

Turning dihydrogen gas into a strong acid. Formation and reactions of the very acidic ruthenium dihydrogen complexes $trans\text{-}[\text{Ru}(\text{H}_2)\text{-}(\text{CNH})\{\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2\}_2][\text{O}_3\text{SCF}_3]_2$ ($n = 2$ or 3)[†]

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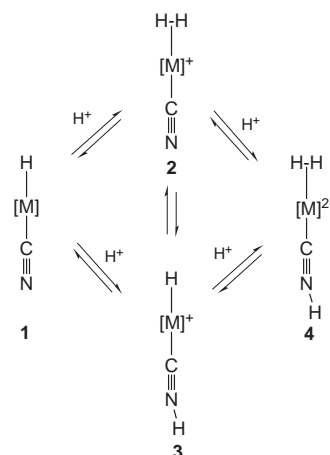
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New, very acidic ruthenium dihydrogen complexes containing the hydrogen isocyanide ligand have been synthesised; when formed under 1 atm H₂ they have been shown to spontaneously eliminate trifluoromethylsulfonic acid.

Some of us recently reported that the protonation of $trans\text{-}[\text{FeH}(\text{CN})(\text{dppe})_2]$ or $trans\text{-}[\text{FeH}(\text{CNH})(\text{dppe})_2]\text{OTf}$ with CF₃SO₃H (HOTf)[‡] in the appropriate ratio gives $trans\text{-}[\text{Fe}(\text{H}_2)(\text{CNH})(\text{dppe})_2][\text{OTf}]_2$, which is very acidic but surprisingly stable with respect to loss of H₂(g).¹ Similar reaction pathways are observed for the related ruthenium and osmium complexes (Scheme 1).² We now find that the very acidic ruthenium analogues $trans\text{-}[\text{Ru}(\text{H}_2)(\text{CNH})\text{L}_2][\text{OTf}]_2$ (L = dppe **4a**, L = dppp **4b**) can be generated by reaction of the new triflate complexes $trans\text{-}[\text{Ru}(\text{OTf})(\text{CNH})\text{L}_2]\text{OTf}$ (**5a**, **5b**) with dihydrogen gas. These complexes then eliminate HOTf in the absence of excess acid although it is not known whether the proton comes from the H₂ or the CNH ligand. This is a significant new reaction pathway involving dihydrogen complexes: the *in situ* production of a very strong acid, in this case HOTf, triggered by the reaction of non-acidic H₂(g) with a co-ordination complex which is not a strong Brønsted acid. Although very acidic dihydrogen complexes have been reported,^{1,3–8} there is only one other complex which is prepared from dihydrogen gas.⁹ This one case involves an unstable iridium dihydrogen complex which can protonate the tetraphenylborate anion in THF.⁹ There is evidence for the elimination of triflic acid from some iridium hydride complexes but it is not known whether dihydrogen complexes are involved.^{10–12}

The reaction of the complexes $trans\text{-}[\text{RuH}(\text{CN})\text{L}_2]$ **1**² in CH₂Cl₂ solution under 1 atm of H₂ with an excess of HOTf gives the dihydrogen complexes $trans\text{-}[\text{Ru}(\text{H}_2)(\text{CNH})\text{L}_2][\text{OTf}]_2$ **4a**, **4b**.[¶] They can also be prepared by reaction of complexes $trans\text{-}[\text{RuH}(\text{CNH})\text{L}_2]\text{OTf}$ **3a**, **3b**² with excess HOTf in CH₂Cl₂ (Scheme 1). The related osmium complexes have also been prepared.² The highly acidic ruthenium dihydrogen complexes have so far only been characterized in solution. The ³¹P-¹H NMR spectrum of **4a** is a sharp singlet at room temperature while that of **4b** is a broad singlet. At 183 K the latter complex gives the A₂X₂ pattern that has been observed for $trans\text{-}[\text{MXY}(\text{dppp})_2]$

species.⁴ The presence of the NH group in complexes **4** is signalled by a broad resonance in the ¹H NMR spectrum in the region at δ 9.6 for **4a** and 13.7 for **4b**. The latter signal is observed only at 183 K; at 293 K the resonance is averaged with



Scheme 1 [M] is the fragment [Ru(dppe)₂] or [Ru(dppp)₂]

§ $trans\text{-}[\text{Ru}(\eta^2\text{-H}_2)(\text{CNH})(\text{dppe})_2][\text{OTf}]_2$ **4a**. Method 1: $trans\text{-}[\text{RuH}(\text{CN})(\text{dppe})_2]$ (**1a**, 100 mg, 0.11 mmol) was dissolved in 10 mL of CH₂Cl₂ 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 2: $trans\text{-}[\text{RuH}(\text{CNH})(\text{dppe})_2][\text{OTf}]$ (**3a**, 15 mg, 0.02 mmol) was dissolved in 5 mL of CD₂Cl₂ and triflic acid (7 mg, 0.05 mmol) was added to the solution. The spectra were recorded immediately. ¹H NMR (300 MHz, CD₂Cl₂): δ 12.7 (s, HOTf), 9.6 (br, NH), 7.8–6.8 (m, Ph), 2.9–2.4 (m, 8 H, CH₂), –5.9 [br, Ru(η²-H₂)]. T₁(min): 300 MHz, CD₂Cl₂, 13.6 ms, 246 K. ³¹P-¹H NMR (120.5 MHz, CD₂Cl₂): δ 52.2 (s). $trans\text{-}[\text{Ru}(\text{HD})(\text{CN})(\text{dppe})_2][\text{OTf}]_2$, **4a-d₂**. Method 2 was followed except deuterated triflic acid (DOTf) was used instead. ¹H NMR (300 MHz, CD₂Cl₂): δ –6.0 [t, ¹J(HD) = 32.4 Hz, Ru(HD)]. ³¹P-¹H NMR (120.5 MHz, CD₂Cl₂): δ 52.2 (s).

¶ $trans\text{-}[\text{Ru}(\eta^2\text{-H}_2)(\text{CNH})(\text{dppp})_2][\text{OTf}]_2$ **4b**. $trans\text{-}[\text{RuH}(\text{CN})(\text{dppp})_2]$ (20 mg, 21 μmol) was dissolved in 0.5 mL of CD₂Cl₂ under H₂ in an NMR tube and CF₃SO₃H (6 μL, 68 μmol) was added thereto by means of a syringe. IR (CH₂Cl₂), cm⁻¹: ν(CN) 2125 (s). ¹H NMR (CD₂Cl₂, 293 K, 200 MHz): δ 7.6–6.9 (m, Ph), 2.4 (br, 8 H, PCH₂), 1.9 (br, 2 H, PCH₂CH₂), 1.6 (br, 2 H, PCH₂CH₂), –4.2 (br, 2 H, RuH₂). ³¹P-¹H NMR (CD₂Cl₂, 293 K, 81 MHz): δ 8.9 (br), T = 183 K, δ 3.2 (t), 15.6 [t, J(P,P') = 30.1 Hz]. $trans\text{-}[\text{Ru}(\text{HD})(\text{CN})(\text{dppp})_2][\text{OTf}]_2$, **4b-d₂**. Excess DOTf was used in the method above. ¹H NMR (200 MHz, CD₂Cl₂): δ –4.2 [t, ¹J(HD) = 31.8 Hz, Ru(HD)]. $trans\text{-}[\text{Ru}(\eta^2\text{-H}_2)(^{13}\text{CNH})(\text{dppp})_2][\text{OTf}]_2$. ³¹P-¹H NMR (CD₂Cl₂): δ 8.9 [d, J(¹³C³¹P) 13.5 Hz]. ¹³C-¹H NMR (CD₂Cl₂): δ 149.9 [q, J(¹³C³¹P) 13.6 Hz].

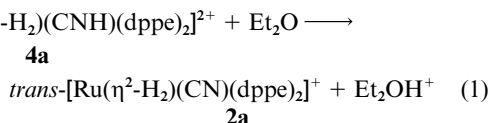
[†] Non-SI unit employed: atm = 101 325 Pa.

[‡] Abbreviations used: dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dtpe = 1,2-bis(ditolylphosphino)ethane; OTf = trifluoromethylsulfonate.

that of free HOTf because of fast proton exchange. This signal splits into a doublet with $^1J(\text{H}^{15}\text{N})$ 108.1 Hz when **4b** is prepared with the C^{15}NH ligand. The CNH ligand has also been detected by IR and ^{13}C NMR.

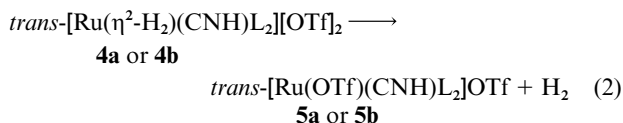
The dihydrogen ligand in complexes **4a** and **4b** gives a broad resonance at δ -5.9 and -4.2, respectively, with a characteristically short minimum T_1 time of 13.6 ms (at 246 K, 300 MHz) and 5.9 ms (at 223 K, 200 MHz). The corresponding η^2 -HD complexes are prepared by reacting complexes **1b** or **3a** with excess DOTf in CD_2Cl_2 . The large $^1J(\text{HD})$ coupling constants of 32.4 Hz for **4a** and 31.8 Hz for **4b** combined with the T_1 (min) data indicate that **4a** and **4b** have rapidly spinning H_2 ligands with H-H distances of 0.88 and 0.89 Å, respectively.¹³

The high acidity of these complexes is illustrated by the chemistry of **4a**. When a CD_2Cl_2 solution of **4a** under $\text{H}_2(\text{g})$ is treated with an excess of the weak base, diethyl ether, complex **2a** forms immediately [equation (1)]. The dihydrogen ligand of



2a is identified by a broad peak at δ -5.5 with a minimum T_1 of 12.4 ms at 240 K, 300 MHz. The corresponding HD complex has $^1J(\text{HD})$ 32.0 Hz. These two data indicate that the H_2 ligand in **2a** is fast spinning with an H-H distance of 0.89 Å. Complexes **4b** are also deprotonated by diethyl ether to give a mixture of the dihydrogen complex $\text{trans-}[\text{Ru}(\eta^2\text{-H}_2)(\text{CN})(\text{dppp})_2]^+$ **2b** and the hydrogen isocyanide complex $\text{trans-}[\text{Ru}(\text{H})(\text{CNH})(\text{dppp})_2]^+$ **3b**.²

The dicationic dihydrogen complexes **4** are less stable with respect to loss of H_2 than the analogous iron complex.¹ Evaporation of solvent leaves yellow oils of complexes **4** and excess acid. These oils slowly lose H_2 under Ar to give mainly the complexes $\text{trans-}[\text{Ru}(\text{OTf})(\text{CNH})\text{L}_2]\text{OTf}$ [equation (2)], $\text{L} = \text{dppe}$ **5a**, ** $\text{L} = \text{dppp}$ **5b**††. Complexes **5** can be identified



|| $\text{trans-}[\text{Ru}(\eta^2\text{-H}_2)(\text{CN})(\text{dppe})_2][\text{HOTf-OTf}]$ **2a**. A yellow oil containing **4a** in HOTf was stirred for 30 min in Et_2O under 1 atm H_2 to form the product. ^1H NMR (300 MHz, CD_2Cl_2): δ 13.1 (s, TfOH-OTf), 7.8-6.6 (m, Ph), 2.5-3.0 (m, 8 H, CH_2), -5.5 [br, $\text{Ru}(\eta^2\text{-H}_2)$]; T_1 (min): 12.4 ms, 240.3 K. $^{31}\text{P}\{-^1\text{H}\}$ NMR (120.5 MHz, CD_2Cl_2): δ 54.2 (s). $\text{trans-}[\text{Ru}(\eta^2\text{-HD})(\text{CN})(\text{dppe})_2]^+$. Diethyl ether was added to the yellow oil of **4a-d** to produce a light yellow precipitate. The solvent was decanted and the product was quickly dried under argon. The product under Ar loses HD and must be isolated and analysed without delay. ^1H NMR (300 MHz, CD_2Cl_2): δ -5.5 [t, $^1J(\text{HD}) = 32.0$ Hz, $\text{Ru}(\text{HD})$]. $^{31}\text{P}\{-^1\text{H}\}$ NMR (120.5 MHz, CD_2Cl_2): δ 54.1 (s).

** $\text{trans-}[\text{Ru}(\text{OTf})(\text{CNH})(\text{dppe})_2]\text{OTf}$ **5a**. Diethyl ether was added to the yellow oil of **4a** under Ar, producing a light yellow precipitate. The solvent was decanted and the precipitate was washed twice with 5 mL of diethyl ether and dried *in vacuo*. Yield of crude **5a** 60%. Yellow crystals were obtained by slow evaporation of a concentrated solution of the product in CH_2Cl_2 . ^1H NMR (300 MHz, CD_2Cl_2): δ 10.5 [t, $^1J(\text{HN}) = 79$ Hz, NH], 7.8-6.6 (m, Ph), 3.0-2.8 (m, 8 H, CH_2). $^{31}\text{P}\{-^1\text{H}\}$ NMR (120.5 MHz, CD_2Cl_2): δ 48.8 (s) (Found: C, 53.66; H, 4.35; N, 1.32. Calc. for $\text{C}_{55}\text{H}_{49}\text{F}_6\text{NO}_6\text{P}_4\text{RuS}_2$: C, 54.01; H, 4.04; N, 1.14%).

†† $\text{trans-}[\text{Ru}(\text{CNH})(\text{OTf})(\text{dppp})_2]\text{OTf}$ **5b**. $\text{trans-}[\text{Ru}(\text{CN})(\text{dppp})_2]$ (**1b**, 200 mg, 0.21 mmol) was dissolved in 20 mL of CH_2Cl_2 . Triflic acid (60 μl , 0.68 mmol) was added and the solution was stirred at room temperature for 20 min under argon bubbling. The solvent was removed *in vacuo* and diethyl ether was added producing a white-pale yellow precipitate. The product was filtered off, washed with diethyl ether, and dried *in vacuo*. Recrystallization from CH_2Cl_2 -diethyl ether yielded 0.21 g, 80% (Found: C, 53.86; H, 4.33; N, 1.10. Calc. for $\text{C}_{57}\text{H}_{53}\text{F}_6\text{NO}_6\text{P}_4\text{RuS}_2$: C, 54.72; H, 4.27; N, 1.12%). IR (Nujol), cm^{-1} : ν (CN) 2074w. ^1H NMR (CD_2Cl_2 , 293 K, 200 MHz): δ 7.6-6.7 (m, PC_6H_5), 2.5 (br, 8 H, PCH_2), 2.1 (br, 4 H, PCH_2CH_2). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CD_2Cl_2 , 293 K, 81 MHz): δ 1.8 (br), $T = 193$ K, δ -7.3 (t), 0.9 [t, $J(\text{P},\text{P}') = 32.7$ Hz].

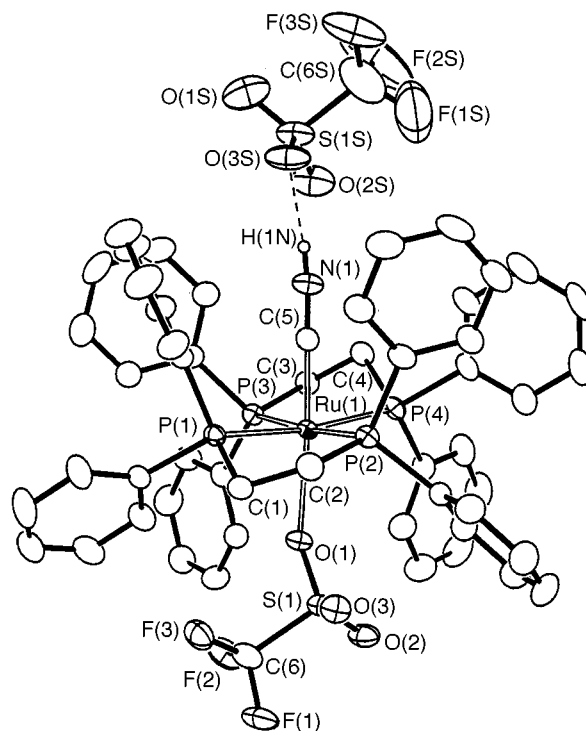
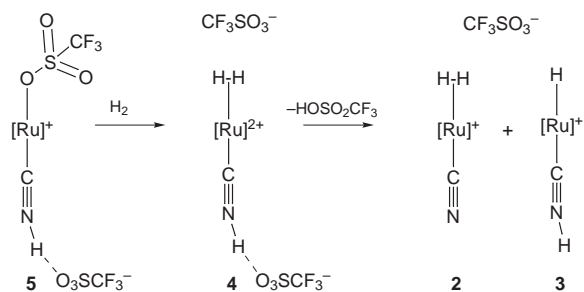


Fig. 1 An ORTEP¹⁴ diagram of complex **5a**. Thermal ellipsoids represent the 50% probability surface. The hydrogen on the nitrogen was located in Fourier electron difference map. Selected bond lengths (Å) and angles (°): Ru-O(1) 2.299(2), Ru-C(5) 1.883(3), Ru-P(1) 2.3938(7), Ru-P(2) 2.3851(8), Ru-P(3) 2.4363(8), Ru-P(4) 2.4144(8), C(5)-N(1) 1.149(4), N(1)-H(1N) 0.77, H(1N)-O(3S) 1.86; O(1)-Ru-C(5) 171.3(1), Ru-C(5)-N(1) 177.2(3), C(5)-N(1)-H(1N) 170.4, N(1)-H(1N)-O(3S) 173.4

by a characteristic ^1HN 1 : 1 : 1 triplet in the ^1H NMR spectrum at δ 10.5 [$^1J(\text{NH})$ 79 Hz] for **5a** or by a broad singlet at δ 11.0 at 183 K for **5b**. Complexes **5** give singlets in the room temperature $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra at δ 48.8 for **5a** and 1.8 for **5b**, respectively. A single-crystal X-ray diffraction study of **5a**†† reveals the presence of a co-ordinated triflate and a triflate anion which is hydrogen bonded to an NH group of a slightly bent CNH unit (C-N-H 170.4°) (Fig. 1). The CNH ligand has similar dimensions to the one of the complex $\text{trans-}[\text{FeH}(\text{CNH})(\text{dtpe})]\text{BF}_4$.¹⁵ The Ru-O(1) distance of 2.299(2) Å is long in comparison to the range of Ru-O distances of 2.177(4) to 2.233(2) Å observed in other ruthenium(II)-triflate complexes.¹⁶⁻¹⁸ The crowded $\text{Ru}(\text{dppe})_2$ site and the high *trans* influence of the CNH ligand cause a weakening of the Ru-O bond and this allows the weak dihydrogen ligand to co-ordinate in its place (see below). Complex **5a** is a weak Brønsted acid. It is not deprotonated by diethyl ether or triphenylphosphine.

When complex **5a** in CD_2Cl_2 with excess HOTf is reacted with 1 atm H_2 , complex **4a** is formed in less than 5 min as expected for the reverse of equation (2). Significantly, when complex **5a** in CD_2Cl_2 is placed under 1 atm H_2 in the absence of HOTf, the dihydrogen complex $\text{trans-}[\text{Ru}(\eta^2\text{-H}_2)(\text{CN})(\text{dppe})_2]^+$ **2a** is produced along with 1 equivalent of triflic acid, probably present mainly as $[\text{TfO-HOTf}]^-$ (Scheme 2). The hydrogen-bonded triflic acid-triflate cluster is identified by ^1H NMR spectroscopy as a broad peak at δ 13.1. Complex **4a** is the likely intermediate in this reaction. However, since it is only

†† Crystal data for **5a**: $\text{C}_{55}\text{H}_{49}\text{F}_6\text{NO}_6\text{P}_4\text{RuS}_2$, $M = 1223.02$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.8064(12)$, $b = 22.121(2)$, $c = 25.213(3)$ Å, $\beta = 93.210(8)^\circ$, $U = 5460.6(11)$ Å³, $D_c = 1.488$ g cm⁻³, $Z = 4$, $T = 173(2)$ K, $\mu = 0.552$ mm⁻¹. For reflections with $2.56 < \theta < 27.00^\circ$, $R(F) = 0.0365$ for 7908 observed reflections [$I > 2\sigma(I)$] and $wR(F^2) = 0.0914$ for all 10 773 reflections. CCDC number 186/1011. See <http://www.rsc.org/suppdata/dt/1998/2111/> for crystallographic files in .cif format.



Scheme 2 [Ru] is the fragment [Ru(dppe)₂] or [Ru(dppp)₂]

stable in the presence of excess HOTf (see above), it must eliminate triflic acid. The product expected from the heterolytic splitting of dihydrogen would be the monohydride complex *trans*-[Ru(H)(CNH)(dppe)₂]OTf **3a**. However as indicated by equation (1), **2a** is the thermodynamically stable product. A similar, slower reaction between **5b** and H₂ produces a mixture of both **2b** and **3b**. However complex **2b** can be quantitatively formed in CH₂Cl₂ solution by treating **5b** with 1 equivalent of NEt₃ and then reacting the product with 1 atm H₂. Studies of the factors that influence the stability of the tautomers **2** and **3** and the properties of related complexes containing iron and osmium and the diphosphine ligands PEt₂CH₂CH₂PEt₂ and PPh₂CH₂PPh₂ are in progress.

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