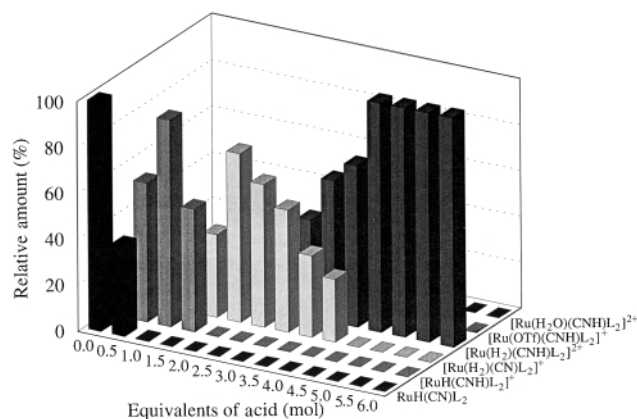
NMR spectrum shows 90% of **2Ru3** and 10% of **3Ru3**; in Cl<sub>2</sub>CDCDCl<sub>2</sub> (after 12 hours) the percentage is 53% for **2Ru3** and 47% for **3Ru3**. The same equilibrium mixtures are slowly obtained starting from the complex **3Ru3**. This complex can be generated by reacting a red solution of [Ru(OTf)(CN)(dppp)<sub>2</sub>] **5Ru3** (see below) with H<sub>2</sub> (step v, Scheme 2).

The addition of an excess of HOTf to a solution of **1Ru3** in C<sub>6</sub>H<sub>6</sub> or CH<sub>2</sub>Cl<sub>2</sub> under 1 atm H<sub>2</sub> gives *trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(CNH)(dppp)<sub>2</sub>](OTf)<sub>2</sub> **4Ru3** as a yellow oil. The dicationic dihydrogen complex is very acidic because, when it is treated with diethyl ether, it produces a mixture of complexes *trans*-[RuH(CNH)(dppp)<sub>2</sub>]OTf **2Ru3** and *trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(CN)(dppp)<sub>2</sub>]OTf **3Ru3** and presumably the strong acid [HOEt<sub>2</sub>]OTf.

**Addition of HOTf to *trans*-[OsH(CN)(dppp)<sub>2</sub>] 1Os3.** When HOTf is added to a CD<sub>2</sub>Cl<sub>2</sub> solution of **1Os3** at room temperature, the CNH derivative **2Os3** is the first species observed by use of <sup>31</sup>P and <sup>1</sup>H NMR. In contrast to **1Ru3**, there is no evidence for the formation of the cyanide dihydrogen complex *trans*-[Os( $\eta^2$ -H<sub>2</sub>)(CN)(dppp)<sub>2</sub>]<sup>+</sup>. Further protonation at the hydride (step vii, Scheme 2) produces the dicationic dihydrogen complex *trans*-[Os( $\eta^2$ -H<sub>2</sub>)(CNH)(dppp)<sub>2</sub>](OTf)<sub>2</sub> **4Os3** as indicated by the appearance of the broad signal at  $\delta$  –4.6 in the high-field range of the <sup>1</sup>H NMR spectrum. The protonation of *trans*-[OsH(CN)(dppp)<sub>2</sub>] **1Os3** in C<sub>6</sub>H<sub>6</sub> or CH<sub>2</sub>Cl<sub>2</sub> solution under 1 atm. of H<sub>2</sub> with an excess of HOTf gives **4Os3** as white solid. This dihydrogen complex is stable with respect to the loss of H<sub>2</sub> both in the solid state and in solution.

#### Addition of HOTf to *trans*-[MH(CN)(dppm)<sub>2</sub>] 1Ru1, 1Os1 and related reactions

When 1 equivalent of HOTf is added to a solution of **1Ru1** in CD<sub>2</sub>Cl<sub>2</sub> under H<sub>2</sub>, the complexes [Ru(H)(CNH)(dppm)<sub>2</sub>]OTf **2Ru1** and [Ru( $\eta^2$ -H<sub>2</sub>)(CN)(dppm)<sub>2</sub>]OTf **3Ru1** appear in the ratio 91:9. The NMR properties of **3Ru1** are listed in Table 2. This ratio is modified to 58:42 if the reaction occurs in Cl<sub>2</sub>CDCDCl<sub>2</sub>. An excess of triflic acid added to a CD<sub>2</sub>Cl<sub>2</sub> solution of **1Ru1** produces a dihydrogen complex, probably **4Ru1**, that is highly unstable at room temperature. It loses the dihydrogen ligand rapidly to give [Ru(OTf)(CNH)(dppm)<sub>2</sub>]OTf **6Ru1**, which is identified by a singlet at  $\delta$  –11.0 in the <sup>31</sup>P NMR spectrum. A solution of this dihydrogen complex **4Ru1** at –80 °C has been characterised by NMR (Table 2). Formation of the dihydrogen complex **3Ru1** can also be observed starting from a **2Ru1** solution in CD<sub>2</sub>Cl<sub>2</sub> or in Cl<sub>2</sub>CDCDCl<sub>2</sub>. The



**Fig. 1** Relative amounts of species observed during the titration of *trans*-RuH(CN)<sub>2</sub>, L = dppe, in CH<sub>2</sub>Cl<sub>2</sub> under H<sub>2</sub> with HOTf. Small amounts of [Ru(OTf)(CNH)L<sub>2</sub>]<sup>+</sup> (10%) are present at 2.0 equiv. of HOTf. Small amounts of [Ru(H<sub>2</sub>O)(CNH)L<sub>2</sub>]<sup>2+</sup> are present at 1.0 equiv. (9%), 2.0 equiv. (16%) and 3.0 equiv. of HOTf (4%).

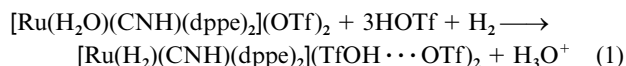
relative percentages measured are the same as found after the protonation of **1Ru1** with 1 equivalent of triflic acid.

The addition of one equivalent of HOTf to **1Os1** in CD<sub>2</sub>Cl<sub>2</sub> at room temperature leads to the formation of exclusively *trans*-[OsH(CNH)(dppm)<sub>2</sub>](OTf)<sup>28</sup> while excess acid produces a violet solution that does not have a dihydrogen resonance in the <sup>1</sup>H NMR spectrum.

#### Addition of HOTf to *trans*-[RuH(CN)(dppe)<sub>2</sub>] **1Ru2** and related reactions

The quantitative titration of complex **1Ru2** in CD<sub>2</sub>Cl<sub>2</sub> with HOTf was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy to determine the approximate relative amounts of the complexes produced (Fig. 1). The acid addition was done under H<sub>2</sub> gas to minimise the formation of the triflate coordinated species *trans*-[Ru(OTf)(CNH)(dppe)<sub>2</sub>](OTf), **6Ru2**. The addition of 0.5 mol of acid to complex **1Ru2** produces a mixture of **1Ru2** and *trans*-[Ru(H)(CNH)(dppe)<sub>2</sub>](OTf) **2Ru2**. Complex **2Ru2** is the predominant species after one equivalent of acid is added. At 1.5 equivalents of acid added, a mixture of the dihydrogen complex *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CN)(dppe)<sub>2</sub>](TfO⋯HOTf), **3'Ru2**, and complex **2Ru2** forms (steps iii, ix, Scheme 2). The **3'** nomenclature indicates that there is an anion effect; this stable complex, which is thought to have the hydrogen-bonded (TfO⋯HOTf)<sup>-</sup> anion, has different solution properties to the unstable dihydrogen complex *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CN)(dppe)<sub>2</sub>](OTf), **3Ru2**, with the OTf<sup>-</sup> anion (see below). When two equivalents of acid have been added, complex **3'Ru2** is the predominant species. The proton of one HOTf is used to protonate the hydride giving the dihydrogen complex while the proton of the other is used to form (TfO⋯HOTf)<sup>-</sup>. This chemical behaviour is different from that of the dppp complexes. Apparently the triflate anion is more basic than the Ru–H bond in **2Ru2** while the metal–hydride bond in **2Ru3** and **2Os3** is more basic than a triflate anion so that protonation produces the dications **4Ru3** and **4Os3**. Between 2.5 and 4.0 equivalents of acid added, the ratio of complex *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CNH)(dppe)<sub>2</sub>](TfO⋯HOTf)<sub>2</sub>, **4'Ru2**, over complex **3'Ru2** increases until it is the only complex present at 4.5 equivalents of acid added (step xi, Scheme 2). In theory, only four equivalents of acid would be required to go from **1Ru2** to **4'Ru2** since two protons from HOTf form complex **4'Ru2** while the rest form the two (TfO⋯HOTf)<sup>-</sup> counter-ions. The requirement of a slight excess reflects the high acidity of complex **4'Ru2**. Under H<sub>2</sub>, only a small amount of complex *trans*-[Ru(OTf)(CNH)(dppe)<sub>2</sub>](OTf), **6Ru2**, forms between 1.5 and 2.5 equivalents of added acid, the maximum relative amount being 10.0% at 2.0 equivalents of acid added.

Between 1.0 and 4.0 equivalents of acid added, a species, suspected to be the aqua complex *trans*-[Ru(H<sub>2</sub>O)(CNH)(dppe)<sub>2</sub>](OTf)<sub>2</sub> (**7Ru2**, see below), is produced from impurities of H<sub>2</sub>O/H<sub>3</sub>O<sup>+</sup>. The relative amount of complex **7Ru2** increases as acid is added, to a maximum of 16% at 2.0 equivalents of acid added. It then decreases as more acid is added until only complex **4'Ru2** is present at 4.5 equivalents of acid added. Therefore this aqua complex can be converted to **4'Ru2** according to eqn. (1).

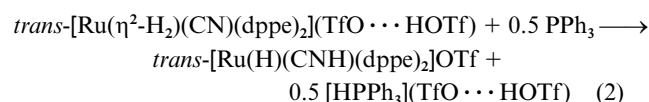


Complex **3'Ru2** appears to be the most unstable of the complexes since the maximum amount of side-reaction complexes **6Ru2** and **7Ru2**, coincides at 2.0 equivalents of acid added, when complex **3'Ru2** is the predominant species. This is consistent with the observation that complex **7Ru2** is only observed in the synthesis of complex **6Ru2** or complex **3'Ru2**. Anytime that complex **3'Ru2** forms, complex **7Ru2** also forms. Therefore, complex **7Ru2** must form by the reaction of trace amounts of water with complex **3'Ru2**. When these reactions are performed under Ar, more than 7 equivalents of acid are required to form complex **4'Ru2** from complex **1Ru2**. Under Ar, when 2 equivalents of acid are added, the amount of complex **6Ru2** present is 46.4% while under H<sub>2</sub>, the amount of complex **6Ru2** present is only 10.0%.

The unstable dihydrogen complex *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CN)(dppe)<sub>2</sub>](OTf), **3Ru2**, has been observed at low temperatures when H<sub>2</sub>(g) is introduced into a solution of *trans*-[Ru(OTf)(CN)(dppe)<sub>2</sub>], **5Ru2** (see below) in CD<sub>2</sub>Cl<sub>2</sub> (step v, Scheme 2). The <sup>1</sup>H NMR spectrum of **3Ru2** recorded at –10 °C shows a broad singlet at δ –7.3 and the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, a singlet at δ 53.7. As the sample was warmed to 10 °C, the appearance of a quintet at δ –9.1 (RuH) and a broad singlet at 10.2 (NH) in the <sup>1</sup>H NMR spectrum signalled the formation of **2Ru2** as did the appearance of a singlet at δ 66.6 in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. Complex **2Ru2** was the major species after 1 h on warming the sample to room temperature. Thus at room temperature, complex **3Ru2** rearranges to the more thermodynamically stable product, complex **2Ru2** (step iv, Scheme 2). The triflate anion is probably weakly hydrogen-bonded to the dihydrogen ligand in **3Ru2** (see below) and could serve as a shuttle to carry the proton from the η<sup>2</sup>-H<sub>2</sub> ligand to the CN ligand, producing **2Ru2**.

There are two routes to the white complex *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CN)(dppe)<sub>2</sub>](TfO⋯HOTf) **3'Ru2**. When the yellow oil of complex **4'Ru2** is stirred in Et<sub>2</sub>O for 30 min, then decanted and quickly dried, complex **3'Ru2** forms (step xii, Scheme 2). In this reaction the very acidic complex **4'Ru2** is deprotonated, presumably to form the strong acid [Et<sub>2</sub>OH](TfO⋯HOTf) which is detected in the <sup>1</sup>H NMR spectrum as a broad singlet at δ 13. The dihydrogen complex **3'Ru2** is soluble in methylene chloride but insoluble in diethyl ether. Under Ar, it is unstable with respect to the loss of H<sub>2</sub> over time to give complex **6Ru2** (step xv, Scheme 2). The addition of H<sub>2</sub> gas to complex **6Ru2** is another route to complex **3'Ru2** (step xvi, Scheme 2).

When one half an equivalent of PPh<sub>3</sub> is added to complex **3'Ru2**, complex **2Ru2** forms (steps x, iv, eqn. (2)). The quintet of complex **2Ru2** is observed in the hydride region of the <sup>1</sup>H NMR spectrum while in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, a singlet at δ 66.6 corresponding to complex **2Ru2** is observed. Resonances for [HPPH<sub>3</sub>](TfO⋯HOTf) at δ 3.4 and complex **7Ru2** at δ 48.4 are also observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. This reaction probably proceeds *via* the formation of complex **3Ru2** as an intermediate.



The addition of excess HOTf (>5 equiv.) to complex *trans*-[RuH(CN)(dppe)<sub>2</sub>] **1Ru2** or complex *trans*-[RuH(CNH)(dppe)<sub>2</sub>]OTf **2Ru2** in CH<sub>2</sub>Cl<sub>2</sub> under Ar produces the complex *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CNH)(dppe)<sub>2</sub>](TfO···HOTf)<sub>2</sub> **4Ru2** which was isolated as a yellow oil. Complex **4Ru2** is a very air sensitive, acidic dihydrogen complex, which is quite stable in the presence of excess acid. It is soluble in methylene chloride and can be deprotonated by diethyl ether. Its spectroscopic properties are discussed below.

#### Protonation of *trans*-[FeH(CN)(dppe)<sub>2</sub>] **1Fe2** and related reactions

The addition of 1 equiv. of HOTf to **1Fe2** in CH<sub>2</sub>Cl<sub>2</sub> produces the hydrogen isocyanide complex **2Fe2** (step i, Scheme 2). The complex *trans*-[Fe(H<sub>2</sub>)(CNH)(dppe)<sub>2</sub>]OTf<sub>2</sub>, **4Fe2**, is prepared by the addition of at least two equivalents of HOTf to **1Fe2** in CH<sub>2</sub>Cl<sub>2</sub> solution (steps i, vii, Scheme 2). The orange colour of **1Fe2** fades to yellow on addition of acid. Some H<sub>2</sub> is liberated from **4Fe2** in solution as revealed by the presence of a signal at δ 4.5 in the <sup>1</sup>H NMR spectrum. Complex **4Fe2** can also be prepared by the addition of HOTf to a yellow CD<sub>2</sub>Cl<sub>2</sub> solution of **2Fe2** (step vii, Scheme 2). Complex **4Fe2** is stable to the loss of dihydrogen in the solid state under vacuum for short periods.

This dihydrogen complex is very acidic as indicated by the deprotonation of **4Fe2** on addition of excess Et<sub>2</sub>O to produce an orange solution of *trans*-[Fe(η<sup>2</sup>-H<sub>2</sub>)(CN)(dppe)<sub>2</sub>]OTf, **3Fe2**. Complex **3Fe2** can be isolated as an impure solid by washing the oil, produced by removal of the solvent from a CH<sub>2</sub>Cl<sub>2</sub> solution of **4Fe2**, with Et<sub>2</sub>O. The yellow oil turns to an orange powder on contact with the ether. Compound **3Fe2** is stable in the solid state as determined by recording the <sup>1</sup>H and <sup>31</sup>P NMR spectra after a period of weeks. It is unstable with respect to tautomeric rearrangement to **2Fe2** in CD<sub>2</sub>Cl<sub>2</sub> solution (step iv, Scheme 2). A solution of **3Fe2** in CD<sub>2</sub>Cl<sub>2</sub> shows resonances in the <sup>31</sup>P spectrum due to both **3Fe2** and **2Fe2** after standing overnight. This process can be promoted by the addition of a small amount of triphenylphosphine as in the case of **3Ru2**.

**Protonation of *trans*-[OsH(CN)(dppe)<sub>2</sub>] **1Os2** and *trans*-[OsH(<sup>13</sup>CNH)(dppe)<sub>2</sub>]OTf **2Os2-c**.** The addition of acid to **1Os2** usually results in the formation of **2Os2**. However if one equivalent of HBF<sub>4</sub>·Et<sub>2</sub>O is added to a solution of **1Os2** in benzene, white *trans*-[Os(η<sup>2</sup>-H<sub>2</sub>)(CN)(dppe)<sub>2</sub>]BF<sub>4</sub>, **3Os2** precipitates (where \* denotes the BF<sub>4</sub><sup>-</sup> salt). This dihydrogen compound in CD<sub>2</sub>Cl<sub>2</sub> is stable to H<sub>2</sub> evolution under Ar but it slowly converts to **2\*Os2** and another complex tentatively identified as *trans*-[OsH(CNBF<sub>3</sub>)(dppe)<sub>2</sub>].<sup>28</sup> The addition of water or ether causes the rearrangement to **2\*Os2**. For example when D<sub>2</sub>O–HBF<sub>4</sub> was used as the acid to prepare **3\*Os2-d** under the same conditions as the preparation of **3Os2**, a significant amount of **2\*Os2-d** also formed.

When 2 equiv. of HOTf or 1 equiv. of DOTf are added to **2Os2-c**, colourless solutions of the complexes *trans*-[Os(η<sup>2</sup>-H<sub>2</sub>)(<sup>13</sup>CNH)(dppe)<sub>2</sub>](OTf)<sub>2</sub>, **4Os2-c**, or *trans*-[Os(η<sup>2</sup>-HD)(<sup>13</sup>CNH)(dppe)<sub>2</sub>](OTf)<sub>2</sub>, **4Os2-c,d** form (step vii, Scheme 2). The NH resonance is averaged with the free acid peak at room temperature in the <sup>1</sup>H NMR spectrum, but at –40 °C it appears as a doublet at δ 10.8 (<sup>2</sup>J(<sup>13</sup>CH) = 31 Hz). Other NMR properties are listed in Table 2.

**Protonation of *trans*-[MH(CN)(depe)<sub>2</sub>] **1M4**, M = Fe, Ru, Os.** When one equivalent or an excess of triflic acid is added to a solution of complex **1Ru4** in CH<sub>2</sub>Cl<sub>2</sub>, the yellow solution changes to a light green colour and effervesces vigorously. Apparently a triflate complex is formed but the characterization of the product was not pursued. Complex **1Fe4** reacts in a similar fashion to give a red solution.

One equivalent of HBF<sub>4</sub>·Et<sub>2</sub>O reacts with complexes **1M4** in CH<sub>2</sub>Cl<sub>2</sub> to give the dihydrogen complexes *trans*-[M(η<sup>2</sup>-H<sub>2</sub>-

(CN)(depe)<sub>2</sub>]BF<sub>4</sub> (**3Ru4**, **3Fe4**) as analyzed by NMR spectroscopy (see Table 2). One equivalent of the weaker acid [Ph<sub>3</sub>PH]BF<sub>4</sub> can also be used to prepare **3Fe4**. Similarly one equivalent of [Ph<sub>3</sub>PH]OTf is used to prepare [Os(η<sup>2</sup>-H<sub>2</sub>)-(<sup>13</sup>CN)(depe)<sub>2</sub>]OTf, **3Os4-c**.

The formation of *trans*-[M(η<sup>2</sup>-H<sub>2</sub>)(CNBF<sub>3</sub>)(depe)<sub>2</sub>]BF<sub>4</sub> by the known reaction of BF<sub>4</sub><sup>-</sup> with CNH ligands can be ruled out because only one equivalent of acid is added. At least two equivalents of acid would be required to supply both the BF<sub>3</sub> and BF<sub>4</sub><sup>-</sup> of such a complex.

The addition of excess HBF<sub>4</sub>·Et<sub>2</sub>O to complex **1Ru4** at room temperature causes immediate gas evolution. Thus a dicationic dihydrogen complex such as **4Ru4** is not stable under these conditions. The addition of two equivalents of 85% [Et<sub>2</sub>OH]BF<sub>4</sub> to **1Fe4** produces *trans*-[Fe(η<sup>2</sup>-H<sub>2</sub>)(CNH)(depe)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, **4Fe4**. The <sup>1</sup>H NMR spectrum of **4Fe4** contains a broad singlet at high field attributed to the dihydrogen ligand. The infrared spectrum of **4Fe4** shows a strong absorption due to the hydrogen isocyanide ligand at 2100 cm<sup>-1</sup> (Nujol mull) or 2103 cm<sup>-1</sup> (CH<sub>2</sub>Cl<sub>2</sub> solution). Preliminary results indicate that **4Os4** can be prepared and is stable under vacuum in solution.

#### Characterisation of the dihydrogen complexes *trans*-[M(η<sup>2</sup>-H<sub>2</sub>)(CN)L<sub>2</sub>]OTf **3Mj**, **3Ru2**, **3Mj**

The properties of these complexes depend on the anion present. Solutions of complexes **3Ru1**, **3Fe2**, **3Ru2**, **3Ru3**, **3Os4** with the triflate anion can be prepared by one of the methods discussed above. These compounds tend to be unstable, readily losing H<sub>2</sub> to give **5Mj** or rearranging to the CNH form **2Mj**. The most stable complex is the osmium one. Similarly the BF<sub>4</sub><sup>-</sup> complex **3Os2** is stable with respect to the loss of H<sub>2</sub>. In the case of the depe complexes, the BF<sub>4</sub><sup>-</sup> complexes **3Fe4** and **3Ru4** are much more stable than the OTf<sup>-</sup> complexes. This can be explained by a M–OTf bond strength that is greater than that of M–F<sub>3</sub>B. Attempts to grow crystals of complex **3Ru2** by slow diffusion of Et<sub>2</sub>O into a saturated solution of complex **3Ru2** in CH<sub>2</sub>Cl<sub>2</sub> under H<sub>2</sub> produced complex **2Ru2** as identified by NMR spectroscopy.

These complexes are in the *trans* configuration according to the <sup>31</sup>P NMR spectra. The spectra are singlets at room temperature while that of **3Ru3**, at –90 °C, resolves to an A<sub>2</sub>X<sub>2</sub> pattern with triplets at δ 2.7 and 16.8 (*J*(P,P') = 28.9 Hz). This is typical of *trans*-M(dppp)<sub>2</sub>XY complexes. The usual periodic trend of δ(PFe) > δ(PRu) > δ(POs) is observed. Compound **3Ru2** with the (TfO···HOTf)<sup>-</sup> anion has a slightly different chemical shift (δ 54.2) than **3Ru2** (53.7) with the OTf<sup>-</sup> anion, although the sample temperatures were different (Table 2). This may reflect the difference in ion-pairing and hydrogen-bonding that is more marked in the <sup>1</sup>H spectra (see below).

The dihydrogen ligand is identified by a broad resonance located at between δ –8 and –14 for iron and between –4 and –10 for ruthenium and osmium (Table 2). The *T*<sub>1</sub>(min) values of the η<sup>2</sup>-H<sub>2</sub> ligand in all of the complexes **3Mj** are quite similar when converted to a common frequency: about 11 ms for Fe, 8 to 13 ms for Ru and 15 and 16 ms for the two Os complexes. Typically osmium dihydrogen complexes have longer *T*<sub>1</sub>(min) values than corresponding Fe and Ru analogues, indicative of a longer H–H distance in the Os case. This is supported by the correlation between *J*(HD) and *d*(HH)<sup>29</sup> where the **3Fej-d** and **3Ruj-d** complexes have *J*(HD) of 31.6 to 32.7 Hz corresponding to *d*(H–H) of 0.89–0.87 Å while **3Os2-d** and **3Os4-d** have *J*(HD) of 28.7 and 25.4 corresponding to *d*(H–H) of 0.94 and 1.06 Å, respectively. The <sup>1</sup>H NMR resonances of the HD ligand in the complexes **3Ru2-d** and **3Ru3-d** appear as 1 : 1 : 1 triplets of quintets with rarely observed <sup>2</sup>*J*(H,P) couplings of 5 and 3 Hz, respectively while those of the Fe and Os complexes are broad 1 : 1 : 1 triplets. The complexes with dppe and depe ligands appear to have “fast-spinning” dihydrogen ligands on the basis of the agreement of the H–H distances calculated from *J*(HD)

and  $T_1(\text{min})$  (Table 2) while those with the dpmm and dppp ligands have  $\text{H}_2$  moving in a way that does not influence dipolar relaxation as much as free spinning, possibly undergoing a torsional libration in a potential well that restricts rotation.<sup>30</sup> The  $T_1$  data examined fit the conventional  $\ln T_1$  versus  $1/T$  curve (see the Supplementary information for fitting parameters, SUP 57672). The complex  $\text{trans}[\text{Ru}(\text{H}_2)(\text{CCPh})(\text{P}^i\text{Pr}_2\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)]^+$  which has a structure related to that of **3Ru4** has been reported to have a similar  $T_1(\text{min})$ .<sup>31,32</sup>

Carbon-13 labelling provides evidence for the  $^{13}\text{C}$  ligand in **3Ru3-c** and **3Os4-c**. The  $^{31}\text{P}$  NMR spectrum in each case is a doublet with  $^2J(\text{PC}) = 14.3$  and  $11.8$  Hz, respectively, while the  $^{13}\text{C}$  resonances at  $\delta$  142.4 and 120.9, respectively, are quintets. A Nujol mull of **3Os4-c** has a  $^{13}\text{C}-\text{N}$  mode at  $2064\text{ cm}^{-1}$  while a film of **3Fe2** has a  $^{12}\text{C}-\text{N}$  band at  $2006\text{ cm}^{-1}$ .

The proton of the anion  $(\text{TfO}\cdots\text{HOTf})^-$  of **3Ru2** is observed at  $\delta$  13.1. As the temperature is decreased, this peak shifts downfield. At  $-50^\circ\text{C}$ , a new peak at  $\delta$  16.8 is observed. At  $-60^\circ\text{C}$ , three peaks are observed in the acid region of the  $^1\text{H}$  NMR spectrum at  $\delta$  12.5 and 12.9 and 16.8. Bullock *et al.*<sup>9</sup> have studied low temperature  $^1\text{H}$  NMR spectra of HOTf in  $\text{CD}_2\text{Cl}_2$ . They attributed the resonance near  $\delta$  17 to  $(\text{TfO}\cdots\text{HOTf})^-$  while those near  $\delta$  12 to excess HOTf present as  $(\text{HOTf})_n$  aggregates or possibly partially dissolved  $(\text{HOTf})_n$  aggregates in solution at low temperatures. Since excess acid was not present in the sample of **3Ru2**, aggregates of HOTf should not be present. Bullock also noted that the solubility of HOTf increases in the presence of  $\text{TfO}^-$  anions. Therefore the peaks observed at  $\delta$  12.5 and  $\delta$  12.9 are probably due to the formation of some other triflic acid-triflate aggregate species.

Surprisingly, the dihydrogen complexes  $\text{trans}[\text{Ru}(\eta^2\text{-H}_2)(\text{CN})(\text{dppe})_2](\text{TfO}\cdots\text{HOTf})$  **3Ru2** and  $\text{trans}[\text{Ru}(\eta^2\text{-H}_2)(\text{CN})(\text{dppe})_2]\text{OTf}$  **3Ru2** in  $\text{CD}_2\text{Cl}_2$  have quite different  $^1\text{H}$  NMR properties in the hydride region. The former complex exhibits a broad singlet at  $\delta$   $-5.5$  while the latter, a broad singlet at  $\delta$   $-7.3$ . The anion of **3Ru2** is proposed to have conventional  $\text{CF}_3\text{O}_2\text{SO}\cdots\text{HOSO}_2\text{CF}_3$  hydrogen bonding while the  $\text{OTf}^-$  anion of **3Ru2** may be involved in a non-classical  $\text{CF}_3\text{O}_2\text{SO}\cdots(\text{HH})\text{Ru}$  hydrogen bond to the dihydrogen ligand as shown in Scheme 2. This would explain the differences in the NMR spectra of the two complexes and why **3Ru2** rearranges readily at room temperature (see below). Such non-classical hydrogen bonds have been characterised crystallographically for  $\text{IrCl}\cdots(\text{HH})\text{Ir}$  in  $\text{Ir}(\eta^2\text{-H}_2)(\text{Cl})_2(\text{H})(\text{P}^i\text{Pr}_3)_2$ ,<sup>23</sup>  $\text{FeH}\cdots(\text{HH})\text{Fe}$  in  $\text{Fe}(\eta^2\text{-H}_2)(\text{H})_2(\text{PEtPh}_2)_3$ <sup>33</sup> and  $\text{BF}\cdots(\text{HH})\text{Os}$  in  $[\text{Os}(\eta^2\text{-H}_2)(\text{CH}_3\text{CN})(\text{dppe})_2](\text{BF}_4)_2$ .<sup>8</sup> In the last example the acidic  $\eta^2\text{-H}_2$  ligand forms a  $2.4\text{ \AA}$   $\text{H}\cdots\text{F}$  contact with one of the  $\text{BF}_4^-$  anions. The H–H distance of complex **3Ru2** might be expected to be longer than that of **3Ru2** due to the hydrogen bonding but this difference is not detectable by  $J(\text{HD})$  or  $T_1(\text{min})$  (Table 2). The dihydrogen ligand in all of the complexes **3Mj** might act as hydrogen bond donors to triflate but this is difficult to prove.

#### Characterisation of the dihydrogen complexes $\text{trans}[\text{M}(\eta^2\text{-H}_2)(\text{CNH})\text{L}_2](\text{OTf})_2$ **4Mj**

These complexes are characterised in  $\text{CD}_2\text{Cl}_2$  solution, under  $\text{H}_2$  in the presence of an excess of HOTf, by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR and IR spectroscopy in certain cases. The complexes are in the *trans* configuration according to the  $^{31}\text{P}$  spectra. The dpmm and dppe complexes show singlets while the dppp complexes at low temperature show a characteristic set of two triplets probably due to the conformation of the backbones of the dppp ligands. For each pair of complexes **3Mj** and **4Mj**, the resonance for **4Mj** is between 1 and 6 ppm upfield of that of **3Mj** (Table 2). Again the  $^{31}\text{P}$  chemical shifts follow the usual periodic trend  $\text{Fe} > \text{Ru} > \text{Os}$  for analogous complexes.

The dihydrogen ligand in the complexes produce a broad

resonance at between  $\delta$  *ca.*  $-3$  and  $\delta$   $-12$  (Table 2). The chemical shift in each case is downfield of the monocationic dihydrogen complex **3Mj**. The short minimum  $T_1$  values indicate H–H distances in the range  $0.8$  to  $1.0\text{ \AA}$  depending on interpretation of the relative motions of the  $\text{H}_2$  ligand and the molecule as a whole. The values are not significantly different from those of corresponding complexes **3Mj**. The HD analogues were produced by reacting complexes **1Mj** in  $\text{CD}_2\text{Cl}_2$  solution with excess  $\text{CF}_3\text{SO}_3\text{D}$ . The ruthenium complexes all have coupling constants  $J(\text{HD})$  of about  $32\text{ Hz}$ , not significantly different than those of **3Ru3**. The correlation between  $J(\text{HD})$  and distance yields a value of about  $0.88\text{--}0.89\text{ \AA}$ . For the dppe complex **4Ru2** this distance agrees well with the H–H distance calculated from the  $T_1(\text{min})$  value for a fast spinning dihydrogen ligand. For the dpmm and dppp complexes, the distance from  $J(\text{HD})$  is intermediate in the range from the  $T_1$  calculation. This suggests that there may be a barrier to rotation, so that torsional-librational motion becomes important.<sup>30</sup>

The lack of variation in  $J(\text{HD})$  with a variation in ancillary ligands is typical of complexes that have  $\eta^2\text{-HD}$  coordinated *trans* to a strong field,  $\pi$ -acid ligand like CO, CNH or  $\text{CN}^-$ .<sup>34</sup>

There is  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  evidence for the CNH ligands. The NH resonance for **4Fe2** is a 1:1:1 triplet at  $\delta$  8.79 with  $^1J_{\text{NH}} = 80\text{ Hz}$  while that for **4Ru2** is a broad singlet at  $\delta$  10.3 due to rapid proton exchange with the excess free acid present. The acid peak appears in the  $^1\text{H}$  NMR spectra at *ca.*  $12.7$ . The excess acid is most likely to be present as HOTf hydrogen bonded to itself or as dynamic clusters involving the  $\text{TfO}^-$  anion such as  $(\text{TfO}\cdots\text{HOTf})^-$ .<sup>9</sup> Complex **4Os2-c** has a broad doublet at  $\delta$  10.8 with  $^2J(\text{HC}) = 30.8\text{ Hz}$ . For **4Ru3** and **4Os3** the  $^1\text{H}$  resonance of the CNH ligand is not observed at room temperature probably owing to the proton exchange between the coordinated CNH and the HOTf. It appears as a broad singlet at  $\delta$  13.7 and 14.1, respectively, at  $-90^\circ\text{C}$ . This resonance shows a doublet with  $^1J(\text{H},^{15}\text{N}) = 108.1$  and  $101.4\text{ Hz}$ , respectively, in the  $^1\text{H}$  spectrum at the same temperature of the  $^{15}\text{N}$  enriched compounds  $\text{trans}[\text{M}(\eta^2\text{-H}_2)(\text{C}^{15}\text{NH})(\text{dppp})_2](\text{OTf})_2$  **4M3-n**. The  $^{15}\text{N}$  NMR spectrum of **4Os3-n** shows a doublet at  $\delta$   $-205$  with  $^1J(\text{NH})$   $102\text{ Hz}$ . Therefore the ligand is coordinated as MCNH and not MNCH. Similarly the CNH and acid peaks for the species at  $-80^\circ\text{C}$  thought to be **4Ru1** occur at  $\delta$  12.8 (broad) and 11.3, respectively.

Further evidence for the CNH ligand in **4M3** derives from monitoring the protonation of the  $^{13}\text{C}$  enriched compounds  $\text{trans}[\text{M}(\text{H})(^{13}\text{CN})(\text{dppp})_2]$  **1M3-c** to produce  $\text{trans}[\text{M}(\eta^2\text{-H}_2)(^{13}\text{CNH})(\text{dppp})_2](\text{OTf})_2$  **4M3-c**. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum the  $^{13}\text{C}$  quintet of **1M3-c** at  $\delta$  156.7 and 137.9 for  $\text{M} = \text{Ru}$  and  $\text{M} = \text{Os}$ , respectively, broadens and shifts to  $\delta$  149.9 ( $^2J(\text{C,P}) = 13.6\text{ Hz}$ ) and 133.2 ( $^2J(\text{C,P}) = 10.2\text{ Hz}$ ), respectively, with the protonation. The  $^{31}\text{P}$  signal is a doublet at  $\delta$  8.9 ( $^2J(\text{P,C}) = 13.5\text{ Hz}$ ) and  $-29.4$  ( $^2J(\text{P,C}) = 7.9\text{ Hz}$ ), respectively.

The C–N mode at  $2056\text{ cm}^{-1}$  of the CNH ligand was detected by IR spectroscopy of **4Fe2** as a film on NaCl. A  $\text{CH}_2\text{Cl}_2$  solution of **4Ru3** has a  $\text{C}\equiv\text{N}$  mode at  $2125\text{ cm}^{-1}$  while a Nujol mull of **4Os3** gives a  $\text{C}\equiv\text{N}$  stretch at  $2129\text{ cm}^{-1}$ . On this basis, the **Fe2** centre seems to be more  $\pi$ -basic than the **Ru3** and **Os3** centres.

#### Acidity of the dihydrogen complexes

The determination of  $\text{p}K_a$  values for these complexes is complicated by their reactivity and the myriad of equilibria possible. The complex **4Ru2** is the most acidic complex since it is only completely formed in an excess of HOTf in  $\text{CH}_2\text{Cl}_2$ . Therefore its  $\text{p}K_a$  is near to that of HOTf in  $\text{CH}_2\text{Cl}_2$  (the aqueous  $\text{p}K_a$  of HOTf has been estimated to be  $-5$ ).<sup>2</sup> Complexes **4Fe2** and **4Os2** are less acidic because they are completely formed by the addition of two equivalents of HOTf to **1Fe2** or **1Os2**. Com-

plex **4Ru3** requires three equivalents of HOTf from **1Ru3** for complete formation and so it is also very acidic but less acidic than **4Ru2**. This is in keeping with the dppp ligand being more donating than the dppe ligand. Complexes **4Ru2** and **4Fe2** are deprotonated by treatment with diethyl ether (the aqueous  $pK_a$  of  $[\text{Et}_2\text{OH}]^+$  is reported to be  $-2.4$ )<sup>35</sup> and so they are very acidic. Complex **3Ru2** at 163 K in  $\text{CH}_2\text{Cl}_2$  must be less acidic than HOTf because it forms the hydrogen-bonded structure  $\text{Ru}(\text{HH})\cdots\text{OTf}$ . The monocationic complex **3Fe2** is less acidic than the dication **4Fe2** because **3Fe2** is not deprotonated in diethyl ether while **4Fe2** is. The dihydrogen site of **3M2**,  $M = \text{Fe}, \text{Ru}$ , is more acidic than the CNH site of **2M2** because these complexes rearrange from **3M2** to **2M2**. The depe complexes **3\*Fe4** and **3Os4** are less acidic than  $\text{HPPH}_3^+$  in  $\text{CH}_2\text{Cl}_2$  which has an estimated  $pK_a$  of 2.7 in water.<sup>36</sup>

The  $pK_a$  of **3\*Fe4** was determined in THF by monitoring the equilibrium between *trans*- $\text{Fe}(\text{H})(\text{CN})(\text{depe})_2$  with  $[\text{Cy}_3\text{PH}]\text{BF}_4$  by  $^{31}\text{P}\{^1\text{H}\}$  NMR. The gated decoupled spectrum was collected with a 10 s delay time to allow adequate time for relaxation of the  $^{31}\text{P}$  nuclei. The resonance observed at 22.2 ppm is at an average position between those of free  $\text{PCy}_3$  (10.9 ppm) and  $[\text{Cy}_3\text{PH}]^+$  (29.9 ppm). The ratio of  $[\text{Cy}_3\text{PH}]^+$  to  $\text{PCy}_3$  is 0.69. The integrations of the resonances due to *trans*- $\text{Fe}(\text{H})(\text{CN})(\text{depe})_2$ , **1Fe4**, and **3\*Fe4** are used to determine their molar ratio of 3.74. Therefore the  $pK_a$  of **3\*Fe4** is calculated to be 9.0 with respect to the  $pK_a$  of  $[\text{Cy}_3\text{PH}]^+$ , which is estimated to be 9.7 in water<sup>36</sup> and is used as an arbitrary anchor for the THF scale.<sup>37</sup>

The  $pK_a$  of *trans*- $[\text{Fe}(\text{H}_2)(\text{CNH})(\text{depe})_2](\text{BF}_4)_2$ , **4\*Fe4**, was determined in THF by monitoring the equilibrium between  $[\text{Ph}_3\text{PH}](\text{BF}_4)$  and *trans*- $[\text{Fe}(\text{H}_2)(\text{CN})(\text{depe})_2]\text{BF}_4$ , **3\*Fe4**, by  $^1\text{H}$  and  $^{31}\text{P}$  NMR. The resonance at  $\delta -2.47$  in the  $^{31}\text{P}$  NMR spectrum is intermediate between the chemical shifts of  $\text{PPh}_3$  ( $\delta -6$ ) and  $[\text{Ph}_3\text{PH}](\text{BF}_4)$  ( $\delta 4$ ). The integrations of the dihydrogen resonances in the  $^1\text{H}$  NMR spectrum were used to calculate the ratio of **3\*Fe4** to **4\*Fe4** of 1.29. Therefore the  $pK_a$  of **4\*Fe4** in  $\text{CH}_2\text{Cl}_2$  must be similar to that of  $[\text{Ph}_3\text{PH}]^+$  ( $pK_a$  approx. 2.7 in water).

It is significant that the very acidic dihydrogen complexes **4Ru2** and **4Ru3** can be formed by reaction of complexes **6RuJ** in  $\text{HOTf}-\text{CH}_2\text{Cl}_2$  with dihydrogen gas. In the absence of an excess of acid, complex **4Ru2** eliminates HOTf as  $\text{TfO}\cdots\text{HOTf}^-$  (step xvi, Scheme 2). There are only a few other examples of very acidic dihydrogen complexes being generated by reaction with hydrogen gas as mentioned in the introduction.

#### Interconversion of $[\text{M}(\text{H})(\text{CNH})\text{L}_2]^+$ and $[\text{M}(\text{H}_2)(\text{CN})\text{L}_2]^+$

Some qualitative statements can be made about the relative rates of these reactions and implications for the mechanism. The rate of rearrangement of **3Ru2** to **2Ru2** in  $\text{CH}_2\text{Cl}_2$  (step iv, Scheme 2) is much faster than that of **3Ru3** to **2Ru3**. The triflate anion might serve to shuttle the proton from the dihydrogen on one side to the cyanide on the other side of the molecule. There is evidence that the addition of a base or the use of a basic solvent destabilises **3RuJ**, **3Fe2**, and **3\*Os2** with respect to complexes **2Mj** and speeds the rearrangement. For example acetone and THF favour **2Ru3** over **3Ru3**. In the presence of  $\text{Et}_2\text{O}$ , complexes **3Ru2** and **3\*Os2** rearrange to the thermodynamically stable complexes **2Ru2** and **2\*Os2** over time. This reaction of **3Ru2** is similar to the addition of  $\text{PPh}_3$  to complex **3Ru2** to form complex **2Ru2** (eqn. (2)). Basic solvents might destabilise the putative  $\text{Ru}(\text{HH})\cdots\text{OTf}^-$  interaction over the  $\text{CNH}\cdots\text{OTf}^-$  hydrogen bond.

The reverse reaction, step iii (Scheme 2), is not observed for **2Ru2** in the absence of acid while it is slow for **2Ru3** on approaching an equilibrium with **3Ru3** under  $\text{H}_2$  in chlorinated solvents. This is also illustrated by the fact that **2Ru2** is stable

**Table 3** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for *trans*- $[\text{Ru}(\text{OTf})(\text{CNH})(\text{dppe})_2]\text{OTf}$  **6Ru2**<sup>3</sup> and *trans*- $[\text{Ru}(\text{OTf})(\text{CN})(\text{dppe})_2]$  **5Ru2**

	<b>6Ru2</b>	<b>5Ru2</b>
Ru(1)–O(1)	2.299(2)	
Ru(1)–O(3)		2.410(5)
Ru(1)–C(5)	1.882(3)	1.94(1)
Ru(1)–P(1)	2.3938(7)	2.376(2)
Ru(1)–P(2)	2.3848(8)	2.400(2)
Ru(1)–P(3)	2.4364(8)	2.361(2)
Ru(1)–P(4)	2.4144(8)	2.381(2)
N(1)–C(5)	1.150(4)	1.18(1)
N(1)–H(1N)	0.76(4)	
N(1) $\cdots$ O(3S)	2.616(4)	
H(1N) $\cdots$ O(3S)	1.86	
S(1)–O(1)–Ru(1)	148.4(1)	
S(1)–O(3)–Ru(1)		160.5(3)
C(5)–Ru(1)–O(1)	171.3(1)	170.7(3)
N(1)–C(5)–Ru(1)	177.1(3)	176.4(7)
H(1N)–N(1)–C(5)	173(4)	

under Ar while **2Ru3** slowly changes to **3Ru3** and then to **5Ru3**. The addition of HOTf causes the rapid conversion of **2Ru2** to **3Ru2**.

#### Preparation and properties of the complexes *trans*- $[\text{Ru}(\text{OTf})(\text{CNH})\text{L}_2]\text{OTf}$ **6RuJ**

When the excess acid is removed from complexes **4Ru2** and **4Ru2-d<sub>4</sub>** by washing with  $\text{Et}_2\text{O}$ , complexes **3Ru2** or **3Ru2-d<sub>4</sub>** form but the  $\eta^2\text{-H}_2$  or  $\eta^2\text{-HD}$  ligands in these complexes are labile. A slow substitution by triflate produces the complexes *trans*- $[\text{Ru}(\text{OTf})(\text{CNH})(\text{dppe})_2]\text{OTf}$  (**6Ru2**) and *trans*- $[\text{Ru}(\text{OTf})(\text{CN})(\text{dppe})_2]\text{OTf}$  (**6Ru2-d**) (step xv, Scheme 2). Complexes **6Ru2** and **6Ru2-d** are white solids that are soluble in  $\text{CH}_2\text{Cl}_2$  but insoluble in diethyl ether. Complex **6Ru2** has a 1:1:1 triplet corresponding to the NH group at  $\delta 10.2$  ( $^1J(\text{HN}) = 79.2$  Hz) in the  $^1\text{H}$  NMR spectrum. A singlet at  $\delta 48.8$  is observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum for this *trans* complex. An X-ray diffraction study<sup>3</sup> as well as microanalysis confirm the identity of complex **6Ru2**. The bond distances and angles for this complex are listed in Table 3 for comparison with the structure of **5Ru2**.

The IR spectrum of complex **6Ru2** was recorded in Nujol. A weak broad band is observed at  $2533\text{ cm}^{-1}$  as a combination of the  $\text{NH}\cdots\text{O}$  and C–N modes. The deuterated analogue **6Ru2-d** gave a more intense, broad peak at  $2275\text{ cm}^{-1}$ , similar to that shown for complex **2Ru2-d**.<sup>28</sup>

$[\text{Ru}(\text{OTf})(\text{CNH})(\text{dppp})_2]\text{OTf}$  **6Ru3** was prepared by bubbling argon through a stirred solution of excess triflic acid and complex **1Ru3** or **2Ru3** and then by precipitating with diethyl ether. The  $^{31}\text{P}$  NMR spectrum is a singlet at room temperature and an  $\text{A}_2\text{X}_2$  pattern at  $-80^\circ\text{C}$  comprised of two triplets at  $\delta 0.9$  and  $-7.3$  with  $^2J(\text{P,P}') = 32.7$  Hz. The NH resonance is observed in the  $^1\text{H}$  NMR spectrum as a broad singlet at  $\delta 11.0$  at  $-80^\circ\text{C}$  but is not observed at room temperature because of exchange processes. The  $^{13}\text{C}$  enriched complex **6Ru3-c** shows a doublet at  $\delta 1.9$  in the  $^{31}\text{P}$  NMR spectrum with  $^2J(\text{P,C}) = 13.5$  Hz and a broad signal at  $\delta 159.7$  in the  $^{13}\text{C}$  NMR spectrum. A weak C–N vibrational band of the complex in Nujol was detected at  $2074\text{ cm}^{-1}$  by IR spectroscopy.

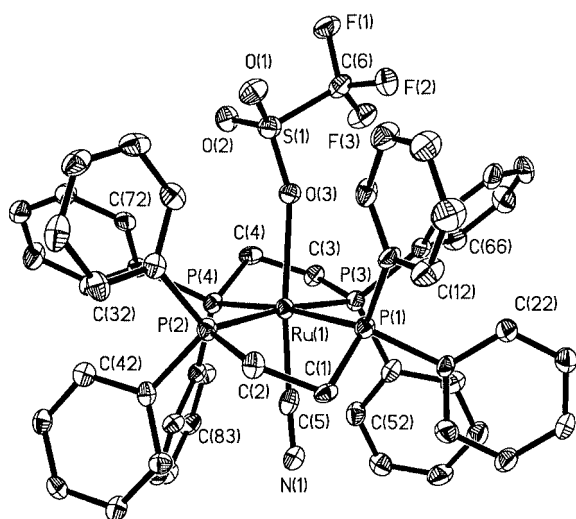
When  $\text{H}_2$  gas is bubbled into a  $\text{CD}_2\text{Cl}_2$  solution of complex **6Ru2** or **6Ru3** in the presence of HOTf, complexes **4Ru2** or **4Ru3** form, respectively (step xiv, Scheme 2).

#### Preparation and properties of the complexes *trans*- $[\text{Ru}(\text{OTf})(\text{CN})\text{L}_2]$ **5RuJ**

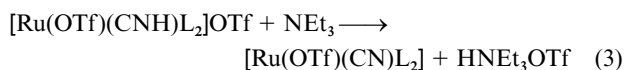
The yellow complexes **5Ru2** and **5Ru3** can be prepared by

**Table 4** Crystallographic data for **5Ru2**

<b>5Ru2</b>	
Empirical formula	C <sub>54</sub> H <sub>48</sub> F <sub>3</sub> NO <sub>3</sub> P <sub>4</sub> RuS
Formula weight	1072.94
<i>T</i> /K	150.0(1)
$\lambda/\text{\AA}$	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> / $\text{\AA}$	16.6236(5)
<i>b</i> / $\text{\AA}$	17.0227(6)
<i>c</i> / $\text{\AA}$	18.0640(8)
$\beta/^\circ$	91.978(5)
<i>V</i> / $\text{\AA}^3$	5108.7(3)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> /Mg m <sup>-3</sup>	1.395
$\mu/\text{mm}^{-1}$	0.527
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0668, <i>wR</i> 2 = 0.1617
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1241, <i>wR</i> 2 = 0.1831

**Fig. 2** The structure and labelling of *trans*-[Ru(OTf)(CN)(dppe)<sub>2</sub>]**5Ru2**. Thermal ellipsoids represent the 30% probability surfaces.

removing one equivalent of HOTf from the corresponding complexes **6Ru<sub>j</sub>** by use of triethylamine (eqn. (3)).



In addition, complexes **5Ru<sub>1</sub>**, **5Ru<sub>2</sub>** and **5Ru<sub>3</sub>** have been observed to form from corresponding complexes **3Ru<sub>j</sub>** by loss of H<sub>2</sub> (step vi of Scheme 2). In a similar fashion the unstable dihydrogen complex [Cp\*Re(H<sub>2</sub>)(NO)(CO)](OTf) loses H<sub>2</sub> at 253 K to give Cp\*Re(OTf)(NO)(CO).<sup>6</sup>

The structure of a crystal of **5Ru<sub>2</sub>** was determined by X-ray diffraction (Fig. 2, Tables 3, 4). Complexes **6Ru<sub>2</sub>** and **5Ru<sub>2</sub>** have very similar structures with very similar bond lengths and bond angles. Since both complexes readily lose the triflate ligand to form dihydrogen complexes under H<sub>2</sub>, it is not surprising to find very long Ru–O distances. Complex **6Ru<sub>2</sub>** contains an Ru(1)–O(1) distance of 2.299(2) Å with a C(5)–Ru(1)–O(1) angle of 171.3(1)°, while complex **5Ru<sub>2</sub>** contains an exceptionally long Ru(1)–O(3) distance of 2.410(5) Å and a C(5)–Ru(1)–O(1) angle of 170.7(3)°. The long Ru–O distances may be due to the steric interactions of the oxygen and fluorine atoms on the triflate ligand with the Ph groups of the dppe ligands. A typical Ru–O distance is approximately 2.1 Å.<sup>38</sup> For example the complex CpRu(P(CF<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P(CF<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>)(OTf) has a Ru–O distance of 2.2 Å.<sup>39</sup>

The <sup>1</sup>H NMR spectrum of complex **5Ru<sub>2</sub>** in CD<sub>2</sub>Cl<sub>2</sub> is very similar to that observed for complex **6Ru<sub>2</sub>** except for the lack of

an NH resonance. A singlet at  $\delta$  52.1 is observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. The IR spectrum of **5Ru<sub>2</sub>** in Nujol has two sharp bands at 2078 cm<sup>-1</sup> (strong) and at 2068 cm<sup>-1</sup> (medium intensity). Complexes **5Ru<sub>1</sub>** and **5Ru<sub>3</sub>** are characterised by broad singlets at  $\delta$  -9.1 and 4.8, respectively, in their <sup>31</sup>P NMR spectra. The latter changes to a doublet with <sup>13</sup>CN labeling (*J*(<sup>13</sup>CP) = 13.5 Hz).

It is interesting that when complex **5Ru<sub>2</sub>** is dissolved in THF, the solution remains yellow but when complex **5Ru<sub>2</sub>** is dissolved in CH<sub>2</sub>Cl<sub>2</sub>, a red solution forms but becomes yellow after approximately 1 h. Yellow crystals of complex **5Ru<sub>2</sub>** were formed by dissolving it in CH<sub>2</sub>Cl<sub>2</sub> and diffusing in Et<sub>2</sub>O. When the yellow crystals are redissolved in CH<sub>2</sub>Cl<sub>2</sub>, a red solution reforms. Perhaps the red species is [Ru(CN)(dppe)<sub>2</sub>](OTf) while the yellow species in a THF or CH<sub>2</sub>Cl<sub>2</sub> solution is [Ru(CN)-(solv)(dppe)<sub>2</sub>](OTf) with a coordinated solvent molecule. For example Huhmann-Vincent *et al.* have recently synthesised and structurally characterised the complexes *cis*-[Re(CO)<sub>4</sub>(PR<sub>3</sub>)-(CH<sub>2</sub>Cl<sub>2</sub>)<sup>+</sup>] (R = Ph or Cy) containing a monodentate CH<sub>2</sub>Cl<sub>2</sub> ligand.<sup>5</sup>

### *trans*-[Ru(H<sub>2</sub>O)(CNH)(dppe)<sub>2</sub>](OTf)<sub>2</sub> **7Ru2**

This complex was detected as an impurity in the crude complex **6Ru<sub>2</sub>** when prepared from complex **3Ru<sub>2</sub>** or if pure **6Ru<sub>2</sub>** is left in a moist Ar atmosphere. Complex **7Ru<sub>2</sub>** is associated with a singlet at  $\delta$  48.4 in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (in CD<sub>2</sub>Cl<sub>2</sub>) and a triplet at  $\delta$  11.7 (<sup>1</sup>*J*(HN) = 79.2 Hz) and a sharp singlet at  $\delta$  3.2 (OH<sub>2</sub>) in the <sup>1</sup>H NMR spectrum. A drop of degassed water added to the NMR tube containing impure complex **6Ru<sub>2</sub>** in CD<sub>2</sub>Cl<sub>2</sub> causes the peak at  $\delta$  3.2 in the <sup>1</sup>H spectrum and at  $\delta$  48.4 in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum to intensify. For comparison, the aqua ligand in *trans*-[Os(η<sup>2</sup>-H<sub>2</sub>)(H<sub>2</sub>O)-(dppe)<sub>2</sub>](OTf)<sub>2</sub><sup>40</sup> and [Ru(tpb)(PCy<sub>3</sub>)(OH<sub>2</sub>)(η<sup>2</sup>-H<sub>2</sub>)]BF<sub>4</sub> (tpb = trispyrazolylborate, Cy = cyclohexyl)<sup>41</sup> produce singlets in the <sup>1</sup>H NMR spectra at  $\delta$  3.2 and  $\delta$  3.43, respectively. Crystals of **7Ru<sub>2</sub>** were grown and X-ray diffraction studies were carried out. Unfortunately, the results were inconclusive due to disorder across a centre of symmetry located at Ru.

## Conclusions

A range of dihydrogen complexes of the type *trans*-[M(η<sup>2</sup>-H<sub>2</sub>)(CN)L<sub>2</sub>]<sup>+</sup> and *trans*-[M(η<sup>2</sup>-H<sub>2</sub>)(CNH)L<sub>2</sub>]<sup>2+</sup> where M = Fe, Ru, Os have been characterized. The stability of these complexes **3M<sub>j</sub>** and **4M<sub>j</sub>** with respect to dihydrogen displacement increases qualitatively as Ru < Fe < Os. This order is paralleled in the other known series of complexes with the triad of iron group metals: *trans*-[M(H<sub>2</sub>)(H)L<sub>2</sub>]<sup>+</sup> L = dppe, dtfpe or depe<sup>42,43</sup> and *trans*-[M(H<sub>2</sub>)(H)(PPh<sub>2</sub>OEt)<sub>4</sub>]<sup>44</sup> and *trans*-[M(H<sub>2</sub>)(H)-(meso-tetraphos)]<sup>+</sup> (meso-tetraphos = (*R,S,S,R*)-PPh<sub>2</sub>(CH<sub>2</sub>-CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>).<sup>45</sup> The <sup>1</sup>*J*(HD) and *T*<sub>1</sub>(min) values of **3M<sub>j</sub>** and **4M<sub>j</sub>** are very similar to those of similar complexes *trans*-[M(H<sub>2</sub>)(H)L<sub>2</sub>]<sup>+</sup>.<sup>2,42</sup> This indicates that hydride and cyanide and hydrogen isocyanide all have a high *trans*-influence on the dihydrogen ligand.

The thermodynamically favoured site of protonation of *trans*-[M(H)(CN)(L)<sub>2</sub>] can be directed to hydride when L = depe (producing a dihydrogen ligand tautomer) or to cyanide when L = dppe (producing a hydrogen isocyanide ligand tautomer). In no case does protonation occur at the metal to produce a stable dihydride. In the case of the dppe, dppp and dppm ligands, the tautomers are on a delicate balance that can be tipped one way ([M(η<sup>2</sup>-H<sub>2</sub>)(CN)L<sub>2</sub>]<sup>+</sup>) or the other ([MH(CNH)L<sub>2</sub>]<sup>+</sup>) by changes in solvent and the hydrogen bonding characteristics of the anion. The isocyanide complexes of the type [MH(CNH)(depe)]<sup>+</sup> are not observed and seem to be thermodynamically much less stable than the dihydrogen tautomers. This can be rationalised mainly as an electronic effect that drops off with the number of bonds from the site of change of



the substituent R on phosphorus. The dihydrogen ligand is two bonds from the change at P while the N–H bond is four bonds removed. Therefore the depe complexes are expected to have metal-hydride sites that are more basic than the other complexes but have nitrogen sites that are of similar basicity.<sup>16</sup> The greater donor effect of depe has been demonstrated by studying properties of diphosphine complexes *trans*-[MX(Y)(PR<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>-PR<sub>2</sub>)<sub>2</sub>] by use of IR, electrochemical and pK<sub>a</sub> measurements.<sup>43,46–50</sup> Another important factor is the strength of hydrogen-bonding in the ion pairs in solution. The CNH ligand forms a strong hydrogen bond to the triflate anion as indicated by IR and X-ray studies and this will tend to favour complexes **2Mj** unless the metal hydride site becomes very basic as in the case of the depe complexes.

The thermodynamically less stable isomers can be accessed in some cases by other routes. The reaction of *trans*-[Ru(OTf)(CN)L<sub>2</sub>] **5RuJ** in CD<sub>2</sub>Cl<sub>2</sub> with dihydrogen produces the less stable complexes *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CN)L<sub>2</sub>]OTf **3RuJ**. Complexes **3Mj** are suspected of having ion pairs with M(HH)⋯OTf non-classical hydrogen bonding. The deprotonation of *trans*-[M(η<sup>2</sup>-H<sub>2</sub>)(CNH)(dippe)<sub>2</sub>](OTf)<sub>2</sub> **4M2**, M = Fe, Ru by Et<sub>2</sub>O also leads to the **3'M2** tautomers where the triflate is mainly hydrogen-bonded to HOTf in CH<sub>2</sub>Cl<sub>2</sub>. Under dihydrogen, complexes **3RuJ** rearrange partially (dppp) or completely (dppe) to the hydrogen isocyanide form **2RuJ**. The triflate ion could act as a proton shuttle to facilitate this rearrangement which also appears to be promoted by other bases (Et<sub>2</sub>O, PPh<sub>3</sub>) in the case of **3\*Fe2**, **3'Ru2** and **3\*Os2**.

The highly acidic and stable dicationic dihydrogen complexes, *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CNH)L<sub>2</sub>]<sup>2+</sup> (L = dppe, dppp) are only stable with respect to the loss of protons or dihydrogen under strongly acidic conditions (excess HOTf). The very acidic complex *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CNH)(dppm)<sub>2</sub>]<sup>2+</sup> is observable at temperatures below –40 °C but decomposes at room temperature. The less acidic *trans*-[Os(η<sup>2</sup>-H<sub>2</sub>)(CNH)(dppp)<sub>2</sub>]<sup>2+</sup> can be obtained as a white solid, while *trans*-[Os(η<sup>2</sup>-H<sub>2</sub>)(CNH)(dppm)<sub>2</sub>]<sup>2+</sup> does not form. The pK<sub>a</sub> of the complexes **4Fe2**, **4'Ru2**, **4Ru3** are less than that of HOEt<sub>2</sub><sup>+</sup> since they are deprotonated by Et<sub>2</sub>O. The dihydrogen complexes *trans*-[M(η<sup>2</sup>-H<sub>2</sub>)(CNH)L<sub>2</sub>]<sup>2+</sup> (L = dppe, dppp) are stable despite the fact that there is very little π-backbonding because of the strong σ bond component. The high Lewis acidity of the metal is created by the 2+ charge and the presence of the π-acidic CNH ligand *trans* to H<sub>2</sub>. The H–H bond length was determined by use of accepted NMR methods to be short (0.9 Å) in these complexes.

The dihydrogen complexes *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CN)L<sub>2</sub>]<sup>+</sup> (L = dppm, dppe, dppp) are unstable under Ar, liberating H<sub>2</sub> and forming *trans*-[Ru(OTf)(CN)L<sub>2</sub>] (L = dppm, dppe, dppp). It is interesting to note that the monocationic dihydrogen complexes **3Ru2**, **3'Ru2**, **3Ru3** are less stable with respect to H<sub>2</sub> loss than the dicationic dihydrogen complexes, **4RuJ**. This could reflect the lower Lewis acidity of the metal centre in **3RuJ** and also possibly the greater *trans* influence of CN over CNH (the latter could be influenced by hydrogen bonding to the counter anion). A greater M–H<sub>2</sub> bond weakening in **3Mj**, M = Fe, Ru would explain why the H–H bond lengths are comparable in **3Mj** and **4Mj**. Otherwise the monocationic complexes would be expected to be more π-basic, an effect that usually results in H–H bond lengthening by dπ→σ\* backdonation. There is theoretical support for the idea that the dσ interaction increases as dπ electrons become unavailable for π-bonding (e.g. on going from complexes **3RuJ** to **4RuJ**).<sup>51</sup> This difference in stability might also be explained by the fact that in **4Mj** the TfO<sup>–</sup> is not as nucleophilic because it is hydrogen bonded to HOTf.

When *trans*-[Ru(OTf)(CNH)(dppe)<sub>2</sub>]OTf **6Ru2** is placed under H<sub>2</sub>, a very strong acid is released (HOTf) in the form of (TfO⋯HOTf)<sup>–</sup> and the complex *trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CN)(dppe)<sub>2</sub>](TfO⋯HOTf) **3'Ru2** is formed. This is a rare example of the formation of an acidic dihydrogen complex from H<sub>2</sub> gas. The reaction of complexes **5RuJ** with dihydrogen also generates

the acidic dihydrogen complexes **3RuJ**. The reactivity of the triflate complexes **6RuJ** and **5RuJ** is attributed to the long Ru–O bonds identified in the structure determinations of **5Ru2** and **6Ru2**.

The iron dihydrogen complexes are of interest because of the recent infrared and crystallographic work on hydrogenase enzymes that suggest that cyanide ligands on iron are present in nature. Our work indicates that iron(II), when it is low spin due to the presence of strong field cyanide, hydrogenisocyanide and phosphine ligands, is an excellent binding site for dihydrogen and that the proton from the H<sub>2</sub> ligand can move to cyanide and back again easily. Such a migration has not been discussed in studies of the mechanism of hydrogenase action.<sup>52–54</sup> We have reported IR data for the CN and CNH ligands that might be useful in enzymatic studies.

## Experimental

### General procedures

All manipulations involving solutions of the complexes were performed under argon with use of Schlenk-line techniques or in a vacuum atmosphere glovebox under Ar unless otherwise noted. HD gas was prepared *via* reaction of NaH with 99.92% D<sub>2</sub>O (generously donated by Ontario Hydro). Solvents were purified by standard methods. All chemicals used were of reagent grade or comparable purity. NMR solvents were obtained from Sigma-Aldrich. The ligand dppp, RuCl<sub>3</sub>·H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>OsCl<sub>6</sub> were purchased from Aldrich. The phosphine ligand dppe was donated by Digital Specialty Chemicals Ltd. [HPPPh<sub>3</sub>]OTf was prepared by reaction with HOTf in a similar fashion to the preparation of [HPPPh<sub>3</sub>]BF<sub>4</sub>.<sup>55</sup> The preparation of the complexes **1Mj** and **2Mj** are reported elsewhere.<sup>28</sup> The yields of complexes reported below were calculated on the basis of the starting metal complex. Crystals were obtained by the slow evaporation of the solvent into an Ar glovebox atmosphere. Infrared spectra were recorded on a Nicolet Magna 550 FT-IR or on a Nicolet 5DX FTIR spectrometer as Nujol mulls on NaCl plates. Microanalyses were performed by the Microanalytical Laboratory of the Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine or by Guelph Chemical Laboratories Ltd., Guelph, ON. <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained with Bruker AC 200 or with Varian Gemini 300 spectrometers. <sup>15</sup>N{<sup>1</sup>H} NMR spectra were obtained with a Bruker AC 500 spectrometer. <sup>31</sup>P chemical shifts are relative to 85% H<sub>3</sub>PO<sub>4</sub> and (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> for solutions and solids, respectively, and <sup>15</sup>N chemical shifts to external aqueous solution of KC<sup>15</sup>N. Inverse-gated decoupling was used to record the <sup>31</sup>P NMR spectra when their integration was required. All <sup>31</sup>P NMR spectra were proton decoupled. <sup>1</sup>H NMR T<sub>1</sub> measurements were made using the inversion recovery method. Further experimental details and <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR data for the complexes can be found in the supplementary information (SUP 57672).

### Preparations

*trans*-[Ru(η<sup>2</sup>-H<sub>2</sub>)(CNH)(dppm)<sub>2</sub>](OTf)<sub>2</sub> **4Ru1**. *trans*-[RuH(CN)(dppm)<sub>2</sub>] (21.8 mg, 24 μmol) was dissolved in 0.5 mL of CD<sub>2</sub>Cl<sub>2</sub> under H<sub>2</sub> in an NMR tube and, after cooling at –80 °C, HOTf (6.4 μL, 72 μmol) was added thereto by means of a syringe. *trans*-[Ru(η<sup>2</sup>-HD)(CND)(dppm)<sub>2</sub>](OTf)<sub>2</sub> **4Ru1-d<sub>2</sub>** was prepared in a similar fashion by use of DOTf.

*trans*-[Fe(η<sup>2</sup>-H<sub>2</sub>)(CN)(dppe)<sub>2</sub>]OTf, **3Fe2**. *Method A*. Excess triflic acid (70 mg; 0.4 mmol) was added to a CH<sub>2</sub>Cl<sub>2</sub> solution of *trans*-Fe(H)(CN)(dppe)<sub>2</sub> (57 mg; 0.06 mmol) and the solution was stirred for 5 min. The solvent was removed *in vacuo* and the resultant yellow oil washed twice with Et<sub>2</sub>O (5 mL) producing a brown powder. Yield 61 mg (98%). *Method B*. Et<sub>2</sub>O was added to a solution of **4Fe2** generated *in situ* by Method B

(see below). IR ( $\text{cm}^{-1}$ , solid on NaCl) 2006 (s,  $\nu\text{CN}$ ). *trans*-[Fe(HD)(CN)(dppe)<sub>2</sub>](OTf), **3Fe2-d** was made using DOTf as in Method A.

*trans*-[Fe(H<sub>2</sub>)(CNH)(dppe)<sub>2</sub>](OTf)<sub>2</sub>, **4Fe2**. *Method A*. **1Fe2**, (13 mg; 0.015 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and cold (0 °C) triflic acid (15 mg; 0.1 mmol) was added. The initial orange colour of the solution fades to yellow immediately. *Method B*. Triflic acid (3 drops) is added to **2Fe2** (20 mg) in CD<sub>2</sub>Cl<sub>2</sub>. IR (film on NaCl) 2056  $\text{cm}^{-1}$  (CN); (CH<sub>2</sub>Cl<sub>2</sub> solution) 2059  $\text{cm}^{-1}$ . *trans*-[Fe( $\eta^2$ -HD)(CND)(dppe)<sub>2</sub>](OTf)<sub>2</sub>, **4Fe2-d<sub>2</sub>** was made with DOTf according to Method A.

*trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(CN)(dppe)<sub>2</sub>](OTf) **3Ru2**. An NMR tube containing *trans*-[Ru(OTf)(CN)(dppe)<sub>2</sub>] (20 mg, 0.02 mmol) in CD<sub>2</sub>Cl<sub>2</sub> was cooled to -78 °C. H<sub>2</sub> gas was bubbled through the solution until the pale yellow solution turned colourless. The NMR spectra were recorded at -10 °C. *trans*-[Ru( $\eta^2$ -HD)(CN)(dppe)<sub>2</sub>](OTf) **3Ru2-d** was prepared by use of HD(g).

*trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(CN)(dppe)<sub>2</sub>](TfO...HOTf) **3'Ru2**. *Method A*. A yellow oil containing *trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(CNH)(dppe)<sub>2</sub>](TfO...HOTf)<sub>2</sub> in HOTf was stirred for 30 min in 10 mL Et<sub>2</sub>O. The solvent was decanted and the product was quickly dried under Ar. The NMR spectra were recorded quickly since the dihydrogen ligand was found to be very labile. *Method B*. H<sub>2</sub> gas was bubbled into an NMR tube containing complex **6Ru2** in CD<sub>2</sub>Cl<sub>2</sub>.

*trans*-[Ru( $\eta^2$ -HD)(CN)(dppe)<sub>2</sub>](TfO...DOTf) **3'Ru2-d<sub>2</sub>**. Diethyl ether was added to the yellow oil of **4'Ru2-d<sub>4</sub>** (see below) to produce a light yellow precipitate. The solvent was decanted and the product was quickly dried under argon.

*trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(CNH)(dppe)<sub>2</sub>](TfO...HOTf)<sub>2</sub> **4'Ru2**. *Method A*. *trans*-[RuH(CN)(dppe)<sub>2</sub>] (100 mg, 0.11 mmol) was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> producing a clear colourless solution. Excess triflic acid (60 mg, 0.40 mmol) was added to the solution and the resulting light yellow solution was stirred for 1 h. The solvent was removed *in vacuo*, producing a yellow oil. *Method B*. *trans*-[RuH(CNH)(dppe)<sub>2</sub>](OTf) (15 mg, 0.02 mmol) was dissolved in 5 mL of CD<sub>2</sub>Cl<sub>2</sub> and triflic acid (7 mg, 0.05 mmol) was added to the solution. The spectra were recorded immediately. *trans*-[Ru( $\eta^2$ -HD)(CND)(dppe)<sub>2</sub>](TfO...DOTf)<sub>2</sub> **4'Ru2-d<sub>4</sub>** was prepared by use of Method A and DOTf.

*trans*-[Os( $\eta^2$ -H<sub>2</sub>)(CN)(dppe)<sub>2</sub>](BF<sub>4</sub>) **3\*Os2**. A solution of *trans*-[OsH(CN)(dppe)<sub>2</sub>] **1Os2** (28 mg, 0.028 mmol) in 1.5 mL benzene was treated with HBF<sub>4</sub>·Et<sub>2</sub>O (5  $\mu\text{L}$  of 85% in Et<sub>2</sub>O, 0.028 mmol) under argon. The white precipitate that formed after 30 s was isolated after 5 min of stirring. The yield appeared to be quantitative.

*trans*-[Os( $\eta^2$ -HD)(CN)(dppe)<sub>2</sub>](BF<sub>4</sub>) **3\*Os2-d**. An acid solution was prepared containing HBF<sub>4</sub>·Et<sub>2</sub>O (50  $\mu\text{L}$ , 0.3 mmol) and D<sub>2</sub>O (0.1 mL) in benzene. Then 1 mL of this solution was added to a solution of **1Os2** (30 mg, 0.03 mmol) in 1 mL benzene. After 2 min, a white precipitate formed. The solvent was decanted by use of a syringe and the white solid was dried in vacuum for 5 min. The sample dissolved in CD<sub>2</sub>Cl<sub>2</sub> was sealed in an NMR tube under Ar.

*trans*-[Os( $\eta^2$ -H<sub>2</sub>)(<sup>13</sup>CNH)(dppe)<sub>2</sub>](OTf)<sub>2</sub> **4Os2-c**. Two equivalents of HOTf (9 mg, 0.055 mmol) were added to *trans*-[OsH(<sup>13</sup>CNH)(dppe)<sub>2</sub>](OTf) **2Os2-c** in 0.7 mL CD<sub>2</sub>Cl<sub>2</sub>. The solution remained colourless and there was no gas evolution.

*trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(CN)(dppp)<sub>2</sub>](OTf) **3Ru3**. H<sub>2</sub> gas was bubbled through a solution of *trans*-[Ru(OTf)(CN)(dppp)<sub>2</sub>], **5Ru3**, in

CD<sub>2</sub>Cl<sub>2</sub> (see below) in an NMR tube until the red solution turned colourless. *trans*-[Ru( $\eta^2$ -HD)(CN)(dppp)<sub>2</sub>](OTf) **3Ru3-d** was made by use of **5Ru3** and HD(g). *trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(<sup>13</sup>CN)(dppp)<sub>2</sub>](OTf) **3Ru3-c** was prepared starting with **5Ru3-c**.

*trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(CNH)(dppp)<sub>2</sub>](OTf)<sub>2</sub> **4Ru3**. *trans*-[RuH(CN)(dppp)<sub>2</sub>] (20 mg, 21  $\mu\text{mol}$ ) was dissolved in 0.5 mL of CD<sub>2</sub>Cl<sub>2</sub> under H<sub>2</sub> in an NMR tube and HOTf (6  $\mu\text{L}$ , 68  $\mu\text{mol}$ ) was added thereto by means of a syringe. IR (CH<sub>2</sub>Cl<sub>2</sub>),  $\text{cm}^{-1}$ :  $\nu(\text{CN})$  2125 (s). *trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(<sup>13</sup>CNH)(dppp)<sub>2</sub>](OTf)<sub>2</sub> **4Ru3-c** and *trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(C<sup>15</sup>NH)(dppp)<sub>2</sub>](OTf)<sub>2</sub> **4Ru3-n** were prepared starting with **1Ru3-c** and **1Ru3-n**, respectively. *trans*-[Ru( $\eta^2$ -HD)(CND)(dppp)<sub>2</sub>](OTf)<sub>2</sub> **4Ru3-d<sub>2</sub>**. DOTf was used as in the preparation of **4Ru3**.

*trans*-[Os( $\eta^2$ -H<sub>2</sub>)(CNH)(dppp)<sub>2</sub>](OTf)<sub>2</sub> **4Os3**. *trans*-[OsH(CN)(dppp)<sub>2</sub>] (0.10 g, 0.10 mmol) was dissolved in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> under H<sub>2</sub> and CF<sub>3</sub>SO<sub>3</sub>H (30  $\mu\text{L}$ , 0.34 mmol) was added by means of a syringe. The solution was stirred at room temperature for 10 minutes and then 15 mL of hexane were added to precipitate the white product, which was filtered off, washed with hexane, dried in vacuum and recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-hexane. Yield: 121 mg, 90%. Anal. calc. for C<sub>57</sub>H<sub>55</sub>F<sub>6</sub>NO<sub>6</sub>OsP<sub>4</sub>S<sub>2</sub>: C, 51.01; H, 4.13; N, 1.04. Found: C, 50.34; H, 4.09; N, 1.03%. IR (Nujol),  $\text{cm}^{-1}$ :  $\nu(\text{CN})$  2129 (s). *trans*-[Os( $\eta^2$ -HD)(CND)(dppp)<sub>2</sub>](OTf)<sub>2</sub> **4Os3-d<sub>2</sub>** was observed by reaction of DOTf with **1Os3**. *trans*-[Os( $\eta^2$ -H<sub>2</sub>)(<sup>13</sup>CNH)(dppp)<sub>2</sub>](OTf)<sub>2</sub> **4Os3-c** and *trans*-[Os( $\eta^2$ -H<sub>2</sub>)(C<sup>15</sup>NH)(dppp)<sub>2</sub>](OTf)<sub>2</sub> **4Os3-n** were prepared starting from **1Os3-c** and **1Os3-n**, respectively.

*trans*-[Fe(H<sub>2</sub>)(CN)(depe)<sub>2</sub>](BF<sub>4</sub>) **3\*Fe4**. The addition of 1 equiv. of acid (85% [Et<sub>2</sub>OH]BF<sub>4</sub> in Et<sub>2</sub>O or [Ph<sub>3</sub>PH]BF<sub>4</sub> in CD<sub>2</sub>Cl<sub>2</sub>) to **1Fe4** produces **3\*Fe4** as revealed by NMR. The compound is isolated by removal of the solvent and washing the yellow powder with Et<sub>2</sub>O. Yield >90%.

*trans*-[Ru( $\eta^2$ -H<sub>2</sub>)(CN)(depe)<sub>2</sub>](BF<sub>4</sub>) **3\*Ru4**. *trans*-[RuH(CN)(depe)<sub>2</sub>] (63 mg, 0.116 mmol) was dissolved in 5 mL of Et<sub>2</sub>O. HBF<sub>4</sub>·Et<sub>2</sub>O (19 mg, 0.117 mmol) was added to the yellow solution producing a white precipitate. The solvent was removed *in vacuo* and the NMR spectra were recorded.

*trans*-[Os( $\eta^2$ -H<sub>2</sub>)(<sup>13</sup>CN)(depe)<sub>2</sub>](OTf) **3Os4-c**. Complex *trans*-[OsH(<sup>13</sup>CN)(depe)<sub>2</sub>] **1Os4-c** (20 mg, 0.032 mmol) was dissolved in 3 mL toluene and [HPPH<sub>3</sub>](OTf) (13 mg, 0.032 mmol) was added with stirring. The white precipitate that formed was isolated, washed with hexanes three times and then dried in vacuum. IR (Nujol),  $\text{cm}^{-1}$ :  $\nu(^{13}\text{CN})$  2064. [Os( $\eta^2$ -HD)(<sup>13</sup>CN)(depe)<sub>2</sub>](OTf) **3Os4-c,d** was generated by use of [DPPH<sub>3</sub>](OTf).

*trans*-[Os( $\eta^2$ -H<sub>2</sub>)(CNH)(depe)<sub>2</sub>](OTf)<sub>2</sub> **4Os4**. Excess HOTf (26 mg, 0.17 mmol) were added to *trans*-[OsH(CN)(depe)<sub>2</sub>] **1Os4** (20 mg, 0.032 mmol) in 3 mL toluene. The solution was stirred for 5 min and then the solvent was evaporated under vacuum to give a beige powder. This was washed with hexanes and then two times with ether and dried for 1 h in vacuum.

*trans*-[Ru(OTf)(CN)(dppe)<sub>2</sub>] **5Ru2**. Under Ar, *trans*-[Ru(OTf)(CNH)(dppe)<sub>2</sub>](OTf) (80.0 mg, 0.65 mmol) was suspended in 5 mL of toluene. To this white suspension, NEt<sub>3</sub> (7 mg, 0.7 mmol) was added and allowed to stir for 1/2 h forming a yellow suspension. The yellow precipitate was filtered and washed with 2 mL of toluene. An orange-red solution was formed when the product was dissolved in a minimal amount of CH<sub>2</sub>Cl<sub>2</sub>. Diethyl ether was diffused in and after 24 h, yellow needles suitable for X-ray structure determination were obtained (53% yield). Anal. calc. for C<sub>54</sub>H<sub>48</sub>F<sub>3</sub>NO<sub>3</sub>P<sub>4</sub>RuS: C, 60.44; H, 4.51; N, 1.30. Found: C, 59.49; H, 4.78; N, 1.26%. IR (Nujol),  $\text{cm}^{-1}$ :  $\nu(\text{CN})$  2078 (s), 2068 (m).

*trans*-[Ru(OTf)(CN)(dppp)<sub>2</sub>] **5Ru3**. Under Ar, *trans*-[Ru(OTf)(CNH)(dppp)<sub>2</sub>]OTf (**6Ru3**, 22 mg, 18 μmol) was dissolved in 0.5 mL of CD<sub>2</sub>Cl<sub>2</sub>. To this colourless solution, NEt<sub>3</sub> (3 μL, 22 μmol) was added and a red solution of **5Ru3** was produced. *trans*-[Ru(OTf)(<sup>13</sup>CN)(dppp)<sub>2</sub>] **5Ru3-c** was prepared by use of **6-Ru3-c**.

*trans*-[Ru(OTf)(CNH)(dppe)<sub>2</sub>]OTf **6Ru2**. Diethyl ether was added to the yellow oil of **4'Ru2** producing a light yellow precipitate. This suspension was stirred for 30 min. and the solvent was decanted. The precipitate was washed twice with 5 mL of diethyl ether and dried *in vacuo*. Purification of the product involved slow diffusion of Et<sub>2</sub>O into a saturated solution of the complex in CH<sub>2</sub>Cl<sub>2</sub>. White crystals suitable for X-ray structure determination were obtained by slow evaporation of a concentrated solution of the product in CH<sub>2</sub>Cl<sub>2</sub> (70.3% yield). Anal. calc. for C<sub>55</sub>H<sub>49</sub>F<sub>6</sub>NO<sub>6</sub>P<sub>4</sub>RuS<sub>2</sub>: C, 54.01; H, 4.04; N, 1.14. Found: C, 53.66; H, 4.35; N, 1.32%. IR (Nujol), cm<sup>-1</sup>: ν(CN) + ν(NH) 2532.6 (w). *trans*-[Ru(OTf)(CN)(dppe)<sub>2</sub>]OTf **6Ru2-d** was prepared in a similar fashion from **4'Ru2-d**. IR (Nujol), cm<sup>-1</sup>: ν(CN) + ν(ND) 2275.4 (m).

*trans*-[Ru(OTf)(CNH)(dppp)<sub>2</sub>]OTf **6Ru3**. *trans*-[RuH(CN)(dppp)<sub>2</sub>] (200 mg, 0.21 mmol) was dissolved in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. Upon addition of HOTf (60 μL, 0.68 mmol) the solution was stirred at room temperature for 20 min with argon bubbling, concentrated in vacuum and then was treated with ether to precipitate the pale yellow product. The product was filtered off, washed with ether, dried in vacuum and recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-ether. Yield: 0.21 g, 80%. Anal. calc. for C<sub>57</sub>H<sub>53</sub>F<sub>6</sub>NO<sub>6</sub>P<sub>4</sub>RuS<sub>2</sub>: C, 54.72; H, 4.27; N, 1.12. Found: C, 53.86; H, 4.33; N, 1.10%. IR (Nujol), cm<sup>-1</sup>: ν(CN) 2074 (w). *trans*-[Ru(OTf)(<sup>13</sup>CNH)(dppp)<sub>2</sub>]OTf **6Ru3-c** was prepared starting from **1Ru3-c**.

*trans*-[Ru(H<sub>2</sub>O)(CNH)(dppe)<sub>2</sub>](OTf)<sub>2</sub> **7Ru2**. *Method A*. Over time, complex **6Ru2** converts to complex **7Ru2** via trace amounts of water in the Ar glove box. *Method B*. Any trace amounts of water in the solvents or in the acid used to prepare complex **6Ru2** or complex **3'Ru2** produces some complex **7Ru2**. *Method C*. In a Schlenk flask, in the Ar glove box, complex **1Ru2** (0.050 g, 0.054 mmol) was dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. A solution of HOTf (45 mg, 0.300 mmol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to the ruthenium complex and allowed to stir for 30 min. After 30 min, the solvent was removed *in vacuo* and the yellow oil was washed twice with 5 mL of Et<sub>2</sub>O. The white solid was dried under vacuum and the flask was removed from the glovebox and introduced to H<sub>2</sub> gas. Approximately 1 mL of degassed water was added to the flask and allowed to stir for 2 days. The water was removed under vacuum and the flask was brought back into the Ar glovebox. White crystals were grown by slow evaporation of a concentrated solution of complex **7Ru2** in CH<sub>2</sub>Cl<sub>2</sub>.

#### Single crystal X-ray diffraction analysis

Data for a yellow crystal of **5Ru2** were collected on Nonius KappaCCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å). The structure was solved and refined using the SHELXTL PC V5.0 package.<sup>56</sup> A combination of 1° phi and omega (with kappa offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the DENZO-SMN package.<sup>57</sup> Refinement was by full-matrix least-squares on F<sup>2</sup> using all data (negative intensities included). Hydrogen atoms were included in calculated positions. The crystallographic data for the complex are listed in Table 4.

CCDC reference number 186/1711.

See <http://www.rsc.org/suppdata/dt/1999/4475/> for crystallographic files in .cif format.

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