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FULL PAPER

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

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Very acidic complexes *trans*-[$M(\eta^2\text{-}H_2)(CN)L_2]^+$ and *trans*-[$M(\eta^2\text{-}H_2)(CNH)L_2]^{2+}$, 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 (dppm = [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*-[$Ru(OTf)(CN)(dppe)_2$] is reported. The Ru–OTf bond is weak and so the triflate ligand can be displaced by H_2(g) to give *trans*-[$Ru(\eta^2\text{-}H_2)(CN)L_2$]OTf. There is a delicate balance of stability between the complexes *trans*-[$M(\eta^2\text{-}H_2)(CN)L_2]^+$ and *trans*-[$M(H)(CNH)L_2]^+$, 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*-[$Ru(\eta^2\text{-}H_2)(CNH)L_2$]OTf is observed to form from the reaction of the weak Brønsted acids H_2 and *trans*-[$Ru(OTf)(CNH)L_2$]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 η^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 π-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*-[$Fe(\eta^2\text{-}H_2)(CO)(dppe)_2]^{2+}$,[1] *trans*-[$M(CO)(\eta^2\text{-}H_2)(dppp)_2]^{2+}$ (M = Ru, Os)[2] and *trans*-[$Ru(\eta^2\text{-}H_2)(CNH)(dppe)_2]^{2+}$.[3] These complexes are surprisingly stable with respect to the loss of H_2(g).[1] This was rationalised in terms of an increase in importance of the metal–H_2 σ bond to compensate for the lack of π-backdonating ability of these electrophilic metal centres. Other highly acidic dihydrogen complexes included [$Os(\eta^2\text{-}H_2)(PPh_3)_2(bpy)(CO)]^{2+}$,[4] *cis*-[$Re(CO)_4(\eta^2\text{-}H_2)(PR_3)]^+$,[5] [$Ru(C_5Me_5)(\eta^2\text{-}H_2)(CO)_2]BF_4$,[6] [$Ru(\eta^2\text{-}H_2)(PPh_3)(CO)(tacn)]^{2+}$ (tacn = 1,4,7-triazacyclononane),[7] *trans*-[$Os(\eta^2\text{-}H_2)(CH_3CN)(dppe)_2]^{2+}$,[8] [$Cp^*Os(CO)_2(\eta^2\text{-}H_2)]OTf$[9] and [(triphos)$Ir(\eta^2\text{-}H_2)(H)_2]BPh_4$ (triphos = $MeC(CH_2PPh_2)_3$).[10]

In this paper we give the complete details of our studies of dihydrogen complexes **3Mj** or **4Mj** derived from protonating complexes *trans*-[$MH(CN)L_2$], **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.[11] 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.[12] 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 [$Os(H_2)(quinS)(CO)(PPh_3)_2]^+$ (quinS = quinoline-8-thiolate)[13,14] and [{$\eta^5\text{-}C_5H_4(CH_2)_3NMe_2H^+$}$RuH(dppm)]BF_4$.[15] Some of us have already reported the important effect of the ancillary ligand on the protonation of hydridocyano complexes.[16] With the basic depe ligand, protonation at the Fe–H bond in *trans*-[$FeH(CN)(depe)_2$] **1Fe4** is thermodynamically favored to give

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

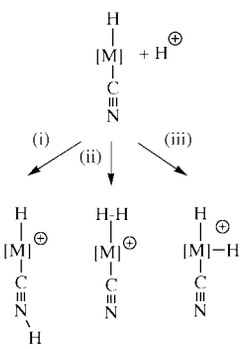
Also available: additional experimental and spectroscopic data. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/4475/, otherwise available from BLDSC (No. SUP 57672, 6 pp.) or the RSC library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

Table 1 The numbering scheme for the complexes **iMJ** as triflate salts and other salts[a]

iMj	i	M	j	L	Abbreviation
$[MH(CN)L_2]$	**1**	**Fe**	**1**	$PPh_2CH_2PPh_2$	dppm
$[MH(CNH)L_2]OTf$	**2**	**Ru**	**2**	$PPh_2(CH_2)_2PPh_2$	dppe
$[M(\eta^2\text{-}H_2)(CN)L_2]OTf$	**3**	**Os**	**3**	$PPh_2(CH_2)_3PPh_2$	dppp
$[M(\eta^2\text{-}H_2)(CNH)L_2](OTf)_2$	**4**		**4**	$PEt_2(CH_2)_2PEt_2$	depe
$[M(OTf)(CN)L_2]$	**5**				
$[M(OTf)(CNH)L_2]OTf$	**6**				

Other salts	i	M	j
$[Ru(\eta^2\text{-}H_2)(CN)(dppe)_2](TfO\cdots HOTf)$	**3′**	**Ru**	**2**
$[Ru(\eta^2\text{-}H_2)(CNH)(dppe)_2](TfO\cdots HOTf)_2$	**4′**	**Ru**	**2**
$[Os(\eta^2\text{-}H_2)(CN)(dppe)_2]BF_4$	**3***	**Os**	**2**
$[M(\eta^2\text{-}H_2)(CN)(depe)_2]BF_4$	**3***	**Fe**	**4**
	3*	**Ru**	**4**
$[Fe(\eta^2\text{-}H_2)(CNH)(depe)_2](BF_4)_2$	**4***	**Fe**	**4**

[a] In addition further symbols are used for ^{13}C labelled complexes (**c**), ^{2}H labelled complexes (**d**) and ^{15}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-$[Fe(\eta^2\text{-}H_2)(CN)(depe)_2]OTf$ **3Fe4** while with the analogous dppe complex **1Fe2**, the proton ends up on the nitrogen to give *trans*-$[Fe(H)(CNH)(dppe)_2]OTf$ **2Fe2**. Further chemistry of **2Fe2** has recently been reported.[17]

In certain cases, as described in our recent communication,[3] very acidic dihydrogen complexes such as *trans*-$[Ru(\eta^2\text{-}H_2)(CNH)(L)_2]^{2+}X^-_2$ L = dppe, X = (TfO···HOTf) **4′Ru2**, L = dppp, X = OTf **4Ru3** can be generated by displacing coordinated triflate in *trans*-$[Ru(OTf)(CNH)(L)_2]OTf$ (**6Ru2** or **6Ru3**) with dihydrogen gas. Only a few other highly acidic complexes have been generated by use of dihydrogen gas. These are $[(triphos)Ir(\eta^2\text{-}H_2)(H)_2]BPh_4$ by hydrogenation of the ethene complex $[(triphos)Ir(\eta^2\text{-}C_2H_4)(H)_2]BPh_4$,[10] and *cis*-$[Re(\eta^2\text{-}H_2)(PR_3)(CO)_4]$ by displacement of CH_2Cl_2 from *cis*-$[Re(\eta^1\text{-}ClCH_2Cl)(PR_3)(CO)_4]^+$.[5]

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_6^- anion and to the oxygen of ethers.[18] Recently, Sapunov *et al.* reported the crystalline structures of $[Ru_2Cp_2(PPh_3)_4(\mu\text{-}CNHNC)]CF_3SO_3$, a bridged complex with a short (2.573 Å) N(H)···N bond length, and of $[RuCp(PPh_3)_2(CNH)]CF_3SO_3$, where the CNH group forms a strong hydrogen bond to the triflate group, N···O = 2.75 Å.[19] We have also previously published the solid-state structure of *trans*-$[Ru(OTf)(CNH)(dppe)_2]OTf$, **6Ru2**, where the N···O distance is found to be 2.62 Å.[3] This complex has a long Ru–OTf bond of 2.299 Å, longer than that of other ruthenium(II)-triflate complexes.[20–22]

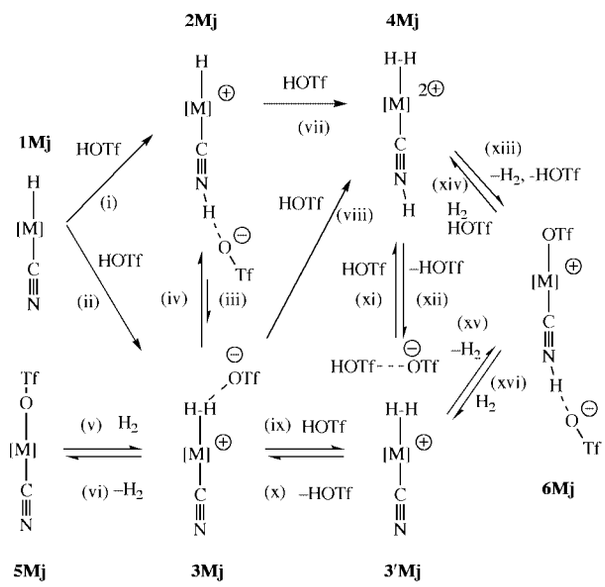
In addition there is the possibility that the dihydrogen ligand might act as an unconventional hydrogen bond donor to triflate. For example there is a related Os(HH)···FBF_3^- interaction in *trans*-$[Os(\eta^2\text{-}H_2)(CH_3CN)(dppe)_2](BF_4)_2$[8] and IrCl···(HH)Ir hydrogen bonds in $Ir(\eta^2\text{-}H_2)(Cl)_2(H)(P^iPr_3)_2$.[23]

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.[24–27] The iron–nickel active site might have dihydrogen coordinated as $(cysteine)_2Ni(\mu\text{-}cysteine)_2Fe(\eta^2\text{-}H_2)(CO)(CN)_2^{n-}$ before it is released as H_2(g) while the iron-only active sites might have $(cysteine)_3Fe_4S_4(\mu\text{-}cysteine)Fe_2(CO)_x(CN)_y(\eta^2\text{-}H_2)$ 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*-$[MH(CN)L_2]$

Scheme 2 outlines the formation of the important hydride and



Scheme 2 The preparative routes. [M] refers to the M(diphosphine)$_2$ fragment. The solvent is CH_2Cl_2 or CD_2Cl_2 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.[28]

Addition of HOTf to *trans*-$[RuH(CN)(dppp)_2]$ 1Ru3 and related reactions

The stepwise protonation of **1Ru3** in CD_2Cl_2 with HOTf can be conveniently followed by NMR spectroscopy. ^{31}P and ^{1}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*-$[RuH(CNH)(dppp)_2]OTf$, **2Ru3** (step i, Scheme 2). When less than one equivalent is added, the hydride resonances and the ^{31}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*-$[Ru(\eta^2\text{-}H_2)(CN)(dppp)_2]OTf$ **3Ru3** (step ii, Scheme 2) as indicated by

Table 2 Characteristics of dihydrogen complexes observed (in CD_2Cl_2)

Complex	^{1}H NMR/δ	^{31}P{^{1}H}NMR/δ	J(HD)/Hz	d(H–H) from J(HD)/Å	T_1(min)/ms	d(H–H) from T_1(min)/Å [a]
3Ru1	−4.7 (br)	−6.1 (br s)	32.0	0.89	5.8 [d] (213 K)	0.81, 1.02
4Ru1	−3.7 (br) [b]	−12.2 (br s) [b]	32.2 [b]	0.88 [b]	6.4 [d] (233 K)	0.82, 1.04
3Fe2	−8.7 (br)	72.2 (s)	32.7	0.87	11.7 [e] (234 K)	0.85, 1.07
4Fe2	−9.1 (br)	70.4 (s)	32.5	0.88	21.5 [f] (262 K)	0.87, 1.09
3Ru2	−7.3 (br) [c]	53.7 (s) [c]	32.5	0.88		
3′Ru2 [g]	−5.5 (br)	54.2 (s)	32.0	0.89	12.4 [e] (240 K)	0.86, 1.08
4′Ru2	−5.9 (br)	52.2 (s)	32.4	0.88	13.6 [e] (247 K)	0.87, 1.10
3*Os2 [h]	−6.4 (br)	21.7 (s)	28.7	0.94	14.7 [e] (233 K)	0.88, 1.11
4Os2-c	−6.1 (br)	22.0 (d)	29.1	0.93	14 [e] (253 K)	0.88, 1.11
3Ru3	−5.4 (br)	9.7 (br s)	31.6	0.89	5.4 [d] (223 K)	0.80, 1.01
4Ru3	−4.2 (br)	8.9 (br s)	31.8	0.89	5.9 [d] (233 K)	0.81, 1.02
4Os3	−4.6 (br)	−29.4 (br s)	28.8	0.94	7.6 [d] (233 K)	0.85, 1.07
3*Fe4 [h]	−14.0 (br)	77.7 (s)	31.6	0.89	15.2 [i] (262 K)	0.85, 1.07
4Fe4	−12.1 (br)	72.5 (s)			19.0 [i] (229 K)	0.88, 1.11
3*Ru4 [h]	−9.1 (br)	54.4 (s)			12.8 [e] (191 K)	0.86, 1.09
3Os4-c	−9.5 (br)	21.7 (d)	25.4	1.00	16 [e] (213 K)	0.90, 1.13
4Os4	−8.1 (br)	17.9 (s)			12 [e] (223 K)	0.86, 1.08

[a] The first value is calculated for the fast spinning while the second is referred to the slow spinning. [b] Values measured at 193 K. [c] NMR spectra recorded at 263 K. [d] T_1 measured at 200 MHz. [e] T_1 measured at 300 MHz. [f] T_1 measured at 500 MHz; see ref. 1. [g] $(TfO\cdots HOTf)^-$ counter anion. [h] BF_4^- counter anion. [i] T_1 measured at 400 MHz.

the appearance in the ^{1}H NMR spectrum of a broad signal at δ −5.4 due to a dihydrogen ligand. This new complex is also visible in the ^{31}P NMR spectrum as a broad singlet centered at δ 9.7. The integration of the ^{31}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_2Cl_2 (see below).

For HOTf–**1Ru3** > 1 both complexes **2Ru3** and **3Ru3** react with HOTf to give the dihydrogen complex *trans*-[Ru(η^2-H_2)(CNH)(dppp)$_2$](OTf)$_2$, **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_2 is slowly lost and an increasing amount of the derivative *trans*-[Ru(OTf)(CNH)(dppp)$_2$]OTf **6Ru3** is formed (step xiii, Scheme 2). If the protonation is carried out under H_2 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 ^{13}CN enriched compound *trans*-[RuH(^{13}CN)(dppp)$_2$] **1Ru3-c** to give the corresponding complexes **2Ru3-c**, **3Ru3-c** and **4Ru3-c** was also studied in CD_2Cl_2 by ^{13}C{^{1}H} NMR. The protonation of the ^{13}CN group to produce ^{13}CNH results in a broadening of the ^{13}C resonance which shifts to low field (from δ 156.7 for **1Ru3-c** to δ 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 δ 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 ^{13}CN of **3Ru3-c** with the final formation of **4Ru3-c**, which shows the ^{13}CNH resonance as a broad quintet at δ 149.9. In solution the complex **4Ru3-c** slowly loses H_2 to give *trans*-[Ru(OTf)(^{13}CNH)(dppp)$_2$]OTf **6Ru3-c** which exhibits a ^{13}C signal at δ 159.7.

When the protonation of **1Ru3** with HOTf under H_2 is carried out in $Cl_2CDCDCl_2$, a larger ratio of **3Ru3** to **2Ru3** is observed (47 : 53) compared to the reaction in CD_2Cl_2 solution. Furthermore, when argon is bubbled into the $Cl_2CDCDCl_2$ 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,[28] appears to be stable in solution under H_2 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_2Cl_2 (after 12 hours) the NMR spectrum shows 90% of **2Ru3** and 10% of **3Ru3**; in $Cl_2CDCDCl_2$ (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)$_2$] **5Ru3** (see below) with H_2 (step v, Scheme 2).

The addition of an excess of HOTf to a solution of **1Ru3** in C_6H_6 or CH_2Cl_2 under 1 atm H_2 gives *trans*-[Ru(η^2-H_2)(CNH)(dppp)$_2$](OTf)$_2$ **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)$_2$]OTf **2Ru3** and *trans*-[Ru(η^2-H_2)(CN)(dppp)$_2$]OTf **3Ru3** and presumably the strong acid [$HOEt_2$]OTf.

Addition of HOTf to *trans*-[OsH(CN)(dppp)$_2$] 1Os3. When HOTf is added to a CD_2Cl_2 solution of **1Os3** at room temperature, the CNH derivative **2Os3** is the first species observed by use of ^{31}P and ^{1}H NMR. In contrast to **1Ru3**, there is no evidence for the formation of the cyanide dihydrogen complex *trans*-[Os(η^2-H_2)(CN)(dppp)$_2$]$^+$. Further protonation at the hydride (step vii, Scheme 2) produces the dicationic dihydrogen complex *trans*-[Os(η^2-H_2)(CNH)(dppp)$_2$] (OTf)$_2$ **4Os3** as indicated by the appearance of the broad signal at δ −4.6 in the high-field range of the ^{1}H NMR spectrum. The protonation of *trans*-[OsH(CN)(dppp)$_2$] **1Os3** in C_6H_6 or CH_2Cl_2 solution under 1 atm. of H_2 with an excess of HOTf gives **4Os3** as white solid. This dihydrogen complex is stable with respect to the loss of H_2 both in the solid state and in solution.

Addition of HOTf to *trans*-[MH(CN)(dppm)$_2$] 1Ru1, 1Os1 and related reactions

When 1 equivalent of HOTf is added to a solution of **1Ru1** in CD_2Cl_2 under H_2, the complexes [Ru(H)(CNH)(dppm)$_2$]OTf **2Ru1** and [Ru(η^2-H_2)(CN)(dppm)$_2$]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 $Cl_2CDCDCl_2$. An excess of triflic acid added to a CD_2Cl_2 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)$_2$]OTf **6Ru1**, which is identified by a singlet at δ −11.0 in the ^{31}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_2Cl_2 or in $Cl_2CDCDCl_2$. The

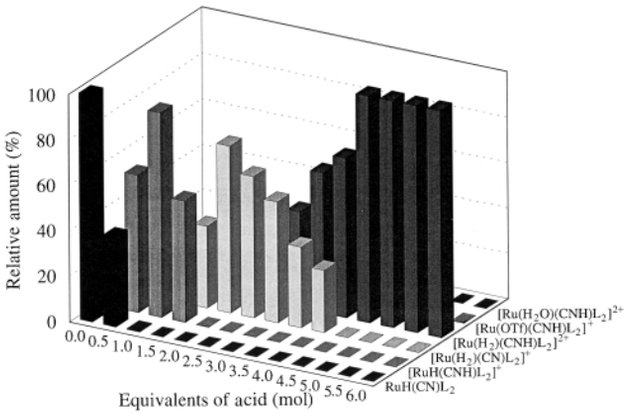


Fig. 1 Relative amounts of species observed during the titration of *trans*-RuH(CN)L_2, L = dppe, in CH_2Cl_2 under H_2 with HOTf. Small amounts of $[Ru(OTf)(CNH)L_2]^+$ (10%) are present at 2.0 equiv. of HOTf. Small amounts of $[Ru(H_2O)(CNH)L_2]^{2+}$ are present at 1.0 equiv. (9%), 2.0 equiv. (16%) 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_2Cl_2 at room temperature leads to the formation of exclusively *trans*-[OsH(CNH)(dppm)$_2$]OTf[28] while excess acid produces a violet solution that does not have a dihydrogen resonance in the ^{1}H NMR spectrum.

Addition of HOTf to *trans*-[RuH(CN)(dppe)$_2$] 1Ru2 and related reactions

The quantitative titration of complex **1Ru2** in CD_2Cl_2 with HOTf was monitored by $^{31}P\{^1H\}$ NMR spectroscopy to determine the approximate relative amounts of the complexes produced (Fig. 1). The acid addition was done under H_2 gas to minimise the formation of the triflate coordinated species *trans*-[Ru(OTf)(CNH)(dppe)$_2$]OTf, **6Ru2**. The addition of 0.5 mol of acid to complex **1Ru2** produces a mixture of **1Ru2** and *trans*-[Ru(H)(CNH)(dppe)$_2$]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^2-H_2)(CN)(dppe)$_2$](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 $(TfO\cdots HOTf)^-$ anion, has different solution properties to the unstable dihydrogen complex *trans*-[Ru(η^2-H_2)(CN)(dppe)$_2$]OTf, **3Ru2**, with the OTf^- 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 $(TfO\cdots HOTf)^-$. 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^2-H_2)(CNH)(dppe)$_2$](TfO···HOTf)$_2$, **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 $(TfO\cdots HOTf)^-$ counter-ions. The requirement of a slight excess reflects the high acidity of complex **4′Ru2**. Under H_2, only a small amount of complex *trans*-[Ru(OTf)(CNH)(dppe)$_2$]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_2O)(CNH)(dppe)$_2$](OTf)$_2$ (**7Ru2**, see below), is produced from impurities of H_2O/H_3O^+. 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).

$$[Ru(H_2O)(CNH)(dppe)_2](OTf)_2 + 3HOTf + H_2 \longrightarrow [Ru(H_2)(CNH)(dppe)_2](TfOH\cdots OTf)_2 + H_3O^+ \quad (1)$$

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_2, the amount of complex **6Ru2** present is only 10.0%.

The unstable dihydrogen complex *trans*-[Ru(η^2-H_2)(CN)(dppe)$_2$]OTf, **3Ru2**, has been observed at low temperatures when H_2(g) is introduced into a solution of *trans*-[Ru(OTf)(CN)(dppe)$_2$], **5Ru2** (see below) in CD_2Cl_2 (step v, Scheme 2). The ^{1}H NMR spectrum of **3Ru2** recorded at −10 °C shows a broad singlet at δ −7.3 and the $^{31}P\{^1H\}$ 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 ^{1}H NMR spectrum signalled the formation of **2Ru2** as did the appearance of a singlet at δ 66.6 in the $^{31}P\{^1H\}$ 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^2-H_2 ligand to the CN ligand, producing **2Ru2**.

There are two routes to the white complex *trans*-[Ru(η^2-H_2)(CN)(dppe)$_2$](TfO···HOTf) **3′Ru2**. When the yellow oil of complex **4′Ru2** is stirred in Et_2O 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 $[Et_2OH](TfO\cdots HOTf)$ which is detected in the ^{1}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_2 over time to give complex **6Ru2** (step xv, Scheme 2). The addition of H_2 gas to complex **6Ru2** is another route to complex **3′Ru2** (step xvi, Scheme 2).

When one half an equivalent of PPh_3 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 ^{1}H NMR spectrum while in the $^{31}P\{^1H\}$ NMR spectrum, a singlet at δ 66.6 corresponding to complex **2Ru2** is observed. Resonances for $[HPPh_3](TfO\cdots HOTf)$ at δ 3.4 and complex **7Ru2** at δ 48.4 are also observed in the $^{31}P\{^1H\}$ NMR spectrum. This reaction probably proceeds *via* the formation of complex **3Ru2** as an intermediate.

$$\textit{trans}\text{-}[Ru(\eta^2\text{-}H_2)(CN)(dppe)_2](TfO\cdots HOTf) + 0.5\ PPh_3 \longrightarrow \textit{trans}\text{-}[Ru(H)(CNH)(dppe)_2]OTf + 0.5\ [HPPh_3](TfO\cdots HOTf) \quad (2)$$

The addition of excess HOTf (>5 equiv.) to complex *trans*-[RuH(CN)(dppe)$_2$] **1Ru2** or complex *trans*-[RuH(CNH)(dppe)$_2$]OTf **2Ru2** in CH_2Cl_2 under Ar produces the complex *trans*-[Ru(η^2-H_2)(CNH)(dppe)$_2$](TfO$\cdots$HOTf)$_2$ **4′Ru2** which was isolated as a yellow oil. Complex **4′Ru2** 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)$_2$] 1Fe2 and related reactions

The addition of 1 equiv. of HOTf to **1Fe2** in CH_2Cl_2 produces the hydrogen isocyanide complex **2Fe2** (step i, Scheme 2). The complex *trans*-[Fe(H_2)(CNH)(dppe)$_2$]OTf_2, **4Fe2**, is prepared by the addition of at least two equivalents of HOTf to **1Fe2** in $\mathbf{CH}_2Cl_2$ solution (steps i, vii, Scheme 2). The orange colour of **1Fe2** fades to yellow on addition of acid. Some H_2 is liberated from **4Fe2** in solution as revealed by the presence of a signal at δ 4.5 in the ^{1}H NMR spectrum. Complex **4Fe2** can also be prepared by the addition of HOTf to a yellow CD_2Cl_2 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_2O to produce an orange solution of *trans*-[Fe(η^2-H_2)(CN)(dppe)$_2$]OTf, **3Fe2**. Complex **3Fe2** can be isolated as an impure solid by washing the oil, produced by removal of the solvent from a CH_2Cl_2 solution of **4Fe2**, with Et_2O. 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 ^{1}H and ^{31}P NMR spectra after a period of weeks. It is unstable with respect to tautomeric rearrangement to **2Fe2** in CD_2Cl_2 solution (step iv, Scheme 2). A solution of **3Fe2** in CD_2Cl_2 shows resonances in the ^{31}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 **3′Ru2**.

Protonation of *trans*-[OsH(CN)(dppe)$_2$] 1Os2 and *trans*-[OsH(^{13}CNH)(dppe)$_2$]OTf 2Os2-c. The addition of acid to **1Os2** usually results in the formation of **2Os2**. However if one equivalent of HBF_4·Et_2O is added to a solution of **1Os2** in benzene, white *trans*-[Os(η^2-H_2)(CN)(dppe)$_2$]BF_4, **3*Os2** precipitates (where * denotes the BF_4^- salt). This dihydrogen compound in CD_2Cl_2 is stable to H_2 evolution under Ar but it slowly converts to **2*Os2** and another complex tentatively identified as *trans*-[OsH($CNBF_3$)(dppe)$_2$].[28] The addition of water or ether causes the rearrangement to **2*Os2**. For example when D_2O–HBF_4 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^2-H_2)(^{13}CNH)(dppe)$_2$](OTf)$_2$, **4Os2-c**, or *trans*-[Os(η^2-HD)(^{13}CNH)(dppe)$_2$](OTf)$_2$, **4Os2-c,d** form (step vii, Scheme 2). The NH resonance is averaged with the free acid peak at room temperature in the ^{1}H NMR spectrum, but at −40 °C it appears as a doublet at δ 10.8 (^2J(^{13}CH) = 31 Hz). Other NMR properties are listed in Table 2.

Protonation of *trans*-[MH(CN)(depe)$_2$] 1M4, M = Fe, Ru, Os. When one equivalent or an excess of triflic acid is added to a solution of complex **1Ru4** in CH_2Cl_2, 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_4·Et_2O reacts with complexes **1M4** in CH_2Cl_2 to give the dihydrogen complexes *trans*-[M(η^2-H_2)(CN)(depe)$_2$]BF_4 (**3*Ru4**, **3*Fe4**) as analyzed by NMR spectroscopy (see Table 2). One equivalent of the weaker acid [Ph_3PH]BF_4 can also be used to prepare **3*Fe4**. Similarly one equivalent of [Ph_3PH]OTf is used to prepare [Os(η^2-H_2)(^{13}CN)(depe)$_2$]OTf, **3Os4-c**.

The formation of *trans*-[M(η^2-H_2)($CNBF_3$)(depe)$_2$]BF_4 by the known reaction of BF_4^- 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_3 and BF_4^- of such a complex.

The addition of excess HBF_4·Et_2O 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_2OH]BF_4 to **1Fe4** produces *trans*-[Fe(η^2-H_2)(CNH)(depe)$_2$](BF_4)$_2$, **4*Fe4**. The ^{1}H NMR spectrum of **4*Fe4** contains a broad singlet at high field attributed to the dihydrogen ligand. The infrared spectrum of **4*Fe4** shows a strong absorption due to the hydrogen isocyanide ligand at 2100 cm^{-1} (Nujol mull) or 2103 cm^{-1} (CH_2Cl_2 solution). Preliminary results indicate that **4Os4** can be prepared and is stable under vacuum in solution.

Characterisation of the dihydrogen complexes *trans*-[M(η^2-H_2)(CN)L_2]OTf 3Mj, 3′Ru2, 3*Mj

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_2 to give **5Mj** or rearranging to the CNH form **2Mj**. The most stable complex is the osmium one. Similarly the BF_4^- complex **3*Os2** is stable with respect to the loss of H_2. In the case of the depe complexes, the BF_4^- complexes **3*Fe4** and **3*Ru4** are much more stable than the OTf^- complexes. This can be explained by a M–OTf bond strength that is greater than that of M–FBF_3. Attempts to grow crystals of complex **3′Ru2** by slow diffusion of Et_2O into a saturated solution of complex **3′Ru2** in CH_2Cl_2 under H_2 produced complex **2Ru2** as identified by NMR spectroscopy.

These complexes are in the *trans* configuration according to the ^{31}P NMR spectra. The spectra are singlets at room temperature while that of **3Ru3,** at −90 °C, resolves to an A_2X_2 pattern with triplets at δ 2.7 and 16.8 (J(P,P′) = 28.9 Hz). This is typical of *trans*-M(dppp)$_2$XY complexes. The usual periodic trend of δ(PFe) > δ(PRu) > δ(POs) is observed. Compound **3′Ru2** with the (TfO$\cdots$HOTf)$^-$ anion has a slightly different chemical shift (δ 54.2) than **3Ru2** (53.7) with the OTf^- 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 ^{1}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_1(min) values of the η^2-H_2 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_1(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)[29] 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 **3*Os2-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 ^{1}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 ^2J(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(min) (Table 2) while those with the dppm and dppp ligands have 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.[30] 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 *trans*-[Ru(H_2)(CCPh)($P^iPr_2CH_2CH_2P^iPr_2$)$_2$]$^+$ which has a structure related to that of **3Ru4** has been reported to have a similar T_1(min).[31,32]

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

The proton of the anion (TfO···HOTf)$^-$ of **3′Ru2** is observed at δ 13.1. As the temperature is decreased, this peak shifts downfield. At −50 °C, a new peak at δ 16.8 is observed. At −60 °C, three peaks are observed in the acid region of the ^{1}H NMR spectrum at δ 12.5 and 12.9 and 16.8. Bullock *et al.*[9] have studied low temperature ^{1}H NMR spectra of HOTf in CD_2Cl_2. They attributed the resonance near δ 17 to (TfO···HOTf)$^-$ while those near δ 12 to excess HOTf present as (HOTf)$_n$ aggregates or possibly partially dissolved (HOTf)$_n$ aggregates in solution at low temperatures. Since excess acid was not present in the sample of **3′Ru2**, aggregates of HOTf should not be present. Bullock also noted that the solubility of HOTf increases in the presence of TfO^- anions. Therefore the peaks observed at δ 12.5 and δ 12.9 are probably due to the formation of some other triflic acid–triflate aggregate species.

Surprisingly, the dihydrogen complexes *trans*-[Ru(η^2-H_2)(CN)(dppe)$_2$](TfO···HOTf) **3′Ru2** and *trans*-[Ru(η^2-H_2)(CN)(dppe)$_2$]OTf **3Ru2** in CD_2Cl_2 have quite different ^{1}H NMR properties in the hydride region. The former complex exhibits a broad singlet at δ −5.5 while the latter, a broad singlet at δ −7.3. The anion of **3′Ru2** is proposed to have conventional $CF_3O_2SO\cdots HOSO_2CF_3$ hydrogen bonding while the OTf^- anion of **3Ru2** may be involved in a non-classical $CF_3O_2SO\cdots$(HH)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 IrCl···(HH)Ir in Ir(η^2-H_2)(Cl)$_2$(H)(P^iPr_3)$_2$,[23] FeH···(HH)Fe in Fe(η^2-H_2)(H)$_2$($PEtPh_2$)$_3$[33] and BF···(HH)Os in [Os(η^2-H_2)(CH_3CN)(dppe)$_2$](BF_4)$_2$.[8] In the last example the acidic η^2-H_2 ligand forms a 2.4 Å H···F contact with one of the BF_4^- anions. The H–H distance of complex **3Ru2** might be expected to be longer than that of **3′Ru2** due to the hydrogen bonding but this difference is not detectable by J(HD) or T_1(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 *trans*-[M(η^2-H_2)(CNH)L_2](OTf)$_2$ 4Mj

These complexes are characterised in CD_2Cl_2 solution, under H_2 in the presence of an excess of HOTf, by ^{1}H, ^{13}C and ^{31}P NMR and IR spectroscopy in certain cases. The complexes are in the *trans* configuration according to the ^{31}P spectra. The dppm 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}P chemical shifts follow the usual periodic trend Fe > Ru > Os for analogous complexes.

The dihydrogen ligand in the complexes produce a broad resonance at betweens δ *ca.* −3 and δ −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 Å depending on interpretation of the relative motions of the 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 CD_2Cl_2 solution with excess CF_3SO_3D. The ruthenium complexes all have coupling constants J(HD) of about 32 Hz, not significantly different than those of **3Ruj**. The correlation between J(HD) and distance yields a value of about 0.88–0.89 Å. For the dppe complex **4′Ru2** this distance agrees well with the H–H distance calculated from the T_1(min) value for a fast spinning dihydrogen ligand. For the dppm and dppp complexes, the distance from J(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.[30]

The lack of variation in J(HD) with a variation in ancillary ligands is typical of complexes that have η^2-HD coordinated *trans* to a strong field, π-acid ligand like CO, CNH or CN^-.[34]

There is ^{1}H, ^{13}C and ^{15}N evidence for the CNH ligands. The NH resonance for **4Fe2** is a 1:1:1 triplet at δ 8.79 with $^1J_{NH}$ = 80 Hz while that for **4′Ru2** is a broad singlet at δ 10.3 due to rapid proton exchange with the excess free acid present. The acid peak appears in the ^{1}H NMR spectra at δ *ca.* 12.7. The excess acid is most likely to be present as HOTf hydrogen bonded to itself or as dynamic clusters involving the TfO^- anion such as (TfO···HOTf)$^-$.[9] Complex **4Os2-c** has a broad doublet at δ 10.8 with ^2J(HC) = 30.8 Hz. For **4Ru3** and **4Os3** the ^{1}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 δ 13.7 and 14.1, respectively, at −90 °C. This resonance shows a doublet with ^1J(H,^{15}N) = 108.1 and 101.4 Hz, respectively, in the ^{1}H spectrum at the same temperature of the ^{15}N enriched compounds *trans*-[M(η^2-H_2)($C^{15}NH$)(dppp)$_2$](OTf)$_2$ **4M3-n**. The ^{15}N NMR spectrum of **4Os3-n** shows a doublet at δ −205 with ^1J(NH) 102 Hz. Therefore the ligand is coordinated as MCNH and not MNCH. Similarly the CNH and acid peaks for the species at −80 °C thought to be **4Ru1** occur at δ 12.8 (broad) and 11.3, respectively.

Further evidence for the CNH ligand in **4M3** derives from monitoring the protonation of the ^{13}CN enriched compounds *trans*-[M(H)(^{13}CN)(dppp)$_2$] **1M3-c** to produce *trans*-[M(η^2-H_2)(^{13}CNH)(dppp)$_2$](OTf)$_2$ **4M3-c**. In the ^{13}C{^{1}H} NMR spectrum the ^{13}CN quintet of **1M3-c** at δ 156.7 and 137.9 for M = Ru and M = Os, respectively, broadens and shifts to δ 149.9 (^2J(C,P) = 13.6 Hz) and 133.2 (^2J(C,P) = 10.2 Hz), respectively, with the protonation. The ^{31}P signal is a doublet at δ 8.9 (^2J(P,C) = 13.5 Hz) and −29.4 (^2J(P,C) = 7.9 Hz), respectively.

The C–N mode at 2056 cm^{-1} of the CNH ligand was detected by IR spectroscopy of **4Fe2** as a film on NaCl. A CH_2Cl_2 solution of **4Ru3** has a C≡N mode at 2125 cm^{-1} while a Nujol mull of **4Os3** gives a C≡N stretch at 2129 cm^{-1}. On this basis, the **Fe2** centre seems to be more π-basic than the **Ru3** and **Os3** centres.

Acidity of the dihydrogen complexes

The determination of pK_a values for these complexes is complicated by their reactivity and the myriad of equilibria possible. The complex **4′Ru2** is the most acidic complex since it is only completely formed in an excess of HOTf in CH_2Cl_2. Therefore its pK_a is near to that of HOTf in CH_2Cl_2 (the aqueous pK_a of HOTf has been estimated to be −5).[2] 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 **4′Ru2**. This is in keeping with the dppp ligand being more donating than the dppe ligand. Complexes **4′Ru2** and **4Fe2** are deprotonated by treatment with diethyl ether (the aqueous pK_a of $[Et_2OH]^+$ is reported to be -2.4)[35] and so they are very acidic. Complex **3Ru2** at 163 K in CH_2Cl_2 must be less acidic than HOTf because it forms the hydrogen-bonded structure Ru(HH)···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 = Fe, 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 $HPPh_3^+$ in CH_2Cl_2 which has an estimated pK_a of 2.7 in water.[36]

The pK_a of **3*Fe4** was determined in THF by monitoring the equilibrium between *trans*-Fe(H)(CN)(depe)$_2$ with $[Cy_3PH]BF_4$ by $^{31}P\{^1H\}$ NMR. The gated decoupled spectrum was collected with a 10 s delay time to allow adequate time for relaxation of the ^{31}P nuclei. The resonance observed at 22.2 ppm is at an average position between those of free PCy_3 (10.9 ppm) and $[Cy_3PH]^+$ (29.9 ppm). The ratio of $[Cy_3PH]^+$ to PCy_3 is 0.69. The integrations of the resonances due to *trans*-Fe(H)(CN)(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 $[Cy_3PH]^+$, which is estimated to be 9.7 in water[36] and is used as an arbitrary anchor for the THF scale.[37]

The pK_a of *trans*-$[Fe(H_2)(CNH)(depe)_2](BF_4)_2$, **4*Fe4**, was determined in THF by monitoring the equilibrium between $[Ph_3PH](BF_4)$ and *trans*-$[Fe(H_2)(CN)(depe)_2]BF_4$, **3*Fe4**, by ^1H and ^{31}P NMR. The resonance at δ -2.47 in the ^{31}P NMR spectrum is intermediate between the chemical shifts of PPh_3 (δ -6) and $[Ph_3PH](BF_4)$ (δ 4). The integrations of the dihydrogen resonances in the ^1H 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 CH_2Cl_2 must be similar to that of $[Ph_3PH]^+$ (pK_a approx. 2.7 in water).

It is significant that the very acidic dihydrogen complexes **4′Ru2** and **4Ru3** can be formed by reaction of complexes **6Ruj** in HOTf–CH_2Cl_2 with dihydrogen gas. In the absence of an excess of acid, complex **4′Ru2** eliminates HOTf as TfO···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 $[M(H)(CNH)L_2]^+$ and $[M(H_2)(CN)L_2]^+$

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 CH_2Cl_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 Et_2O, complexes **3′Ru2** and **3*Os2** rearrange to the thermodynamically stable complexes **2Ru2** and **2*Os2** over time. This reaction of **3′Ru2** is similar to the addition of PPh_3 to complex **3′Ru2** to form complex **2Ru2** (eqn. (2)). Basic solvents might destabilise the putative Ru(HH)···OTf$^-$ interaction over the CNH···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 H_2 in chlorinated solvents. This is also illustrated by the fact that **2Ru2** is stable under Ar while **2Ru3** slowly changes to **3Ru3** and then to **5Ru3**. The addition of HOTf causes the rapid conversion of **2Ru2** to **3′Ru2**.

Table 3 Selected bond distances (Å) and angles (°) for *trans*-[Ru(OTf)(CNH)(dppe)$_2$]OTf **6Ru2**[3] and *trans*-[Ru(OTf)(CN)(dppe)$_2$] **5Ru2**

	6Ru2	**5Ru2**
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)···O(3S)	2.616(4)	
H(1N)···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)	

Preparation and properties of the complexes *trans*-[Ru(OTf)(CNH)L$_2$]OTf 6Ruj

When the excess acid is removed from complexes **4′Ru2** and **4′Ru2-d$_4$** by washing with Et_2O, complexes **3′Ru2** or **3′Ru2-d$_2$** form but the η^2-H_2 or η^2-HD ligands in these complexes are labile. A slow substitution by triflate produces the complexes *trans*-[Ru(OTf)(CNH)(dppe)$_2$]OTf (**6Ru2**) and *trans*-[Ru(OTf)(CND)(dppe)$_2$]OTf (**6Ru2-d**) (step xv, Scheme 2). Complexes **6Ru2** and **6Ru2-d** are white solids that are soluble in CH_2Cl_2 but insoluble in diethyl ether. Complex **6Ru2** has a 1:1:1 triplet corresponding to the NH group at δ 10.2 (^1J(HN) = 79.2 Hz) in the ^1H NMR spectrum. A singlet at δ 48.8 is observed in the $^{31}P\{^1H\}$ NMR spectrum for this *trans* complex. An X-ray diffraction study[3] 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 cm^{-1} as a combination of the NH···O and C–N modes. The deuterated analogue **6Ru2-d** gave a more intense, broad peak at 2275 cm^{-1}, similar to that shown for complex **2Ru2-d**.[28]

[Ru(OTf)(CNH)(dppp)$_2$]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}P NMR spectrum is a singlet at room temperature and an A_2X_2 pattern at -80 °C comprised of two triplets at δ 0.9 and -7.3 with ^2J(P,P′) = 32.7 Hz. The NH resonance is observed in the ^1H NMR spectrum as a broad singlet at δ 11.0 at -80 °C but is not observed at room temperature because of exchange processes. The ^{13}C enriched complex **6Ru3-c** shows a doublet at δ 1.9 in the ^{31}P NMR spectrum with ^2J(P,C) = 13.5 Hz and a broad signal at δ 159.7 in the ^{13}C NMR spectrum. A weak C–N vibrational band of the complex in Nujol was detected at 2074 cm^{-1} by IR spectroscopy.

When H_2 gas is bubbled into a CD_2Cl_2 solution of complex **6Ru2** or **6Ru3** in the presence of HOTf, complexes **4′Ru2** or **4Ru3** form, respectively (step xiv, Scheme 2).

Preparation and properties of the complexes *trans*-[Ru(OTf)(CN)L$_2$] 5Ruj

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

Table 4 Crystallographic data for **5Ru2**

	5Ru2
Empirical formula	$C_{54}H_{48}F_3NO_3P_4RuS$
Formula weight	1072.94
T/K	150.0(1)
λ/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	16.6236(5)
b/Å	17.0227(6)
c/Å	18.0640(8)
β/°	91.978(5)
V/Å^3	5108.7(3)
Z	4
D_{calc}/Mg m^{-3}	1.395
μ/mm^{-1}	0.527
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0668$, $wR2 = 0.1617$
R indices (all data)	$R1 = 0.1241$, $wR2 = 0.1831$

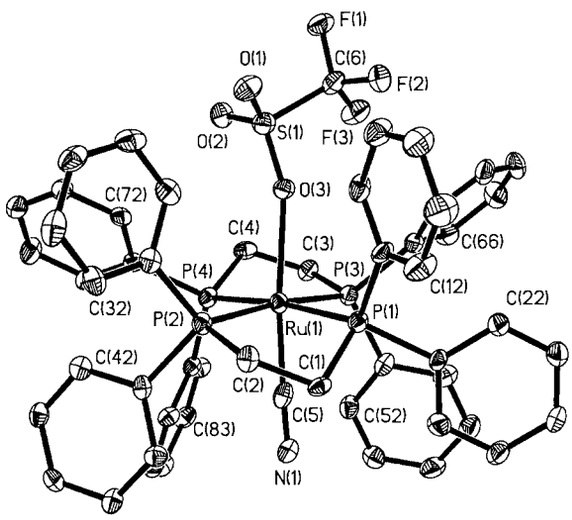


Fig. 2 The structure and labelling of *trans*-[Ru(OTf)(CN)(dppe)$_2$] **5Ru2**. Thermal ellipsoids represent the 30% probability surfaces.

removing one equivalent of HOTf from the corresponding complexes **6Ruj** by use of triethylamine (eqn. (3)).

$$[Ru(OTf)(CNH)L_2]OTf + NEt_3 \longrightarrow [Ru(OTf)(CN)L_2] + HNEt_3OTf \quad (3)$$

In addition, complexes **5Ru1**, **5Ru2** and **5Ru3** have been observed to form from corresponding complexes **3Ruj** by loss of H_2 (step vi of Scheme 2). In a similar fashion the unstable dihydrogen complex [Cp*Re(H$_2$)(NO)(CO)](OTf) loses H_2 at 253 K to give Cp*Re(OTf)(NO)(CO).[6]

The structure of a crystal of **5Ru2** was determined by X-ray diffraction (Fig. 2, Tables 3, 4). Complexes **6Ru2** and **5Ru2** 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_2, it is not surprising to find very long Ru–O distances. Complex **6Ru2** 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 **5Ru2** 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.[38] For example the complex CpRu(P(CF$_2$CF$_3$)$_2$CH$_2$CH$_2$P(CF$_2$CF$_3$)$_2$)(OTf) has a Ru–O distance of 2.2 Å.[39]

The ^{1}H NMR spectrum of complex **5Ru2** in CD_2Cl_2 is very similar to that observed for complex **6Ru2** except for the lack of an NH resonance. A singlet at δ 52.1 is observed in the $^{31}P\{^1H\}$ NMR spectrum. The IR spectrum of **5Ru2** in Nujol has two sharp bands at 2078 cm^{-1} (strong) and at 2068 cm^{-1} (medium intensity). Complexes **5Ru1** and **5Ru3** are characterised by broad singlets at δ −9.1 and 4.8, respectively, in their ^{31}P NMR spectra. The latter changes to a doublet with ^{13}CN labeling ($J(^{13}CP) = 13.5$ Hz).

It is interesting that when complex **5Ru2** is dissolved in THF, the solution remains yellow but when complex **5Ru2** is dissolved in CH_2Cl_2, a red solution forms but becomes yellow after approximately 1 h. Yellow crystals of complex **5Ru2** were formed by dissolving it in CH_2Cl_2 and diffusing in Et_2O. When the yellow crystals are redissolved in CH_2Cl_2, a red solution reforms. Perhaps the red species is [Ru(CN)(dppe)$_2$]OTf while the yellow species in a THF or CH_2Cl_2 solution is [Ru(CN)(solv)(dppe)$_2$]OTf with a coordinated solvent molecule. For example Huhmann-Vincent *et al.* have recently synthesised and structurally characterised the complexes *cis*-[Re(CO)$_4$(PR$_3$)(CH$_2$Cl$_2$)]$^+$ (R = Ph or Cy) containing a monodentate CH_2Cl_2 ligand.[5]

trans-[Ru(H$_2$O)(CNH)(dppe)$_2$](OTf)$_2$ 7Ru2

This complex was detected as an impurity in the crude complex **6Ru2** when prepared from complex **3′Ru2** or if pure **6Ru2** is left in a moist Ar atmosphere. Complex **7Ru2** is associated with a singlet at δ 48.4 in the $^{31}P\{^1H\}$ NMR spectrum (in CD_2Cl_2) and a triplet at δ 11.7 ($^1J(HN) = 79.2$ Hz) and a sharp singlet at δ 3.2 (OH_2) in the ^{1}H NMR spectrum. A drop of degassed water added to the NMR tube containing impure complex **6Ru2** in CD_2Cl_2 causes the peak at δ 3.2 in the ^{1}H spectrum and at δ 48.4 in the $^{31}P\{^1H\}$ NMR spectrum to intensify. For comparison, the aqua ligand in *trans*-[Os(η^2-H$_2$)(H$_2$O)(dppe)$_2$](OTf)$_2$[40] and [Ru(tpb)(PCy$_3$)(OH$_2$)(η^2-H$_2$)]BF$_4$ (tbp = trispyrazolylborate, Cy = cyclohexyl)[41] produce singlets in the ^{1}H NMR spectra at δ 3.2 and δ 3.43, respectively. Crystals of **7Ru2** 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^2-H$_2$)(CN)L$_2$]$^+$ and *trans*-[M(η^2-H$_2$)(CNH)L$_2$]$^{2+}$ where M = Fe, Ru, Os have been characterized. The stability of these complexes **3Mj** and **4Mj** 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$_2$)(H)L$_2$]$^+$ L = dppe, dtfpe or depe[42,43] and *trans*-[M(H$_2$)(H)(PPh$_2$OEt)$_4$]$^+$[44] and *trans*-[M(H$_2$)(H)(*meso*-tetraphos)]$^+$ (*meso*-tetraphos = (*R*,*S*/*S*,*R*)-PPh$_2$(CH$_2$CH$_2$PPh)$_2$CH$_2$CH$_2$PPh$_2$).[45] The ^1J(HD) and T_1(min) values of **3Mj** and **4Mj** are very similar to those of similar complexes *trans*-[M(H$_2$)(H)L$_2$]$^+$.[2,42] 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)$_2$] 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^2-H$_2$)(CN)L$_2$]$^+$) or the other ([MH(CNH)L$_2$]$^+$) by changes in solvent and the hydrogen bonding characteristics of the anion. The isocyanide complexes of the type [MH(CNH)(depe)$_2$]$^+$ 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.[16] The greater donor effect of depe has been demonstrated by studying properties of diphosphine complexes *trans*-[MX(Y)($PR_2(CH_2)_2PR_2)_2$] by use of IR, electrochemical and pK_a measurements.[43,46–50] 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_2] **5Ruj** in CD_2Cl_2 with dihydrogen produces the less stable complexes *trans*-[Ru(η^2-H_2)(CN)L_2]OTf **3Ruj**. Complexes **3Mj** are suspected of having ion pairs with M(HH)···OTf non-classical hydrogen bonding. The deprotonation of *trans*-[M(η^2-H_2)(CNH)(dppe)$_2$](OTf)$_2$ **4M2**, M = Fe, Ru by Et_2O also leads to the **3′M2** tautomers where the triflate is mainly hydrogen-bonded to HOTf in CH_2Cl_2. 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_2O, PPh_3) in the case of **3*Fe2, 3′Ru2** and **3*Os2**.

The highly acidic and stable dicationic dihydrogen complexes, *trans*-[Ru(η^2-H_2)(CNH)L_2]$^{2+}$ (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^2-H_2)(CNH)(dppm)$_2$]$^{2+}$ is observable at temperatures below −40 °C but decomposes at room temperature. The less acidic *trans*-[Os(η^2-H_2)(CNH)(dppp)$_2$]$^{2+}$ can be obtained as a white solid, while *trans*-[Os(η^2-H_2)(CNH)(dppm)$_2$]$^{2+}$ does not form. The pK_a of the complexes **4Fe2**, **4′Ru2**, **4Ru3** are less than that of $HOEt_2^+$ since they are deprotonated by Et_2O. The dihydrogen complexes *trans*-[M(η^2-H_2)(CNH)L_2]$^{2+}$ (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_2. 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^2-H_2)(CN)L_2]$^+$ (L = dppm, dppe, dppp) are unstable under Ar, liberating H_2 and forming *trans*-[Ru(OTf)(CN)L_2] (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_2 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_2 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**).[51] This difference in stability might also be explained by the fact that in **4Mj** the TfO^- is not as nucleophilic because it is hydrogen bonded to HOTf.

When *trans*-[Ru(OTf)(CNH)(dppe)$_2$]OTf **6Ru2** is placed under H_2, a very strong acid is released (HOTf) in the form of (TfO···HOTf)$^-$ and the complex *trans*-[Ru(η^2-H_2)(CN)(dppe)$_2$](TfO···HOTf) **3′Ru2** is formed. This is a rare example of the formation of an acidic dihydrogen complex from H_2 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_2 ligand can move to cyanide and back again easily. Such a migration has not been discussed in studies of the mechanism of hydrogenase action.[52–54] 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_2O (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, $RuCl_3·H_2O$ and $(NH_4)_2OsCl_6$ were purchased from Aldrich. The phosphine ligand dppe was donated by Digital Specialty Chemicals Ltd. [$HPPh_3$]OTf was prepared by reaction with HOTf in a similar fashion to the preparation of [$HPPh_3$]BF_4.[55] The preparation of the complexes **1Mj** and **2Mj** are reported elsewhere.[28] 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. ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were obtained with Bruker AC 200 or with Varian Gemini 300 spectrometers. ^{15}N{^{1}H} NMR spectra were obtained with a Bruker AC 500 spectrometer. ^{31}P chemical shifts are relative to 85% H_3PO_4 and $(NH_4)H_2PO_4$ for solutions and solids, respectively, and ^{15}N chemical shifts to external aqueous solution of K^{15}N. Inverse-gated decoupling was used to record the ^{31}P NMR spectra when their integration was required. All ^{31}P NMR spectra were proton decoupled. ^{1}H NMR T_1 measurements were made using the inversion recovery method. Further experimental details and ^{1}H, ^{13}C, ^{31}P NMR data for the complexes can be found in the supplementary information (SUP 57672).

Preparations

***trans*-[Ru(η^2-H_2)(CNH)(dppm)$_2$](OTf)$_2$ 4Ru1.** *trans*-[RuH(CN)(dppm)$_2$] (21.8 mg, 24 μmol) was dissolved in 0.5 mL of CD_2Cl_2 under H_2 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^2-HD)(CND)(dppm)$_2$](OTf)$_2$ **4Ru1-d$_2$** was prepared in a similar fashion by use of DOTf.

***trans*-[Fe(η^2-H_2)(CN)(dppe)$_2$]OTf, 3Fe2.** *Method A.* Excess triflic acid (70 mg; 0.4 mmol) was added to a CH_2Cl_2 solution of *trans*-Fe(H)(CN)(dppe)$_2$ (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_2O (5 mL) producing a brown powder. Yield 61 mg (98%). *Method B.* Et_2O was added to a solution of **4Fe2** generated *in situ* by Method B

(see below). IR (cm^{-1}, solid on NaCl) 2006 (s, *ν*CN). *trans*-[Fe(HD)(CN)(dppe)$_2$](OTf), **3Fe2-d** was made using DOTf as in Method A.

***trans*-[Fe(H$_2$)(CNH)(dppe)$_2$](OTf)$_2$, 4Fe2.** *Method A.* **1Fe2**, (13 mg; 0.015 mmol) was dissolved in CH_2Cl_2 (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_2Cl_2. IR (film on NaCl) 2056 cm^{-1} (CN); (CH_2Cl_2 solution) 2059 cm^{-1}. *trans*-[Fe(η^2-HD)(CND)(dppe)$_2$](OTf)$_2$, **4Fe2-d$_2$** was made with DOTf according to Method A.

***trans*-[Ru(η^2-H$_2$)(CN)(dppe)$_2$]OTf 3Ru2.** An NMR tube containing *trans*-[Ru(OTf)(CN)(dppe)$_2$] (20 mg, 0.02 mmol) in CD_2Cl_2 was cooled to −78 °C. H_2 gas was bubbled through the solution until the pale yellow solution turned colourless. The NMR spectra were recorded at −10 °C. *trans*-[Ru(η^2-HD)(CN)(dppe)$_2$]OTf **3Ru2-d** was prepared by use of HD(g).

***trans*-[Ru(η^2-H$_2$)(CN)(dppe)$_2$](TfO · · · HOTf) 3′Ru2.** *Method A*. A yellow oil containing *trans*-[Ru(η^2-H$_2$)(CNH)(dppe)$_2$](TfO · · · HOTf)$_2$ in HOTf was stirred for 30 min in 10 mL Et_2O. 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_2 gas was bubbled into an NMR tube containing complex **6Ru2** in CD_2Cl_2.

***trans*-[Ru(η^2-HD)(CN)(dppe)$_2$](TfO · · · DOTf) 3′Ru2-d$_2$.** Diethyl ether was added to the yellow oil of **4′Ru2-d$_4$** (see below) to produce a light yellow precipitate. The solvent was decanted and the product was quickly dried under argon.

***trans*-[Ru(η^2-H$_2$)(CNH)(dppe)$_2$](TfO · · · HOTf)$_2$ 4′Ru2.** *Method A*. *trans*-[RuH(CN)(dppe)$_2$] (100 mg, 0.11 mmol) was dissolved in 10 mL of CH_2Cl_2 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)$_2$]OTf (15 mg, 0.02 mmol) was dissolved in 5 mL of CD_2Cl_2 and triflic acid (7 mg, 0.05 mmol) was added to the solution. The spectra were recorded immediately. *trans*-[Ru(η^2-HD)(CND)(dppe)$_2$](TfO · · · DOTf)$_2$ **4′Ru2-d$_4$** was prepared by use of Method A and DOTf.

***trans*-[Os(η^2-H$_2$)(CN)(dppe)$_2$]BF$_4$ 3*Os2.** A solution of *trans*-[OsH(CN)(dppe)$_2$] **1Os2** (28 mg, 0.028 mmol) in 1.5 mL benzene was treated with HBF_4·Et_2O (5 μL of 85% in Et_2O, 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(η^2-HD)(CN)(dppe)$_2$]BF$_4$ 3*Os2-d.** An acid solution was prepared containing HBF_4·Et_2O (50 μL, 0.3 mmol) and D_2O (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_2Cl_2 was sealed in an NMR tube under Ar.

***trans*-[Os(η^2-H$_2$)(^{13}CNH)(dppe)$_2$](OTf)$_2$ 4Os2-c.** Two equivalents of HOTf (9 mg, 0.055 mmol) were added to *trans*-[OsH(^{13}CNH)(dppe)$_2$]OTf **2Os2-c** in 0.7 mL CD_2Cl_2. The solution remained colourless and there was no gas evolution.

***trans*-[Ru(η^2-H$_2$)(CN)(dppp)$_2$]OTf 3Ru3.** H_2 gas was bubbled through a solution of *trans*-[Ru(OTf)(CN)(dppp)$_2$], **5Ru3**, in CD_2Cl_2 (see below) in an NMR tube until the red solution turned colourless. *trans*-[Ru(η^2-HD)(CN)(dppp)$_2$]OTf **3Ru3-d** was made by use of **5Ru3** and HD(g). *trans*-[Ru(η^2-H$_2$)(^{13}CN)(dppp)$_2$]OTf **3Ru3-c** was prepared starting with **5Ru3-c**.

***trans*-[Ru(η^2-H$_2$)(CNH)(dppp)$_2$](OTf)$_2$ 4Ru3.** *trans*-[RuH(CN)(dppp)$_2$] (20 mg, 21 μmol) was dissolved in 0.5 mL of CD_2Cl_2 under H_2 in an NMR tube and HOTf (6 μL, 68 μmol) was added thereto by means of a syringe. IR (CH_2Cl_2), cm^{-1}: *ν*(CN) 2125 (s). *trans*-[Ru(η^2-H$_2$)(^{13}CNH)(dppp)$_2$](OTf)$_2$ **4Ru3-c** and *trans*-[Ru(η^2-H$_2$)(C^{15}NH)(dppp)$_2$](OTf)$_2$ **4Ru3-n** were prepared starting with **1Ru3-c** and **1Ru3-n**, respectively. *trans*-[Ru(η^2-HD)(CND)(dppp)$_2$](OTf)$_2$ **4Ru3-d$_2$** DOTf was used as in the preparation of **4Ru3**.

***trans*-[Os(η^2-H$_2$)(CNH)(dppp)$_2$](OTf)$_2$ 4Os3.** *trans*-[OsH(CN)(dppp)$_2$] (0.10 g, 0.10 mmol) was dissolved in 2 mL of CH_2Cl_2 under H_2 and CF_3SO_3H (30 μL, 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_2Cl_2–hexane. Yield: 121 mg, 90%. Anal. calc. for $C_{57}H_{55}F_6NO_6OsP_4S_2$: C, 51.01; H, 4.13; N, 1.04. Found: C, 50.34; H, 4.09; N, 1.03%. IR (Nujol), cm^{-1}: *ν*(CN) 2129 (s). *trans*-[Os(η^2-HD)(CND)(dppp)$_2$](OTf)$_2$ **4Os3-d$_2$** was observed by reaction of DOTf with **1Os3**. *trans*-[Os(η^2-H$_2$)(^{13}CNH)(dppp)$_2$](OTf)$_2$ **4Os3-c** and *trans*-[Os(η^2-H$_2$)(C^{15}NH)(dppp)$_2$](OTf)$_2$ **4Os3-n** were prepared starting from **1Os3-c** and **1Os3-n**, respectively.

***trans*-[Fe(H$_2$)(CN)(depe)$_2$]BF$_4$, 3*Fe4.** The addition of 1 equiv. of acid (85% [Et_2OH]BF_4 in Et_2O or [Ph_3PH]BF_4 in CD_2Cl_2) 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_2O. Yield >90%.

***trans*-[Ru(η^2-H$_2$)(CN)(depe)$_2$]BF$_4$ 3*Ru4.** *trans*-[RuH(CN)(depe)$_2$] (63 mg, 0.116 mmol) was dissolved in 5 mL of Et_2O. HBF_4·Et_2O (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(η^2-H$_2$)(^{13}CN)(depe)$_2$]OTf 3Os4-c.** Complex *trans*-[OsH(^{13}CN)(depe)$_2$] **1Os4-c** (20 mg, 0.032 mmol) was dissolved in 3 mL toluene and [$HPPh_3$]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), cm^{-1}: *ν*(^{13}CN) 2064. [Os(η^2-HD)(^{13}CN)(depe)$_2$]OTf **3Os4-c,d** was generated by use of [$DPPh_3$]OTf.

***trans*-[Os(η^2-H$_2$)(CNH)(depe)$_2$](OTf)$_2$ 4Os4.** Excess HOTf (26 mg, 0.17 mmol) were added to *trans*-[OsH(CN)(depe)$_2$] **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)$_2$] 5Ru2.** Under Ar, *trans*-[Ru(OTf)(CNH)(dppe)$_2$]OTf (80.0 mg, 0.65 mmol) was suspended in 5 mL of toluene. To this white suspension, NEt_3 (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_2Cl_2. Diethyl ether was diffused in and after 24 h, yellow needles suitable for X-ray structure determination were obtained (53% yield). Anal. calc. for $C_{54}H_{48}F_3NO_3P_4RuS$: C, 60.44; H, 4.51; N, 1.30. Found: C, 59.49; H, 4.78; N, 1.26%. IR (Nujol), cm^{-1}: *ν*(CN) 2078 (s), 2068 (m).

***trans*-[Ru(OTf)(CN)(dppp)$_2$] 5Ru3.** Under Ar, *trans*-[Ru(OTf)(CNH)(dppp)$_2$]OTf (**6Ru3**, 22 mg, 18 μmol) was dissolved in 0.5 mL of CD_2Cl_2. To this colourless solution, NEt_3 (3 μL, 22 μmol) was added and a red solution of **5Ru3** was produced. *trans*-[Ru(OTf)(^{13}CN)(dppp)$_2$] **5Ru3-c** was prepared by use of **6-Ru3-c**.

***trans*-[Ru(OTf)(CNH)(dppe)$_2$]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_2O into a saturated solution of the complex in CH_2Cl_2. White crystals suitable for X-ray structure determination were obtained by slow evaporation of a concentrated solution of the product in CH_2Cl_2 (70.3% yield). Anal. calc. for $C_{55}H_{49}F_6NO_6P_4RuS_2$: C, 54.01; H, 4.04; N, 1.14. Found: C, 53.66; H, 4.35; N, 1.32%. IR (Nujol), cm^{-1}: ν(CN) + ν(NH) 2532.6 (w). *trans*-[Ru(OTf)(CND)(dppe)$_2$]OTf **6Ru2-d** was prepared in a similar fashion from **4′Ru2-d$_4$**. IR (Nujol), cm^{-1}: ν(CN) + ν(ND) 2275.4 (m).

***trans*-[Ru(OTf)(CNH)(dppp)$_2$]OTf 6Ru3.** *trans*-[RuH(CN)-(dppp)$_2$] (200 mg, 0.21 mmol) was dissolved in 20 mL of CH_2Cl_2. 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_2Cl_2–ether. Yield: 0.21 g, 80%. Anal. calc. for $C_{57}H_{53}F_6NO_6P_4RuS_2$: C, 54.72; H, 4.27; N, 1.12. Found: C, 53.86; H, 4.33; N, 1.10%. IR (Nujol), cm^{-1}: ν(CN) 2074 (w). *trans*-[Ru(OTf)(^{13}CNH)(dppp)$_2$]OTf **6Ru3-c** was prepared starting from **1Ru3-c**.

***trans*-[Ru(H$_2$O)(CNH)(dppe)$_2$](OTf)$_2$ 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_2Cl_2. A solution of HOTf (45 mg, 0.300 mmol) in 2 mL of CH_2Cl_2 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_2O. The white solid was dried under vacuum and the flask was removed from the glovebox and introduced to H_2 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_2Cl_2.

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.[56] 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.[57] Refinement was by full-matrix least-squares on F^2 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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