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Turning dihydrogen gas into a strong acid. Formation and reactions of the very acidic ruthenium dihydrogen complexes *trans*-[Ru(H_2)(CNH){$PPh_2(CH_2)_nPPh_2$}$_2$][O_3SCF_3]$_2$ (n = 2 or 3)†

Tina P. Fong,[a] **Alan J. Lough,**[a] **Robert H. Morris,***[,a] **Antonio Mezzetti,**[b] **Eliana Rocchini**[c] **and Pierluigi Rigo** *[,c]

[a] *Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario, Canada M5S 3H6*

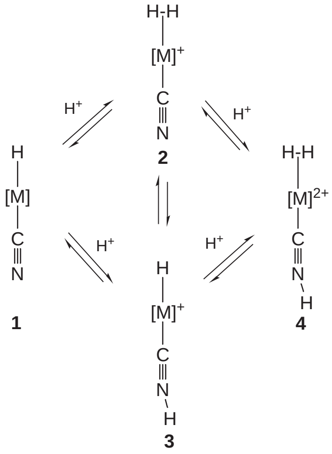
[b] *Laboratorium für Anorganische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland*

[c] *Dip. di Scienze e Tecnol. Chimiche, Università di Udine, Via del Cotonificio 108, I-33100 Udine, Italy*

New, very acidic ruthenium dihydrogen complexes containing the hydrogen isocyanide ligand have been synthesised; when formed under 1 atm H_2 they have been shown to spontaneously eliminate trifluoromethylsulfonic acid.

Some of us recently reported that the protonation of *trans*-[FeH(CN)(dppe)$_2$] or *trans*-[FeH(CNH)(dppe)$_2$]OTf with CF_3SO_3H (HOTf)‡ in the appropriate ratio gives *trans*-[Fe(H_2)(CNH)(dppe)$_2$][OTf]$_2$, which is very acidic but surprisingly stable with respect to loss of H_2(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*-[Ru(H_2)(CNH)L_2][OTf]$_2$ (L = dppe **4a**, L = dppp **4b**) can be generated by reaction of the new triflate complexes *trans*-[Ru(OTf)(CNH)L_2]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 H_2 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 H_2(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*-[RuH(CN)L_2] **1**[2] in CH_2Cl_2 solution under 1 atm of H_2 with an excess of HOTf gives the dihydrogen complexes *trans*-[Ru(H_2)(CNH)L_2][OTf]$_2$ **4a**,§ **4b**.¶ They can also be prepared by reaction of complexes *trans*-[RuH(CNH)L_2]OTf **3a**, **3b**[2] with excess HOTf in CH_2Cl_2 (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 ^{31}P-{^{1}H} 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 A_2X_2 pattern that has been observed for *trans*-[MXY(dppp)$_2$] species.[4] The presence of the NH group in complexes **4** is signalled by a broad resonance in the ^{1}H 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)$_2$]

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† *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.

§ *trans*-[Ru(η^2-H_2)(CNH)(dppe)$_2$][OTf]$_2$ **4a**. Method 1: *trans*-[RuH(CN)(dppe)$_2$] (**1a**, 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 2: *trans*-[RuH(CNH)(dppe)$_2$][OTf] (**3a**, 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. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 12.7 (s, HOTf), 9.6 (br, NH), 7.8–6.8 (m, Ph), 2.9–2.4 (m, 8 H, CH_2), −5.9 [br, Ru(η^2-H_2)]. T_1(min): 300 MHz, CD_2Cl_2, 13.6 ms, 246 K. ^{31}P-{^{1}H} NMR (120.5 MHz, CD_2Cl_2): δ 52.2 (s). *trans*-[Ru(HD)(CND)(dppe)$_2$][OTf]$_2$, **4a**-d_2. Method 2 was followed except deuteriated triflic acid (DOTf) was used instead. ^{1}H NMR (300 MHz, CD_2Cl_2): δ −6.0 [t, ^1J(HD) = 32.4 Hz, Ru(HD)]. ^{31}P-{^{1}H} NMR (120.5 MHz, CD_2Cl_2): δ 52.2 (s).

¶ *trans*-[Ru(η^2-H_2)(CNH)(dppp)$_2$][OTf]$_2$ **4b**. *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 CF_3SO_3H (6 μL, 68 μmol) was added thereto by means of a syringe. IR (CH_2Cl_2), cm^{-1}: ν(CN) 2125 (s). ^{1}H NMR (CD_2Cl_2, 293 K, 200 MHz): δ 7.6–6.9 (m, Ph), 2.4 (br, 8 H, PCH_2), 1.9 (br, 2 H, PCH_2CH_2), 1.6 (br, 2 H, PCH_2CH_2), −4.2 (br, 2 H, RuH_2). ^{31}P-{^{1}H} NMR (CD_2Cl_2, 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*-[Ru(HD)(CND)(dppp)$_2$][OTf]$_2$ **4b**-d_2. Excess DOTf was used in the method above. ^{1}H NMR (200 MHz, CD_2Cl_2): δ −4.2 [t, ^1J(HD) = 31.8 Hz, Ru(HD)]. *trans*-[Ru(η^2-H_2)(^{13}CNH)(dppp)$_2$][OTf]$_2$. ^{31}P-{^{1}H} NMR (CD_2Cl_2): δ 8.9 [d, $J(^{13}C^{31}P)$ 13.5 Hz]. ^{13}C-{^{1}H} NMR (CD_2Cl_2): δ 149.9 [q, $J(^{13}C^{31}P)$ 13.6 Hz].

that of free HOTf because of fast proton exchange. This signal splits into a doublet with $^1J(H^{15}N)$ 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 $^1J(HD)$ 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 $H_2(g)$ is treated with an excess of the weak base, diethyl ether, complex **2a**|| forms immediately [equation (1)]. The dihydrogen ligand of

$$\underset{\textbf{4a}}{trans\text{-}[Ru(\eta^2\text{-}H_2)(CNH)(dppe)_2]^{2+}} + Et_2O \longrightarrow \underset{\textbf{2a}}{trans\text{-}[Ru(\eta^2\text{-}H_2)(CN)(dppe)_2]^{+}} + Et_2OH^+ \quad (1)$$

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 $^1J(HD)$ 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 *trans*-$[Ru(\eta^2\text{-}H_2)(CN)(dppp)_2]^+$ **2b** and the hydrogen isocyanide complex *trans*-$[Ru(H)(CNH)(dppp)_2]^+$ **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 *trans*-$[Ru(OTf)(CNH)L_2]$OTf [equation (2), L = dppe **5a**,** L = dppp **5b**††]. Complexes **5** can be identified by a characteristic ^{1}HN 1 : 1 : 1 triplet in the ^{1}H NMR spectrum at δ 10.5 [^1J(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 $^{31}P\text{-}\{^1H\}$ 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 *trans*-$[FeH(CNH)(dtpe)_2]BF_4$.[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 $Ru(dppe)_2$ 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.

$$\underset{\textbf{4a or 4b}}{trans\text{-}[Ru(\eta^2\text{-}H_2)(CNH)L_2][OTf]_2} \longrightarrow \underset{\textbf{5a or 5b}}{trans\text{-}[Ru(OTf)(CNH)L_2]OTf} + H_2 \quad (2)$$

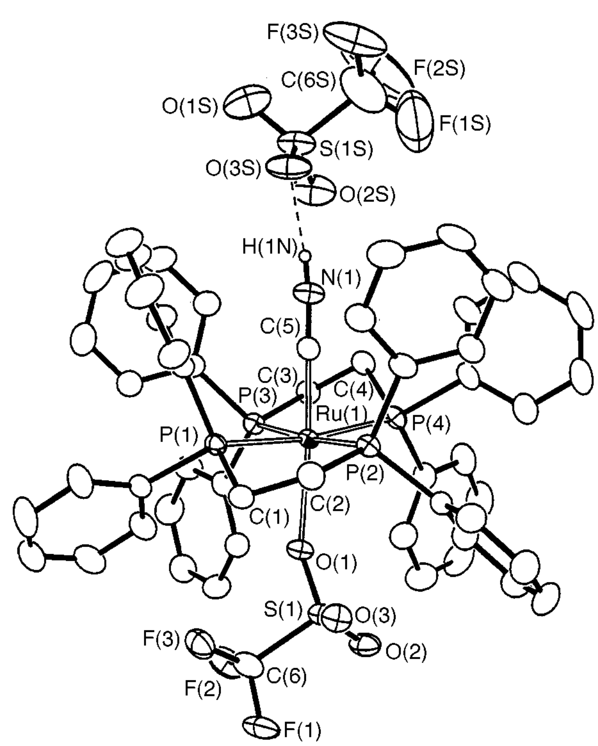

Fig. 1 An ORTEP[14] diagram of complex **5a**. Thermal ellipsoids represent the 50% probability surface. The hydrogen on the nitrogen was located in Fourier electron difference map. Selected bond lengths (Å) and angles (°): Ru–O(1) 2.299(2), Ru–C(5) 1.883(3), Ru–P(1), 2.3938(7), Ru–P(2) 2.3851(8), Ru–P(3) 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

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 *trans*-$[Ru(\eta^2\text{-}H_2)(CN)(dppe)_2]^+$ **2a** is produced along with 1 equivalent of triflic acid, probably present mainly as $[TfO\text{–}HOTf]^-$ [7] (Scheme 2). The hydrogen-bonded triflic acid–triflate cluster is identified by ^{1}H NMR spectroscopy as a broad peak at δ 13.1. Complex **4a** is the likely intermediate in this reaction. However, since it is only

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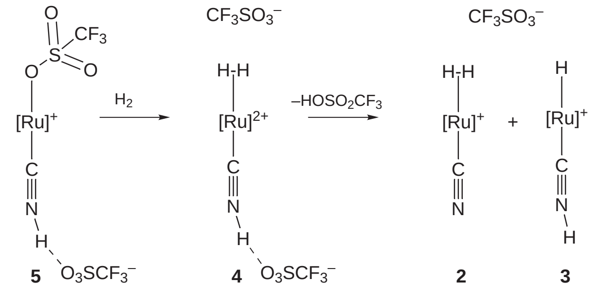
|| *trans*-$[Ru(\eta^2\text{-}H_2)(CN)(dppe)_2][HOTf\text{–}OTf]$ **2a**. A yellow oil containing **4a** in HOTf was stirred for 30 min in Et_2O under 1 atm H_2 to form the product. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 13.1 (s, TfOH–OTf), 7.8–6.6 (m, Ph), 2.5–3.0 (m, 8 H, CH_2), −5.5 [br, $Ru(\eta^2\text{-}H_2)$]; T_1(min): 12.4 ms, 240.3 K. $^{31}P\text{-}\{^1H\}$ NMR (120.5 MHz, CD_2Cl_2): δ 54.2 (s). *trans*-$[Ru(\eta^2\text{-}HD)(CN)(dppe)_2]^+$. Diethyl ether was added to the yellow oil of **4a**-d_2 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. ^{1}H NMR (300 MHz, CD_2Cl_2): δ −5.5 [t, $^1J(HD)$ = 32.0 Hz, Ru(HD)]. $^{31}P\text{-}\{^1H\}$ NMR (120.5 MHz, CD_2Cl_2): δ 54.1 (s).

** *trans*-$[Ru(OTf)(CNH)(dppe)_2]$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. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 10.5 [t, $^1J(HN)$ = 79 Hz, NH], 7.8–6.6 (m, Ph), 3.0–2.8 (m, 8 H, CH_2). $^{31}P\text{-}\{^1H\}$ NMR (120.5 MHz, CD_2Cl_2): δ 48.8 (s) (Found: C, 53.66; H, 4.35; N, 1.32. Calc. for $C_{55}H_{49}F_6NO_6P_4RuS_2$: C, 54.01; H, 4.04; N, 1.14%).

†† *trans*-$[Ru(CNH)(OTf)(dppp)_2]$OTf **5b**. *trans*-$[RuH(CN)(dppp)_2]$ (**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 $C_{57}H_{53}F_6NO_6P_4RuS_2$: C, 54.72; H, 4.27; N, 1.12%). IR (Nujol), cm^{-1}: ν (CN) 2074w. ^{1}H 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). $^{31}P\text{-}\{^1H\}$ NMR (CD_2Cl_2, 293 K, 81 MHz): δ 1.8 (br), T = 193 K, δ −7.3 (t), 0.9 [t, $J(P,P')$ = 32.7 Hz].

‡‡ Crystal data for **5a**: $C_{55}H_{49}F_6NO_6P_4RuS_2$, M = 1223.02, monoclinic, space group $P2_1/c$ (no. 14), a = 9.8064(12), b = 22.121(2), c = 25.213(3) Å, β = 93.210(8)°, U = 5460.6(11) Å^3, D_c = 1.488 g cm^{-3}, Z = 4, T = 173(2) K, µ = 0.552 mm^{-1}. For reflections with 2.56 < θ < 27.00°, $R(F)$ = 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 H_2 produces a mixture of both **2b** and **3b**. However complex **2b** can be quantitatively formed in CH_2Cl_2 solution by treating **5b** with 1 equivalent of NEt_3 and then reacting the product with 1 atm H_2. 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 $PEt_2CH_2CH_2PEt_2$ and $PPh_2CH_2PPh_2$ are in progress.

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