Ruthenium–Dihydrogen Complexes *via* C–H Cleavage in Alk-1-ynes. Crystal Structure of $[Ru(H_2)(C\equiv CPh)(dippe)_2][BPh_4]$ [dippe = 1,2-bis(diisopropylphosphino)ethane]

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The reaction of the monohydride complex $[RuH(dippe)_2]^+$ with alk-1-ynes yields the dihydrogen complexes $[Ru(H_2)(C\equiv CR)(dippe)_2]^+$ [R = Ph or CO_2Me]; the X-ray crystal structure of $[Ru(H_2)(C\equiv CPh)(dippe)_2][BPh_4]$ has been determined, and represents the first structural report of an alkynyl–dihydrogen complex.

The interaction of hydride and dihydrogen complexes, with alkynes has attracted a great deal of attention in recent years, owing mainly to the potential ability of such complexes to act as catalysts for the polymerisation and hydrogenation of alkynes.[1] Depending upon the particular system and the reaction conditions, different metal-containing products, including alkynyl,[2] vinylidene,[3] alkenyl[4] or enynyl[5] complexes, can be isolated. Recently, it has been pointed out that the reactions of some transition metal hydrides with alkynes may give rise to alkynyl–dihydrogen complexes, as in the reaction of $[OsH_4(CO)(PPr^i_3)_2]$ with one equivalent of $HC\equiv CR$ (R = Ph or $SiMe_3$), in which the labile derivatives $[OsH(H_2)(C\equiv CR)(CO)(PPr^i_3)_2]$ are produced.[6] These compounds have been detected in solution only, being short-lived species which are converted into the corresponding bis(alkynyl) or tetrahydride complex depending upon the conditions.[7]

We report that the reaction of the 16-electron, five-coordinate complex $[RuH(dippe)_2][BPh_4]$[8] **1** with an excess of $HC\equiv CR$ (R = Ph or CO_2Me) proceeds with cleavage of the C–H bond, to yield $[RuH_2(C\equiv CR)(dippe)_2][BPh_4]$ (where R = Ph **2** or CO_2Me **3**).† Apparently, oxidative addition of the alkyne molecule to produce an Ru^{IV} acetylido-dihydride has taken place. However, the high-field hydride resonance for **2** and **3** appears as a broad, unresolved signal in their respective ^1H NMR spectra even at low temperature, and the minimum longitudinal relaxation time (T_1) for these signals has a value of 11 and 13 ms for **2** and **3**, respectively (400 MHz, $[^2H_6]$acetone). These data indicate that **2** and **3** are better formulated as Ru^{II} dihydrogen complexes $[Ru(\eta^2\text{-}H_2)(C\equiv CR)(dippe)_2][BPh_4]$, rather than as Ru^{IV} dihydrides. These materials are quite stable and do not lose H_2 in the solid state under dinitrogen or in *vacuo*, in contrast with $[RuH(H_2)(dippe)_2][BPh_4]$,[8] which is only stable under a dihydrogen atmosphere. In acetone solution, however, these compounds exhibit rather peculiar behaviour and exist as equilibrium mixtures with the monohydride **1** and the free alkyne, according to eqn. (1). The equilibrium constant K for this

$$[Ru(\eta^2\text{-}H_2)(C\equiv CR)(dippe)_2]^+ \rightleftarrows [RuH(dippe)_2]^+ + HC\equiv CR \qquad (1)$$

$$R = Ph \text{ or } CO_2Me$$

process has been determined by integration of the NMR hydride signals due to **2** or **3** and the monohydride **1** in the equilibrium mixture, and has an approximate value of 3×10^{-2} mol dm^{-3} for both complexes. The equilibrium can be shifted to the left by addition of an excess of alk-1-yne. No products of hydrogenation of the alkyne, such as styrene or methyl acrylate have been detected. The $^{31}P\{^1H\}$ NMR spectra of complexes **2** and **3** (with an excess of alkyne added) consist of one singlet, which suggests an equatorial arrangement of the phosphines, with the acetylide *trans* to the side-on bound dihydrogen ligand. This has been confirmed by the single crystal X-ray structure analysis of **2**.‡ A view of the complex cation $[Ru(\eta^2\text{-}H_2)(C\equiv CPh)(dippe)_2]^+$ is shown in Fig. 1, together with selected bond lengths and angles. The structure of the ruthenium complex displays a distorted octahedral arrangement around the metal, with the alkynyl and hydrogen ligands in mutually *trans* positions. The fragment Ru–C(1)–C(2)–C(3) appears almost linear, with bond distances and angles in the usual range for other alkynyl complexes.[1,9] The dihydrogen ligand was located on a symmetry-weighted Fourier map, and it was not refined. The dimensions obtained for this ligand are not definite, in view of the relatively poor R-value. Thus, the H atoms appear to be located at 1.5 Å from the Ru atom and 1.1 Å apart, this separation being consistent with the NMR data which point to a dihydrogen rather than a dihydride complex.

The complexes **2** and **3** undergo typical reactions of dihydrogen complexes, namely substitution of coordinated

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† Satisfactory elemental analyses were obtained for all the compounds. Selected spectral data for: **2**, IR (Nujol): $\nu(C\equiv C)$ 2040, 2090 cm^{-1}; NMR (CD_3COCD_3): ^1H δ -8.577 [s, br, Ru(H_2)], T_1 = 11 ms (400 MHz, 253 K); $^{31}P\{^1H\}$ δ 69.1 s.

3, IR (Nujol): $\nu(C\equiv C)$ 2091 cm^{-1}, $\nu(C{=}O)$ 1674 cm^{-1}; NMR (CD_3COCD_3): ^1H δ -8.370 [s, br, Ru(H_2)], T_1 = 13 ms (400 MHz, 248 K); $^{31}P\{^1H\}$ δ 69.3 s.

4, IR (Nujol): $\nu(CN)$ 2101 cm^{-1}, $\nu(C\equiv C)$ 2076, 2051 cm^{-1}; NMR (CD_3COCD_3): ^1H δ 1.436 [s, $CNC(CH_3)_3$], 7.00–7.160 (several multiplets, $C\equiv CC_6H_5$); $^{31}P\{^1H\}$ δ 54.8 s.

5 IR (Nujol): $\nu(CN)$ 2110 cm^{-1}, $\nu(C\equiv C)$ 2060 cm^{-1}, $\nu(C{=}O)$ 1662 cm^{-1}; NMR (CD_3COCD_3): ^1H δ 1.238 [s, $CNC(CH_3)_3$], 3.545 (s, $C\equiv CCO_2CH_3$); $^{31}P\{^1H\}$ δ 55.2 s.

6 IR (Nujol): $\nu(C\equiv C)$ 2040 cm^{-1}, $\nu(RuH)$ 1838 cm^{-1}, reinforced $\nu(C{=}C)$ 1588 cm^{-1}; NMR (C_6D_6): ^1H δ -12.52 (quintet, $^2J_{HP}$ 20 Hz, RuH); $^{31}P\{^1H\}$ δ 75.4 s.

7 IR (Nujol); $\nu(C\equiv C)$ 2034 cm^{-1}, $\nu(RuH)$ 1848 cm^{-1}, $\nu(C{=}O)$ 1656 cm^{-1}; NMR (C_6D_6): ^1H δ -12.02 (quintet, $^2J_{HP}$ 20 Hz, RuH); $^{31}P\{^1H\}$ δ 76.0 s.

‡ *Crystal data*: $C_{36}H_{71}P_4Ru$, $C_{24}H_{20}B$; M = 1048.15, monoclinic, space group $P2_1/c$ (No. 14, setting No. 1), a = 17.330(5), b = 14.674(4), c = 23.715(1) Å, β = 104.27(1)°, V = 5845(4) Å^3, Z = 4, D_c = 1.19 g cm^{-3}, λ(Cu-Kα) = 1.54178 Å, μ(Cu-Kα) = 35.17 cm^{-1}, $F(000)$ = 2240, T = 293 K, R = 0.060 for 3613 observed reflections $[I > 3\sigma(I)]$, R_w = 0.070 (weighted $w = \sigma_F^{-2}$). The sample (a colourless plate of dimensions 0.43 × 0.15 × 0.46 mm) was studied on an AFC6S-Rigaku automatic diffractometer, with graphite-monochromated Cu-Kα radiation. The cell parameters were obtained from the settings of 25 high-angle reflections. The data were collected in the interval $5 < 2\theta < 120°$ at a speed of 4° min^{-1}. Three standard reflections were intensity controlled for decay correction (a negligible decay of 0.8% was found during data collection). Absorption (ψ-scan method), Lorentz and polarisation corrections were applied. The structure was solved by the Patterson method and phase expansion and refinement of the remainder of the structure. All non-hydrogen atoms were anisotropically refined by full-matrix, least-squares methods. The hydrogen atoms were not refined. The two hydrogen atoms in the dihydrogen ligand were localised on a weighted Fourier map, and the remaining hydrogen atoms were included at idealised positions. Refinements concluded with R = 0.060, R_w = 0.070 and goodness of fit 1.97. Scattering curves were taken from those included in the TEXSAN system, running on a DEC VAX 3520 at the Servicios Centralizados de Ciencia y Tecnología, Universidad de Cádiz.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

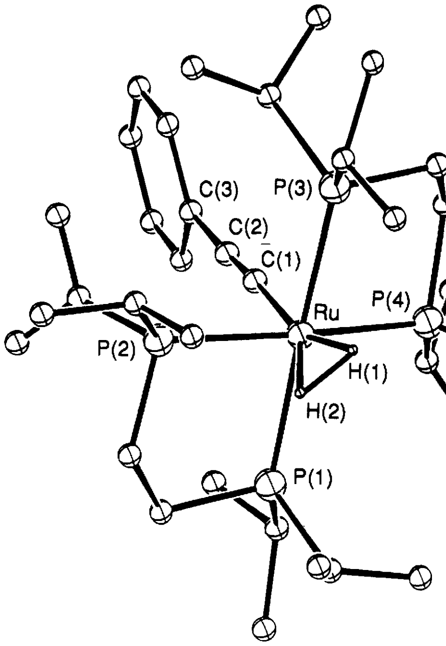

Fig. 1 Molecular structure of $[Ru(H_2)(C{\equiv}CPh)(dippe)_2]^+$ showing the atom labelling scheme. Hydrogen atoms, except those of the dihydrogen ligand (not refined), have been omitted for clarity. Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses: Ru–P(1) 2.403(3); Ru–P(2) 2.406(4); Ru–P(3) 2.429(3); Ru–P(4) 2.402(4); Ru–C(1) 2.01(1); Ru–H(1) or Ru–H(2) 1.5; H(1)–H(2) 1.1; C(1)–C(2) 1.19(2); Ru–C(1)–C(2) 176(1); C(1)–C(2)–C(3) 175(1).

dihydrogen and deprotonation. Thus, the dihydrogen ligand in complexes **2** and **3** is displaced by $CNBu^t$ in acetone in the presence of an excess of alk-1-yne, yielding the corresponding derivatives $[Ru(C{\equiv}CR)(CNBu^t)(dippe)_2][BPh_4]$ (R = Ph **4** or CO_2Me **5**)‡. Complexes **2** and **3** are readily deprotonated by strong bases such as $KOBu^t$, yielding the neutral hydrido-acetylides $[RuH(C{\equiv}CR)(dippe)_2]$ (R = Ph **6** or CO_2Me **7**)‡. All these compounds have *trans*-octahedral structures as inferred from their NMR spectra.

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