Intramolecular proton transfer from a cation to the associated, structurally characterised, hydride-containing anion [(PPh$_3$)$_2$(H)Ru(μ-H)(μ-Cl)$_2$Ru(H)(PPh$_3$)$_2$]$^-$ to give an η^2-H$_2$ complex

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The previously unknown, dinuclear, ionic ruthenium(ɪɪ) species [Hdma][(PPh$_3$)$_2$(H)Ru(μ-H)(μ-Cl)$_2$Ru(H)-(PPh$_3$)$_2$]·dma 1 (dma = *N,N*-dimethylacetamide) is characterised by X-ray crystallography; in solution, intramolecular proton transfer from the cation to the anion gives the known molecular hydrogen complex [(PPh$_3$)$_2$(η^2-H$_2$)Ru(μ-H)(μ-Cl)$_2$Ru(H)(PPh$_3$)$_2$] 2.

A general method for preparing dihydrogen complexes is protonation of transition-metal hydride species,[1] a process that can be viewed as the reverse of heterolytic cleavage of H$_2$. There are reported examples of an equilibrium between a molecular hydrogen complex and the corresponding hydride [*i.e.* M(η^2-H$_2$) ⇌ M(H$^-$) + H$^+$], and some include intramolecular proton transfer from the η^2-H$_2$ ligand to a co-ligand, which acts as a base.[2] To our knowledge, there are no examples where this proton transfer is from a cation to the associated anion of a transition-metal complex. The closest related example is proton transfer from cyclohexanol to the anionic [RuH$_3$(PPh$_3$)$_3$]$^-$ to generate [Ru(η^2-H$_2$)(H)$_2$(PPh$_3$)$_3$].[3] We report here, the X-ray crystal structure of the ionic complex [Hdma][(PPh$_3$)$_2$(H)Ru(μ-H)(μ-Cl)$_2$Ru(H)(PPh$_3$)$_2$]·dma 1,† which in solution undergoes proton transfer to give the known complex [(PPh$_3$)$_2$(η^2-H$_2$)Ru(μ-H)(μ-Cl)$_2$Ru(H)(PPh$_3$)$_2$] 2.[4]

Red prisms of 1 were serendipitously grown in a dma filtrate that was left at *ca.* 20 °C for several months. The reactants were [RuCl$_3$(PPh$_3$)$_2$(dma)]·dma,[5] and 1 equiv. of dppb [1,4-bis(diphenylphosphino)butane], left under 1 atm H$_2$. A pink co-product, established by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy and elemental analysis‡ to be the ionic complex [Hdma][(dppb)Cl-Ru(μ-Cl)$_3$RuCl(dppb)] 3, was also isolated; the anion of 3 has been previously characterised by X-ray crystallography within a complex where the associated cation was 1,1,3-trimethyl-2,3-dihydroperimidinium.[6]

The molecular structure of 1 is shown in Fig. 1. The dinuclear anion, with a C_2 axis, contains one bridging and two terminal hydrides. The cation [Hdma]$^+$, the proton of which was not located or included in the model, has been studied previously by X-ray diffraction within *N,N*-dimethylacetamidonium chloride;[7] the cation here is different from that found for 1, as the H$^+$ is located between the O and Cl, with strong hydrogen bonds. The dma sites in 1 are occupied 50% by a neutral molecule and 50% by a [Hdma]$^+$ moiety. The IR spectrum (KBr pellet) of crystalline 1 shows a strong broad $\nu_{C=O}$ at 1647 cm^{-1}, close to that found for free dma solvent (1640 cm^{-1}). For comparison purposes, the $\nu_{C=O}$ band in [Hdma]Cl was observed at 1670 cm^{-1}.[7]

The Ru–μ-H bond length of 1.72 Å observed in 1 is similar to that observed for one side of the unsymmetrical hydride bridge in [L(η^2-H$_2$)Ru(μ-H)(μ-Cl)$_2$Ru(H)(PPh$_3$)$_2$] (1.71 Å); L = a phosphorus–nitrogen chelating, ferrocene-based ligand,[4] but is significantly longer than the other Ru–μ-H bond length in the η^2-H$_2$ species (1.49 Å). The Ru–terminal hydride bond length (1.59 Å) is similar to that in the species containing L.[4] The locations of the hydrogen atoms in 2 and the analogous [{P(C$_6$H$_4$Me-*p*)$_3$}$_2$(η^2-H$_2$)Ru(μ-H)(μ-Cl)$_2$Ru(H){P(C$_6$H$_4$Me-

p)$_3$}$_2$] complex were not established in earlier X-ray crystallographic studies; however, these complexes did not contain a C_2 axis.[4,8,9] For 1 and the molecular (L)(η^2-H$_2$) complex,[4] the hydride and the η^2-H$_2$ ligands were located. Of note, complex 2 has recently been studied by X-ray crystallography using CCD detection with all the hydride and η^2-H$_2$ hydrogens now located.[10] Comparison of the bond lengths and angles of 1 with those of 2[10] are entirely consistent with the formulation of 1 as [Hdma][(PPh$_3$)$_2$(H)Ru(μ-H)(μ-Cl)$_2$Ru(H)(PPh$_3$)$_2$]·dma.
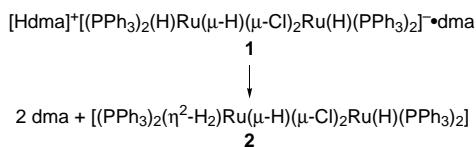
The Ru–Ru bond length of 2.83 Å in 1 is the same as that in 2 (from the partial structure) and is in the range generally reported for a Ru–Ru single bond (2.632–3.034 Å).[4] The Ru–Cl–Ru (69.20°) and Cl–Ru–Cl (81.58°) bond angles of 1 are also indicative of a Ru–Ru single bond within the general class of dinuclear Ru$_2$ complexes containing face-sharing bioctahedra.[11]

^{31}P{^{1}H} and ^{1}H NMR spectroscopic studies on [^{2}H$_8$]toluene solutions of the crystalline sample of 1 show spectra essentially
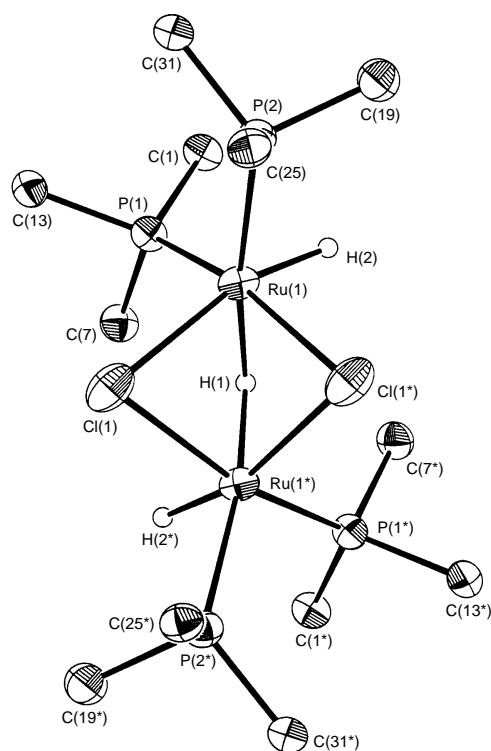
Fig. 1 ORTEP plot of the anion of [Hdma][(PPh$_3$)$_2$(H)Ru(μ-H)(μ-Cl)$_2$Ru(H)(PPh$_3$)$_2$]·dma 1. Thermal ellipsoids for non-hydrogen atoms are drawn at 33% probability (some of the phenyl carbons have been omitted for clarity); * refers to the symmetry operation: $-x$, y, $\frac{1}{2} - z$. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(1*) 2.8251(5), Ru(1)–Cl(1) 2.510(1), Ru(1)–Cl(1*) 2.4649(9), Ru(1)–P(1) 2.2576(9), Ru(1)–P(2) 2.3483(9), Ru(1)–H(2) 1.59(3), Ru(1)–H(1) 1.72(3); Cl(1)–Ru(1)–Cl(1*) 81.58(4), Ru(1)–Cl(1)–Ru(1*) 69.20(3), Ru(1*)–Ru(1)–H(2) 109.1(9), Ru(1*)–Ru(1)–H(1) 35(1), H(1)–Ru(1)–H(2) 86(1).

identical to those of the neutral η^2-H$_2$ complex **2**, thus demonstrating conversion of **1** into **2** in this solvent (Scheme 1). The ^{31}P{^{1}H} spectrum of **1** in C$_7$D$_8$ at 20 °C shows two broad resonances at δ 71.3 and 46.3, while at -89 °C the spectrum gives an ABCD spin system, the data corresponding exactly to those previously observed for **2**;[4,8,9] the 20 °C spectrum also shows a small amount (*ca.* 5%) of another species associated with an AB pattern (δ_A 56.8, δ_B 54.7, $^2J_{AB}$ 30 Hz) and this possibly results from the presence of **1**.

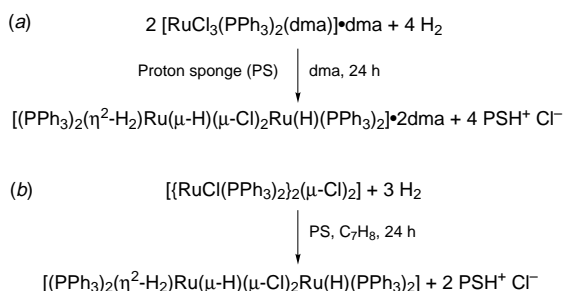[Hdma]$^+$[(PPh$_3$)$_2$(H)Ru(μ-H)(μ-Cl)$_2$Ru(H)(PPh$_3$)$_2$]$^-$•dma

1

$\downarrow$

2 dma + [(PPh$_3$)$_2$(η^2-H$_2$)Ru(μ-H)(μ-Cl)$_2$Ru(H)(PPh$_3$)$_2$]

2

Scheme 1

The ^{1}H NMR spectrum of **1** in C$_7$D$_8$ at 20 °C shows a single broad resonance in the hydride region at δ -12.8, but at -79 °C signals are seen at δ -8.7 (br d), -12.6 (br s) and -17.3 (br s), and these data correspond to those for the μ-hydride, η^2-H$_2$ and terminal hydride, respectively, of **2**, as established by the T_1 measurements and exchange-spectra simulations for these protons [similar data are found for the P(C$_6$H$_4$Me-*p*)$_3$ analogue].[4,8,9] Two other resonances of lower intensity observed at δ -14.9 (t, $^2J_{PH}$ 31.1 Hz) and δ -17.7 (br s) could again be attributed to the terminal- and bridging-hydrides of **1**. We have been unable to detect the ^{1}H resonance for the proton of [Hdma]$^+$. {Of interest, the resonance for the proton of this cation in a CH$_2$Cl$_2$ solution of [Hdma]Cl has been reported at δ 12.[7] The [H(dma)$_2$]$^+$ cation is also known, *e.g.* within [H(dma)$_2$][AuCl$_4$] where δ_H was reported at -17.45,[12,13] but we have repeated this work and find δ_H at +18}.

The observation of NMR signals that are consistent with the presence of small amounts of **1** in Scheme 1 implies an equilibrium reaction, but unfortunately this could not be confirmed by measuring the ^{31}P{^{1}H} NMR spectra of **2** in C$_7$D$_8$ solutions containing several equivalents of dma; only signals due to **2** were seen (trace water in the added dma could complicate these measurements on the 'reverse' process).

Nevertheless, despite our failure to establish Scheme 1 as an equilibrium, the spectral and X-ray structural data taken together demonstrate unequivocally the proton-transfer reaction shown in the forward reaction.

(*a*)   2 [RuCl$_3$(PPh$_3$)$_2$(dma)]•dma + 4 H$_2$

Proton sponge (PS) | dma, 24 h

[(PPh$_3$)$_2$(η^2-H$_2$)Ru(μ-H)(μ-Cl)$_2$Ru(H)(PPh$_3$)$_2$]•2dma + 4 PSH$^+$ Cl$^-$

(*b*)   [{RuCl(PPh$_3$)$_2$}$_2$(μ-Cl)$_2$] + 3 H$_2$

PS, C$_7$H$_8$, 24 h

[(PPh$_3$)$_2$(η^2-H$_2$)Ru(μ-H)(μ-Cl)$_2$Ru(H)(PPh$_3$)$_2$] + 2 PSH$^+$ Cl$^-$

Scheme 2

Of note, we have reported two synthetic routes to the η^2-H$_2$ complex **2** (Scheme 2).[4,8] In retrospect, in light of the data given here, the solid-state product from Scheme 2(*a*) should be reformulated as the ionic complex **1**, while in solution the neutral species **2** would be present. Reaction in the absence of dma allows the isolation of the neutral complex **2** in the solid state [Scheme 2(*b*)].

A key step in the mechanism of the well known hydrogenation catalyst [Ru(H)Cl(PPh$_3$)$_3$] is initial dissociation of a phosphine ligand to generate species containing the 'Ru(PPh$_3$)$_2$' moiety,[8,9] but whether dinuclear species such as the anion of **1**, or the η^2-H$_2$ complex **2**, play any role in the catalysis still remains to be established.

Footnotes

† Crystals of **1** are monoclinic, space group *C*2/*c*, a = 23.762(3), b = 13.372(2), c = 25.937(3) Å, β = 119.575(7)°, Z = 4; μ(Mo-Kα) = 6.34 cm^{-1}, T = 21 °C. The structure was solved by the Patterson method and was refined by full-matrix least-squares procedures to R = 0.036 (R_w = 0.033) for 5504 reflections with $I \geqslant 3\sigma(I)$. Satisfactory elemental analysis was obtained for **1**. CCDC no. 182/519.
‡ *Data* for **3**: ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C): δ 1.58 (br m, 4 H, CH$_2$), 1.65 (br m, 4 H, CH$_2$), 2.05 (s, 3 H, CH$_3$), 2.15 (br m, 2 H, CH$_2$), 2.55 (br m, 4 H, CH$_2$), 2.88 (br m, 2 H, CH$_2$), 2.90 (s, 3 H, CH$_3$), 3.00 (s, 3 H, CH$_3$), 6.7–7.6 (m, 40 H, Ph), 8.2 (br s, 1 H, *H*dma). ^{31}P{^{1}H} NMR (121.42 MHz, CDCl$_3$, 20 °C): δ 48.9 (s). Satisfactory elemental analysis was obtained for **3**.

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