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Preparation and reactivity of dihydrogen complexes $[MX(\eta^2\text{-}H_2)P_4]BF_4$ (M = Ru or Os; X = halogenide or SEt^-; P = phosphite)

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Monohydride complexes $MHXP_4$ [M = Ru or Os; X = Cl^-, Br^-, I^-, SEt^- or N_3^-; P = $P(OEt)_3$, $PPh(OEt)_2$ or PPh_2OEt] were prepared by treating dihydride species MH_2P_4 first with CF_3SO_3Me and then with an excess of the anionic ligand X. In an argon atmosphere, protonation of $MHXP_4$ with $HBF_4{\cdot}Et_2O$ gives dihydrogen cations $[MX(\eta^2\text{-}H_2)P_4]^+$, with X = Cl, Br, I or SEt; the classical dihydride $[MH_2(N_3)P_4]^+$ was obtained with the azide ligand. Instead, in a hydrogen atmosphere, protonation of $MHXP_4$ with $HBF_4{\cdot}Et_2O$ gives hydride–dihydrogen $[MH(\eta^2\text{-}H_2)P_4]^+$ species, according to a proposed mechanism involving interaction of Brønsted acid with ligand X. Some $[MX(\eta^2\text{-}H_2)P_4]^+$ cations were thermally unstable and fully characterised in solution (^1H and ^{31}P NMR, variable temperature T_1 measurements), whereas the $[OsX(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$ complexes were stable and isolated as solids. Treatment of $[MX(\eta^2\text{-}H_2)P_4]^+$ cations with alkyne PhC≡CH gave evolution of H_2 and formation of the vinylidene intermediate $[MX\{{=}C{=}C(H)Ph\}P_4]^+$ which, by reaction with base, afforded the final acetylide $M(C{\equiv}CPh)XP_4$ derivatives. Treatment with propargyl alcohols HC≡CC(OH)RR′ of the $[MX(\eta^2\text{-}H_2)P_4]^+$ cations, instead, gave propadienylidene derivatives $[MX({=}C{=}C{=}CRR')P_4]BPh_4$ (M = Ru or Os; R = R′ = Ph or R = Ph, R′ = Me). Hydrazine complexes $[MX(NH_2NH_2)P_4]BPh_4$ were also prepared by substitution of the dihydrogen ligand in the new $\eta^2\text{-}H_2$ derivatives.

The chemistry of transition metal dihydrogen complexes has extensively been developed in the past fifteen years, and numerous studies on their synthesis, structure bonding and reactivity have been reported.[1–4] They have also shown how the nature of the ancillary ligands in a $\eta^2\text{-}H_2$ complex may have a dramatic influence on the structure and reactivity of the dihydrogen ligand. However, while a large amount of information has been reported on the influence of phosphine, carbonyl, amine or other neutral ligands, relatively little is known about that anionic ligands X (H^-, Cl^-, Br^-, I^-, N_3^-, SEt^-, CN^-, *etc.*) may have on the properties of $[MX(\eta^2\text{-}H_2)L_4]^{n+}$ complexes.[1–4] Some studies on the effects of hydride H^- and halogenide Cl^-, Br^-, I^- on the H–H distance and J_{HD} values have recently been reported[5,6] for $[RuX(\eta^2\text{-}H_2)L_2]^+$ (X = Cl^- or H^-; L_2 = bidentate phosphine) and $[OsX(\eta^2\text{-}H_2)L_4]^+$ (X = Cl^-, Br^- or I^-; L = NH_3) derivatives.

We have previously reported[7,8] the synthesis and reactivity of dihydrogen complexes stabilised by monodentate phosphite ligands and have shown how the steric and electronic properties of the ligand influence[7a,8b] H–H distance and J_{HD} values. As an extension of these studies, we report here the preparation and protonation reactions of a series of $MHXP_4$ complexes (M = Ru or Os), with the aim of synthesizing new "classical" or "non-classical" $[MX(H_2)P_4]^+$ hydride complexes stabilised by monodentate phosphite ligands. Furthermore, study of their chemical and spectroscopic properties should give information on the influence of the anionic ligand on the $\eta^2\text{-}H_2$ group and allow comparisons with related hydride[8] $[MH(\eta^2\text{-}H_2)P_4]^+$ or halogenide[5,6] $[MCl(\eta^2\text{-}H_2)(P\text{–}P)_2]^+$ derivatives.

Experimental

All synthetic work was carried out in an inert atmosphere using standard Schlenk techniques or a Vacuum Atmosphere drybox. Once isolated, the complexes were found to be relatively stable in air, but were stored in an inert atmosphere (H_2, argon) at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Triethyl phosphite was an Aldrich product, purified by distillation under nitrogen; phosphites $PPh(OEt)_2$ and PPh_2OEt were prepared by the method of Rabinowitz and Pellon.[9] Salts $RuCl_3{\cdot}xH_2O$ (ChemPur) and $(NH_4)_2OsCl_6$ (Johnson Matthey) were used as received. Methyl triflate (CF_3SO_3Me), triflic acid (CF_3SO_3H), $HBF_4{\cdot}Et_2O$ (54% solution in Et_2O), NaN_3, Na(SEt) and alkynes PhC≡CH, HC≡CC(Ph)$_2$OH and HC≡CC(Me)(Ph)OH were Aldrich products used without further purification. Hydrazine NH_2NH_2 was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method.[10] Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on Digilab Bio-Rad FTS-40 or Nicolet Magna 750 FT-IR spectrophotometers, NMR spectra (^1H, ^{13}C, ^{31}P) on a Bruker AC200 spectrometer at temperatures varying between −90 and +30 °C, unless otherwise noted. ^1H and ^{13}C spectra are referred to internal tetramethylsilane. $^{31}P\text{-}\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The SWAN-MR software package[11] was used to treat NMR data. Proton T_1 values were measured by the inversion–recovery method between +30 and −90 °C with a standard 180°–τ–90° pulse sequence: the error in T_1 measurements is typically ±10%. The conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in $MeNO_2$ at 25 °C were measured with a Radiometer CDM 83 instrument.

Synthesis of complexes

Hydrides RuH_2P_4 and OsH_2P_4 [P = $PPh(OEt)_2$, $P(OEt)_3$ or $PPh_2(OEt)$] and $[RuH(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$ were prepared following the methods previously reported.[8a,b,12,13]

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$OsHXP_4$ 1–3 [P = $PPh(OEt)_2$ 1, $P(OEt)_3$ 2 or PPh_2OEt 3; X = Cl^- a, Br^- b, I^- c, SEt^- d or N_3^- e]. To a solution of OsH_2P_4 (0.25 mmol) in 10 cm^3 of toluene cooled to −80 °C was added an equimolar amount of CF_3SO_3Me (0.25 mmol, 28 μL) and the reaction mixture, brought to room temperature, was stirred for 1 h. An excess of the appropriate lithium or sodium salt of anionic ligand X^- (0.75 mmol of NaX or LiX) in 5 cm^3 of ethanol was added, and the resulting solution stirred for 3 h. The solvent was removed under reduced pressure, giving an oil which was triturated with ethanol (2–3 cm^3). A white or yellow solid slowly separated from the resulting solution, which was filtered off and crystallised from ethanol; yield between 40 and 70% (Found: C, 47.2; H, 5.8; Cl, 3.65. $C_{40}H_{61}ClO_8OsP_4$ **1a** requires C, 47.1; H, 6.0; Cl, 3.5. Found: C, 45.0; H, 5.7. $C_{40}H_{61}BrO_8OsP_4$ **1b** requires C, 45.2; H, 5.8. Found: C, 43.4; H, 5.7. $C_{40}H_{61}IO_8OsP_4$ **1c** requires C, 43.25; H, 5.5. Found: C, 48.15; H, 6.5. $C_{42}H_{66}O_8OsP_4S$ **1d** requires C, 48.3; H, 6.4. Found: C, 47.0; H, 5.9; N, 4.05. $C_{40}H_{61}N_3O_8OsP_4$ **1e** requires C, 46.8; H, 6.0; N, 4.10. Found: C, 29.1; H, 6.2. $C_{24}H_{61}IO_{12}OsP_4$ **2c** requires C, 29.3; H, 6.3. Found: C, 56.7; H, 5.1. $C_{56}H_{61}BrO_4OsP_4$ **3b** requires C, 56.4; H, 5.2. Found: C, 54.2; H, 4.9. $C_{56}H_{61}IO_4OsP_4$ **3c** requires C, 54.3; H, 5.0%).

$OsHBr[P(OEt)_3]_4$ 2b. This complex was prepared like related species **1**–**3** resulting, in this case, in an oily product with low yield (about 30%).

$RuHXP_4$ 4, 5 [P = $PPh(OEt)_2$ 4 or $P(OEt)_3$ 5; X = Br^- b, I^- c or N_3^- e]. These complexes can be obtained by two methods.

(*i*) An equimolar amount of CF_3SO_3Me (0.25 mmol, 28 μL) was added to a solution of RuH_2P_4 (0.25 mmol) in 10 cm^3 of toluene cooled to −80 °C and the reaction mixture, brought to 0 °C, was stirred for 30 min. An excess of the appropriate lithium or sodium salt of anionic ligand X (0.40 mmol of NaX or LiX) in 5 cm^3 of ethanol was added, and the solution stirred for 1 h. The solvent was removed under reduced pressure, giving an oil which was treated with 3 cm^3 of ethanol. Cooling of the resulting solution to −25 °C gave a white or pale yellow microcrystalline solid, which was slowly separated, filtered off, and dried under vacuum; yield was between 35 and 70%.

(*ii*) An excess of the appropriate lithium or sodium salt of anionic ligand X (0.4 mmol) and compound $[RuH(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$ (0.2 mmol, 0.20 g) were placed in a 25 cm^3 three-necked round-bottomed flask and, after cooling to −80 °C, treated with 10 cm^3 of ethanol. The reaction mixture, brought to room temperature, was stirred for 1 h, and the volume of the solution then reduced to about 3 cm^3 by evaporation under reduced pressure. Cooling to −25 °C of the resulting solution gave white or pale yellow microcrystals, which were separated, filtered off, and dried under vacuum; yield was between 40 and 70% (Found: C, 49.1; H, 6.4. $C_{40}H_{61}BrO_8P_4Ru$ **4b** requires C, 49.3; H, 6.3. Found: C, 46.95; H, 6.05. $C_{40}H_{61}IO_8P_4Ru$ **4c** requires C, 47.0; H, 6.0. Found: C, 51.4; H, 6.7; N, 4.4. $C_{40}H_{61}N_3O_8P_4Ru$ **4e** requires C, 51.3; H, 6.6; N, 4.5. Found: C, 33.8; H, 7.4. $C_{24}H_{61}BrO_{12}P_4Ru$ **5b** requires C, 34.05; H, 7.3%).

$[OsX(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$ 6 (X = Cl^- a, Br^- b or I^- c). A slight excess of $HBF_4{\cdot}Et_2O$ (0.137 mmol, 20 μL of 54% solution in Et_2O) was added to a solution of $OsHX[PPh(OEt)_2]_4$ (0.12 mmol) in 5 cm^3 of diethyl ether cooled to −80 °C and allowed to stand under argon. The reaction mixture was brought to room temperature and stirred for about 1 h. A white solid began to separate from the solution at 0 °C, and precipitation was complete after 1 h of stirring at room temperature. The solid was filtered off and dried under vacuum; yield ≥90%; $\Lambda_M = 90.4$ for **6a**, 93.1 for **6b**, 88.9 S cm^2 mol^{-1} for **6c** (Found: C, 43.5; H, 5.8; Cl, 3.1. $C_{40}H_{62}BClF_4O_8OsP_4$ **6a** requires C, 43.4; H, 5.6; Cl, 3.20. Found: C, 41.55; H, 5.5. $C_{40}H_{62}BBrF_4O_8OsP_4$ **6b** requires C, 41.7; H, 5.4. Found: C, 40.0; H, 5.3. $C_{40}H_{62}BF_4IO_8OsP_4$ **6c** requires C, 40.1; H, 5.2%).

$[Os(SEt)(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+BF_4^-$ 6d. This compound is thermally unstable and was prepared only in solution by adding 3.9 μL (0.027 mmol) of $HBF_4{\cdot}Et_2O$ to a solution of $OsH(SEt)[PPh(OEt)_2]_4$ (0.025 mmol, 0.026 g) in 0.5 cm^3 of CD_2Cl_2 placed in a 5 mm NMR tube cooled to −80 °C. The tube was shaken and brought to −10 °C to complete the reaction, and then ^1H and ^{31}P NMR spectra were recorded: $\delta_H(CD_2Cl_2$, 273 K) 3.80–3.21 (18 H, m, CH_2), 1.23 (3 H, t, CH_3 sulfide), 1.13 (24 H, t, CH_3 phosphite) and −10.38 (2 H, br, $\eta^2\text{-}H_2$); $\delta_P(CD_2Cl_2$, 273 K) 105.0 (s); (183 K) A_2BC spin system, δ_A 113.1, δ_B 102.1, δ_C 101.5, $J_{AB} = 29.5$, $J_{AC} = 31.9$, $J_{BC} = 36.8$ Hz.

$[OsH_2(N_3)\{PPh(OEt)_2\}_4]^+BF_4^-$ 6e. This compound too is thermally unstable and decomposes above −5 to −10 °C, both as a solid and in solution. It was therefore prepared only in solution by adding 3.9 μL (0.027 mmol) of $HBF_4{\cdot}Et_2O$ to a solution of $OsH(N_3)[PPh(OEt)_2]_4$ (0.025 mmol, 0.026 g) in 0.5 cm^3 of CD_2Cl_2 placed in a 5 mm NMR tube cooled to −80 °C. The tube was shaken and brought to −10 °C to complete the reaction, and then ^1H and ^{31}P NMR spectra were recorded: $\delta_H(CD_2Cl_2$, 203 K) 3.35 (16 H, m, CH_2), 1.06 (24 H, t, CH_3) and −15.62 (2 H, br, hydride); $\delta_P(CD_2Cl_2$, 203 K) 123.0 (s, br).

$[OsX(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]^+BF_4^-$ 7 and $[OsX(\eta^2\text{-}H_2)(PPh_2OEt)_4]^+BF_4^-$ 8 (X = Br^- b or I^- c). These complexes were prepared in CD_2Cl_2 solution at low temperature by protonation with $HBF_4{\cdot}Et_2O$ of the corresponding hydrides, but not isolated as solids owing to easy loss of H_2 above 0 °C. A typical preparation involved the addition by microsyringe of $HBF_4{\cdot}Et_2O$ (0.022 mmol, 3.2 μL) to a solution of the appropriate hydride (0.020 mmol) in 0.5 cm^3 of CD_2Cl_2 placed in a 5 mm NMR tube cooled to −80 °C. The tube was shaken to complete the reaction and then NMR spectra were recorded. $[OsBr(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]^+$ **7b**: $\delta_H(CD_2Cl_2$, 203 K) 4.06, 3.96 (24 H, m, CH_2), 1.27, 1.15 (36 H, t, CH_3); $\delta_P(CD_2Cl_2$, 203 K) A_2B_2 spin system, δ_A 87.2, δ_B 74.4, $J_{AB} = 42$ Hz. $[OsI(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BF_4$ **7c**: $\delta_H(CD_2Cl_2$, 273 K) 4.19, 4.05 (24 H, m, CH_2), 1.33, 1.28 (36 H, t, CH_3); $\delta_P(CD_2Cl_2$, 193 K) A_2B_2 spin system, δ_A 87.6, δ_B 71.8, $J_{AB} = 42$ Hz. $[OsBr(\eta^2\text{-}H_2)(PPh_2OEt)_4]^+$ **8b**: $\delta_H(CD_2Cl_2$, 203 K) 3.40 (8 H, m, CH_2), 1.11 (12 H, t, CH_3) and −9.35 (2 H, br, $\eta^2\text{-}H_2$); $\delta_P(CD_2Cl_2$, 203 K) 87.0 (s). $[OsI(\eta^2\text{-}H_2)(PPh_2OEt)_4]^+$ **8c**: $\delta_H(CD_2Cl_2$, 273 K) 3.98 (8 H, qnt, CH_2), 1.35 (12 H, t, CH_3) and −9.07 (2 H, qnt, $\eta^2\text{-}H_2$, $J_{PH} = 12$ Hz); $\delta_P(CD_2Cl_2$, 298 K) 108.3 (s).

$[RuX(\eta^2\text{-}H_2)P_4]^+BF_4^-$ 9, 10 (P = $PPh(OEt)_2$ 9 or $P(OEt)_3$ 10; X = Br^- b or I^- c). Owing to easy loss of H_2 above −10 °C, these complexes too were prepared only at low temperature by protonation with $HBF_4{\cdot}Et_2O$ (0.022 mmol, 3.2 μL) of the appropriate hydride $RuHXP_4$ (0.020 mmol) dissolved in 0.5 cm^3 of CD_2Cl_2 placed in a 5 mm NMR tube cooled to −80 °C. After shaking the tube to complete the reaction, the NMR spectra were as follows. $[RuBr(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$ **9b**: $\delta_H(CD_2Cl_2$, 183 K) 3.36 (16 H, m, CH_2), 1.09 (24 H, t, CH_3) and −10.83 (2 H, br, $\eta^2\text{-}H_2$), (260 K) 3.70, 3.43 (16 H, m, CH_2), 1.18 (24 H, t, CH_3) and −10.75 (2 H, qnt, br, $\eta^2\text{-}H_2$); $\delta_P(CD_2Cl_2$, 183 K) 145 (m), (246 K) 145.0 (s, br). $[RuI(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$ **9c**: $\delta_H(CD_2Cl_2$, 203 K) 3.37 (16 H, m, CH_2), 1.10 (24 H, t, CH_3) and −9.66 (2 H, br, $\eta^2\text{-}H_2$); $\delta_P(CD_2Cl_2$, 203 K) 146.0 (s, br). $[RuBr(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]^+$ **10b**: $\delta_H(CD_2Cl_2$, 223 K) 4.03 (24 H, m, CH_2), 1.19 (36 H, t, CH_3) and −11.96 (2 H, br, $\eta^2\text{-}H_2$); $\delta_P(CD_2Cl_2$, 203 K) 135.5 (s).

$[RuH_2(N_3)\{PPh(OEt)_2\}_4]^+BF_4^-$ 9e. This compound was prepared exactly like related species **9** and **10** by protonation with $HBF_4{\cdot}Et_2O$ of $RuH(N_3)[PPh(OEt)_2]_4$ in an NMR tube at

−80 °C. δ_H(CD_2Cl_2, 203 K) 3.90–3.30 (16 H, m, CH_2), 1.10 (24 H, t, CH_3) and −14.81 (2 H, qnt, br, hydride); δ_P(CD_2Cl_2, 203 K) 167–158 (m).

$OsBr(C{\equiv}CPh)[PPh(OEt)_2]_4$ 11b. An excess of $PhC{\equiv}CH$ (0.45 mmol, 50 μL) was added to a solution of $[OsBr(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$ (0.15 mmol, 0.170 g) in 10 cm^3 of CH_2Cl_2 under an argon atmosphere, and the reaction mixture stirred for about 1 h. Triethylamine (1.5 mmol, 208 μL) was added and, after 2 h of stirring, the solvent removed under reduced pressure giving an oil which was treated with ethanol (2 cm^3). Cooling to −25 °C gave a solution from which a yellow solid separated, this was filtered off and crystallised from toluene (1 cm^3) and ethanol (5 cm^3); yield ≥60% (Found: C, 49.7; H, 5.7. $C_{48}H_{65}BrO_8OsP_4$ requires C, 49.5; H, 5.6%).

$RuBr(C{\equiv}CPh)[PPh(OEt)_2]_4$ 12b. To a solution of $RuHBr[PPh(OEt)_2]_4$ (0.15 mmol, 0.15 g) in 10 cm^3 of CH_2Cl_2, cooled to −80 °C, was added a slight excess of $HBF_4{\cdot}Et_2O$ (0.165 mmol, 24 μL) and the resulting solution, brought to −40 °C, stirred for 30 min. An excess of $PhC{\equiv}CH$ (0.45 mmol, 50 μL) was added and, after 30 min of stirring, triethylamine (0.45 mmol, 62 μL). The reaction mixture was brought to room temperature and, after 1 h, the solvent removed under reduced pressure giving an oil which was treated with 5 cm^3 of ethanol. Stirring the resulting solution gave a yellow solid which was separated, filtered off, and crystallised from ethanol; yield ≥40% (Found: C, 53.75; H, 6.0. $C_{48}H_{65}BrO_8P_4Ru$ requires C, 53.6; H, 6.1%).

$[OsBr(=C=C=CPh_2)\{PPh(OEt)_2\}_4]BF_4$ 13b and $[OsBr\{=C=C=C(Me)Ph\}\{PPh(OEt)_2\}_4]BF_4$ 14b. An excess of the appropriate alkyne [$HC{\equiv}CC(Ph_2)OH$ or $HC{\equiv}CC(Me)(Ph)OH$] (0.15 mmol) was added to a solution of $[OsBr(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$ (0.15 mmol, 0.17 g) in 10 cm^3 of CH_2Cl_2, and the reaction mixture stirred for about 3 h. The solvent was removed under reduced pressure, giving an oil which was treated with 5 cm^3 of ethanol. Vigorous stirring of the resulting solution caused the separation of a reddish brown solid which was filtered off and dried under vacuum; yield ≥70%; Λ_M = 93.6 for **13b**, 90.9 S cm^2 mol^{-1} for **14b** (Found: C, 49.5; H, 5.4. $C_{55}H_{70}BBrF_4O_8OsP_4$ **13b** requires C, 49.30; H, 5.3. Found: C, 46.9; H, 5.5. $C_{50}H_{68}BBrF_4O_8OsP_4$ **14b** requires C, 47.00; H, 5.4%).

$[RuBr(=C=C=CPh_2)\{PPh(OEt)_2\}_4]BPh_4$ 15b. A slight excess of $HBF_4{\cdot}Et_2O$ (0.165 mmol, 24 μL) was added to a solution of $RuHBr[PPh(OEt)_2]_4$ (0.15 mmol, 0.15 g) in 10 cm^3 of CH_2Cl_2 cooled to −80 °C, and the reaction mixture, brought to −40 °C, was stirred for 30 min. 1,1-Diphenyl-2-propyn-1-ol ($HC{\equiv}CCPh_2OH$, 0.15 mmol, 0.031 g) was then added and the solution, brought to room temperature, stirred for about 3 h. The solvent was removed under reduced pressure, giving an oil which was treated with ethanol containing an excess of $NaBPh_4$ (0.3 mmol, 0.10 g). A reddish orange solid slowly separated from the resulting solution, which was filtered off and crystallised from CH_2Cl_2 (3 cm^3) and ethanol (5 cm^3); yield ≥60%; Λ_M = 53.4 S cm^2 mol^{-1} (Found: C, 64.1; H, 6.3. $C_{79}H_{90}BBrO_8P_4Ru$ requires C, 64.0; H, 6.1%).

$[OsBr(NH_2NH_2)\{PPh(OEt)_2\}_4]BPh_4$ 16b. To a solution of $[OsBr(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$ (0.15 mmol, 0.17 g) in 10 cm^3 of CH_2Cl_2 was added a slight excess of NH_2NH_2 (0.30 mmol, 10 μL) and the reaction mixture stirred for about 3 h. The solvent was removed under reduced pressure, giving an oil which was treated with ethanol containing an excess of $NaBPh_4$ (0.30 mmol, 0.10 g). A white solid separated from the resulting solution, which was filtered off and crystallised from CH_2Cl_2 (2 cm^3) and ethanol (5 cm^3); yield ≥70%; Λ_M = 51.7 S cm^2 mol^{-1} (Found: C, 54.2; H, 6.1; N, 2.0. $C_{64}H_{84}BBrN_2O_8OsP_4$ requires C, 54.4; H, 6.0; N, 2.0%).

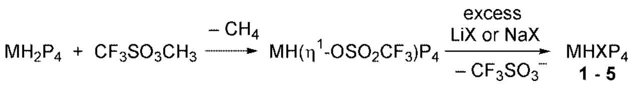
$[RuBr(NH_2NH_2)\{P(OEt)_3\}_4]BPh_4$ 17b. To a solution of $RuHBr[P(OEt)_3]_4$ (0.15 mmol, 0.13 g) in 10 cm^3 of CH_2Cl_2 cooled to −80 °C was added $HBF_4{\cdot}Et_2O$ (0.165 mmol, 24 μL) and the reaction mixture, brought to −40 °C, stirred for 2 h. An excess of NH_2NH_2 (0.30 mmol, 10 μL) was slowly added, then the solution was brought to room temperature and stirred for 30 min. The solvent was removed under reduced pressure, giving an oil which was treated with ethanol containing an excess of $NaBPh_4$ (0.30 mmol, 0.10 g). A white solid separated from the resulting solution, and was filtered off and crystallised from CH_2Cl_2 (2 cm^3) and ethanol (5 cm^3); yield ≥70%; Λ_M = 52.6 S cm^2 mol^{-1} (Found: C, 48.35; H, 7.3; N, 2.2. $C_{48}H_{84}BBrN_2O_{12}P_4Ru$ requires C, 48.2; H, 7.1; N, 2.3%).

Oxidation reactions. The oxidation of hydrazine complexes was carried out at low temperature (−30 °C) using $Pb(OAc)_4$ as oxidant. In a typical experiment, a sample of the appropriate complex (0.1 mmol) was placed in a 25 cm^3 three-necked flask fitted with a solid-addition sidearm containing an equimolar amount or an excess of $Pb(OAc)_4$. Dichloromethane was added, the solution cooled to −40 °C, and the oxidant added portionwise, in about 20–30 min, to the cold stirred solution. The reaction mixture was brought to 0 °C, stirred for 10 min, and the solvent then removed under reduced pressure, giving an oil which was treated with ethanol (3 cm^3) containing an excess of $NaBPh_4$ (0.2 mmol, 0.070 g). A white solid slowly separated out, which was filtered off and dried under vacuum.

Results and discussion

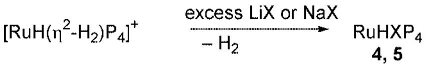
Monohydride complexes

The new monohydride complexes $MHXP_4$ **1**–**5** were prepared by allowing the MH_2P_4 species to react first with CF_3SO_3Me and then with the appropriate anionic ligand X, as shown in Scheme 1. The reaction of dihydride MH_2P_4 with methyl triflate proceeds with the evolution of CH_4 (by ^{1}H NMR) and formation of the triflate complex[14] $MH(\eta^1\text{-}OSO_2CF_3)P_4$ which, by substitution with anionic ligand X, gives the final complexes $MHXP_4$ **1–5**. Alternatively, ruthenium complexes $RuHXP_4$ can be prepared by substituting the η^2-H_2 ligand in $[RuH(\eta^2\text{-}H_2)P_4]^+$ cations[8a] with the appropriate ligand X, as shown in Scheme 2.



$$MH_2P_4 + CF_3SO_3CH_3 \xrightarrow{-CH_4} MH(\eta^1\text{-}OSO_2CF_3)P_4 \xrightarrow[-CF_3SO_3^-]{\text{excess LiX or NaX}} MHXP_4\ \mathbf{1-5}$$

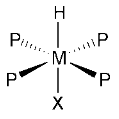
Scheme 1 M = Os **1**, **2**, **3** or Ru **4**, **5**; P = $PPh(OEt)_2$ **1**, **4**, $P(OEt)_3$ **2**, **5** or PPh_2OEt **3**; X = Cl^- **a**, Br^- **b**, I^- **c**, SEt^- **d** or N_3^- **e**.



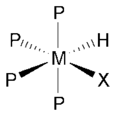
$$[RuH(\eta^2\text{-}H_2)P_4]^+ \xrightarrow[-H_2]{\text{excess LiX or NaX}} RuHXP_4\ \mathbf{4, 5}$$

Scheme 2

All the new hydride complexes **1–5** were isolated as white or pale yellow solids, stable in air (except **3**), diamagnetic and non-electrolytic. Analytical and spectroscopic data (Table 1) support the proposed formulations. Furthermore, IR and NMR data allowed *trans* geometry **I** to be established in solution for hydride complexes **1**, **3**, **4** and **5**; *cis* geometry **II** was shown by



I
trans



II
cis

Table 1 Selected infrared and NMR data for osmium and ruthenium complexes

Compound		IR[a]		^{1}H NMR[b,c]		Spin system	^{31}P-{^{1}H} NMR[b,d]
		ṽ/cm^{-1}	Assignment	δ (*J*/Hz)	Assignment		δ (*J*/Hz)
1a	*trans*-OsHCl[PPh(OEt)$_2$]$_4$	2089w	ν(OsH)	3.72 (qnt)	CH$_2$	A$_4$	121.1 (s)
				3.35 (m)			
				1.01 (t)	CH$_3$		
				−19.20 (qnt)	OsH		
				$J_{PH} = 18$			
				3.97 (qnt)[e]	CH$_2$	A$_4$[e]	120.5 (s)
				3.57 (m)			
				1.08 (t)	CH$_3$		
				−18.47 (qnt)	OsH		
				$J_{PH} = 18$			
1b	*trans*-OsHBr[PPh(OEt)$_2$]$_4$	2098w	ν(OsH)	3.98 (qnt)[e]	CH$_2$	A$_4$[e]	119.2 (s, br)
				3.60 (qnt)			
				1.08 (t)	CH$_3$		
				−18.10 (qnt)	OsH		
				$J_{PH} = 18$			
1c	*trans*-OsHI[PPh(OEt)$_2$]$_4$	2122w	ν(OsH)	3.96 (qnt)[e]	CH$_2$	A$_4$[e]	117.6 (s)
				3.62 (qnt)			
				1.09 (t)	CH$_3$		
				−16.53 (qnt)	OsH		
				$J_{PH} = 18$			
1d	*trans*-OsH(SEt)[PPh(OEt)$_2$]$_4$	2006w	ν(OsH)	3.70 (m)	CH$_2$	A$_4$	121.1 (s)
				3.34 (m)			
				1.26 (t)	SCH$_2$*CH$_3$*		
				1.00 (t)	POCH$_2$*CH$_3$*		
				−19.21 (qnt)	OsH		
				$J_{PH} = 18$			
1e	*trans*-OsH(N$_3$)[PPh(OEt)$_2$]$_4$	2099w	ν(OsH)	3.59 (s)	CH$_2$	A$_4$	123.8 (s)
		2070m	ν(N$_3$)	3.23 (m)			
				1.01 (t)	CH$_3$	A$_2$B$_2$[f]	δ_A 129.7
				−18.47 (qnt)	OsH		δ_B 123.5
				$J_{PH} = 18$			$J_{AB} = 38$
2b	*cis*-OsHBr[P(OEt)$_3$]$_4$	1960m	ν(OsH)	4.15–3.80 (m)	CH$_2$	AB$_2$C	δ_A 120.3
				1.22 (t)	CH$_3$		δ_B 116.6
				1.17 (t)			δ_C 103.9
				1.01 (t)			$J_{AB} = 31.3$
				−8.71 to −9.57 (m)	OsH		$J_{AC} = 23.6$
							$J_{BC} = 39.1$
2c	*cis*-OsHI[P(OEt)$_3$]$_4$	1966m	ν(OsH)	4.21 (m)[e]	CH$_2$	AB$_2$C[e]	δ_A 105.7
				1.31 (m)	CH$_3$		δ_B 102.2
				−9.57 to −10.42 (m)	OsH		δ_C 93.5
							$J_{AB} = 33.8$
							$J_{AC} = 21.6$
							$J_{BC} = 38.3$
3b	*trans*-OsHBr(PPh$_2$OEt)$_4$			3.02 (m)	CH$_2$	A$_4$[f]	101.5 (s, br)
				0.52 (t)	CH$_3$		
				−18.34 (qnt)	OsH		
				$J_{PH} = 18$			
3c	*trans*-OsHI(PPh$_2$OEt)$_4$	2118w	ν(OsH)	3.06 (m)	CH$_2$	A$_4$	96.2 (s, br)
				0.62 (t)	CH$_3$		
				−16.60 (qnt)	OsH		
				$J_{PH} = 18$			
4b	*trans*-RuHBr[PPh(OEt)$_2$]$_4$	1992m	ν(RuH)	3.75 (m)	CH$_2$	A$_4$	161.2 (s)
				3.42 (m)			
				1.03 (t)	CH$_3$		
				−16.45 (qnt)	RuH		
				$J_{PH} = 22$			
				3.99 (m)[e]	CH$_2$	A$_4$[e]	160.8 (s)
				3.66 (m)			
				1.09 (t)	CH$_3$		
				−15.77 (qnt)	RuH		
				$J_{PH} = 22$			
4c	*trans*-RuHI[PPh(OEt)$_2$]$_4$	2027m	ν(RuH)	3.77 (m)	CH$_2$	A$_4$	161.5 (s)
				3.47 (m)			
				1.07 (t)	CH$_3$		
				−14.65 (qnt)	RuH		
				$J_{PH} = 20$			
4e	*trans*-RuH(N$_3$)[PPh(OEt)$_2$]$_4$	2087s	ν(N$_3$)	3.60 (m)	CH$_2$	A$_4$	162.8 (s)
		1983w	ν(RuH)	3.25 (m)			
				1.00 (t)	CH$_3$		
				−16.94 (qnt)	RuH		
				$J_{PH} = 22$			
5b	*trans*-RuHBr[P(OEt)$_3$]$_4$	2027m	ν(RuH)	4.11 (m)	CH$_2$	A$_4$	134.8 (s)
				1.27 (t)	CH$_3$		
				1.22 (t)			
				−17.46 (qnt)	RuH		
				$J_{PH} = 22$			

Table 1 (*Contd.*)

Compound		IR[a]		^{1}H NMR[b,c]		Spin system	^{31}P-{^{1}H} NMR[b,d]
		$\tilde{\nu}$/cm^{-1}	Assignment	δ (*J*/Hz)	Assignment		δ (*J*/Hz)
6a	*trans*-$[OsCl(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$			3.72 (m) 3.54 (m) 1.16 (t) −10.31 (qnt) J_{PH} = 12	CH_2 CH_3 η^2-H_2	A_4	105.0 (s)
6b	*trans*-$[OsBr(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$			3.67 (m) 1.17 (t) −10.34 (qnt, br) J_{PH} = 12	CH_2 CH_3 η^2-H_2	A_4	102.8 (s)
6c	*trans*-$[OsI(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$			3.60 (m) 1.19 (t) −10.13 (qnt, br) J_{PH} = 12	CH_2 CH_3 η^2-H_2	A_4 A_2B_2[f]	100.3 (s) δ_A 112.5 δ_B 100.0 J_{AB} = 30
11b	*cis*-$OsBr(C{\equiv}CPh)[PPh(OEt)_2]_4$	2083m	ν(C≡C)	4.10–3.60 (m) 1.40 (t) 1.27 (t) 1.23 (t) 1.11 (t)	CH_2 CH_3	AB_2C	δ_A 118.5 δ_B 109.8 δ_C 107.3 J_{AB} = 31.0 J_{AC} = 17.3 J_{BC} = 33.9
12b	*trans*-$RuBr(C{\equiv}CPh)[PPh(OEt)_2]_4$	2091s	ν(C≡C)	3.89 (m) 3.76 (m) 1.30 (t)	CH_2 CH_3	A_4	163.8 (s)
13b	*cis*-$[OsBr(=C=C=CPh_2)\{PPh(OEt)_2\}_4]BF_4$	1969s	ν(C=C=C)	3.86 (m) 3.67 (m) 1.32 (t) 1.29 (t) 1.25 (t)	CH_2 CH_3	AB_2C	δ_A 117.6 δ_B 96.8 δ_C 94.3 J_{AB} = 47.2 J_{AC} = 24.1 J_{BC} = 26.6
14b	*cis*-$[OsBr\{=C=C=C(Me)Ph\}\{PPh(OEt)_2\}_4]BF_4$	1973s	ν(C=C=C)	3.81 (m) 3.61 (m) 1.35–1.20 (m)	CH_2 CH_3	AB_2C	δ_A 117.0 δ_B 97.6 δ_C 94.7 J_{AB} = 45.8 J_{AC} = 25.6 J_{BC} = 26.8
15b	*trans*-$[RuBr(=C=C=CPh_2)\{PPh(OEt)_2\}_4]BPh_4$	1952s	ν(C=C=C)	3.86 (m) 3.75 (m) 1.30 (t)	CH_2 CH_3	A_4	163.9 (s)
16b	*cis*-$[OsBr(NH_2NH_2)\{PPh(OEt)_2\}_4]BPh_4$	3332m 3317w 3263w 1595sh	ν(NH) δ(NH_2)	4.48 (br) 4.00–3.50 (m) 3.25 (br) 1.34 (t) 1.28 (t) 1.25 (t)	$OsNH_2$ CH_2 NH_2 CH_3	A_2BC	δ_A 112.8 δ_B 106.1 δ_C 100.0 J_{AB} = 32.2 J_{AC} = 33.6 J_{BC} = 31.5
17b	*cis*-$[RuBr(NH_2NH_2)\{P(OEt)_3\}_4]BPh_4$	3344sh 3335m 3263m	ν(NH)	4.41 (br) 4.20–3.90 (m) 2.93 (br) 1.30 (m)	$RuNH_2$ CH_2 NH_2 CH_3	ABC_2	δ_A 134.8 δ_B 126.6 δ_C 121.6 J_{AB} = 63.3 J_{AC} = 59.2 J_{BC} = 59.8

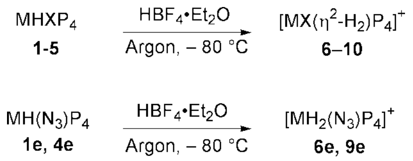
[a] In KBr pellets. [b] In CD_2Cl_2 at 25 °C. [c] Phenyl proton resonances are omitted. [d] Positive shift downfield from 85% H_3PO_4. [e] In C_6D_6. [f] At −70 °C.

the $P(OEt)_3$ derivatives $OsHX[P(OEt)_3]_4$ **2b** and **2c**. In the hydride region, the ^{1}H NMR spectra showed a quintet for the *trans* complexes and a multiplet for the *cis*. The ^{31}P-{^{1}H} NMR spectra are consistent with the proposed geometries, showing only one sharp singlet for *trans* complexes **1**, **3**, **4** and **5**, while an AB_2C multiplet appears in the spectra of *cis* derivatives **2**. It may be observed, however, that the spectra of some *trans* complexes do not remain unchanged between +30 and −90 °C, and the sharp singlet observed to −60 °C resolves, in the case of **1e**, into an A_2B_2 multiplet at −90 °C. This result implies the presence of inequivalent phosphorus nuclei, and seems to be in contrast with both the proposed *trans* and *cis* geometry, for which an AB_2C multiplet should be expected. However, the spectra may be interpreted on the basis of *trans* geometry, in which the four $PPh(OEt)_2$ ligands are made inequivalent by restricted rotation around M–P as the temperature is lowered. The probable different arrangement of the phenyl and ethoxy groups of one phosphite with respect to the other may give the observed ^{31}P spectra. Examples of inequivalent phosphorus nuclei in octahedral complexes containing four $PPhMe_2$[15] or $PPh(OEt)_2$ ligand[7c,16] in a plane have recently been reported and these precedents further support the *trans* geometry proposed for complexes **1**, **3**, **4** and **5**.

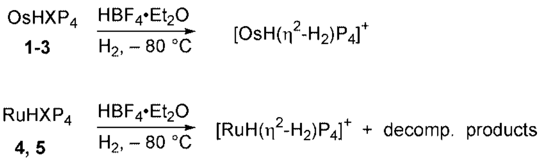
Protonation reactions

Protonation reactions of monohydrides $MHXP_4$ with $HBF_4{\cdot}Et_2O$ were studied at low temperature in both argon and hydrogen atmospheres. The results are summarised in Schemes 3 and 4.

In an argon atmosphere, hydrides $MHXP_4$ **1**–**5** react with $HBF_4{\cdot}Et_2O$ to give dihydrogen complexes $[MX(\eta^2\text{-}H_2)P_4]^+$ **6**–**10** which are stable at room temperature only in the case of osmium with $PPh(OEt)_2$ (**6**), and were isolated as BF_4^- salts and characterised. Instead, the related $[OsX(\eta^2\text{-}H_2)P_4]^+$ **7**, **8** and $[RuX(\eta^2\text{-}H_2)P_4]^+$ **9**, **10** cations are thermally unstable and lose



Scheme 3 M = Os **6**, **7**, **8** or Ru **9**, **10**; P = $PPh(OEt)_2$ **6**, **9**, $P(OEt)_3$ **7**, **10** or PPh_2OEt **8**; X = Cl^- **a**, Br^- **b**, I^- **c** or SEt^- **d**.

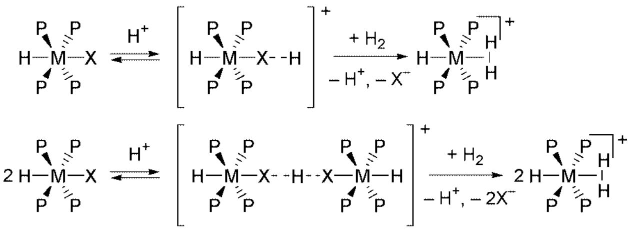


Scheme 4 X = Cl^-, Br^-, I^- or SEt^-.

H_2 even at temperatures below −10 °C, preventing their separation as solids. In solution, however, they are stable to −5 to −10 °C and were characterised spectroscopically.

Azido complexes $MH(N_3)P_4$ also react with $HBF_4{\cdot}Et_2O$ but, in this case, they afford the classical dihydride species $[MH_2(N_3)P_4]^+$ **6e**, **9e**, which are thermally unstable and were characterised in solution at low temperature.

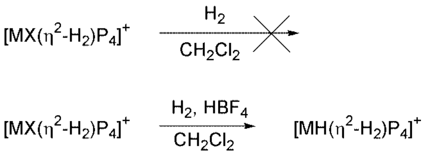
Surprisingly, operating in a hydrogen atmosphere, protonation of $OsHXP_4$ gives hydride–dihydrogen cations $[OsH(\eta^2\text{-}H_2)P_4]^+$, which were isolated as BF_4^- salts in very high yields (Scheme 4). Protonation of the related $RuHXP_4$ also afforded $[RuH(\eta^2\text{-}H_2)P_4]^+$, but in low yield and with some decomposition products. The formation of hydride-dihydrogen species under H_2 may be due to substitution of ligand X with H_2 in the starting complex $MHXP_4$. In order to test this hypothesis, we treated all $MHXP_4$ species with H_2, but no reaction was observed after 24 h at room temperature, and only further addition of $HBF_4{\cdot}Et_2O$ caused the formation of $[MH(\eta^2\text{-}H_2)P_4]^+$ derivatives. It may also be noted that the addition of even a small amount (less than the 1 : 1 ratio) of $HBF_4{\cdot}Et_2O$ or another Brønsted acid to a solution of $MHXP_4$ under H_2 led to $[MH(\eta^2\text{-}H_2)P_4]^+$ cationic species. These results may be interpreted on the basis of labilisation of ligand X in $MHXP_4$, caused by interaction with the Brønsted acid (or with H^+) and subsequent substitution of X with H_2, affording the final complex shown in Scheme 5.



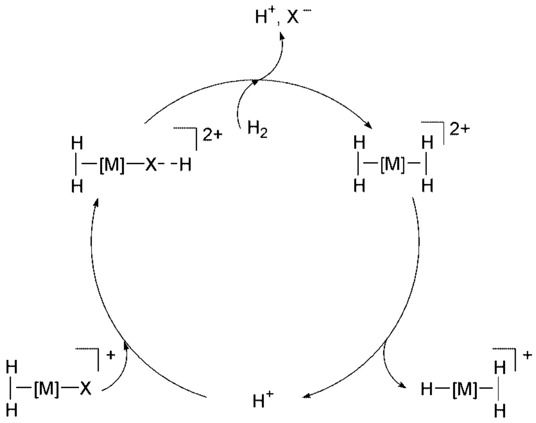
Scheme 5

Although this mechanism, involving the interaction of H^+ with one or two M–X fragments, is plausible, it is probably not the only possible or only operating one in this transformation, because treatment of $MHXP_4$ with an acid, even in H_2, and at least in small amounts, should give $[MX(\eta^2\text{-}H_2)P_4]^+$ species. In fact, the potential protonation sites present in the $MHXP_4$ complexes are the X ligand, the metal, the oxygen atoms of the phosphites and the hydride ligand, whose protonation gives the $[MX(\eta^2\text{-}H_2)P_4]^+$ cation. Instead, no trace of any halide–dihydrogen complex was detected when the protonation reaction was carried out under H_2.

These results prompted us to study the stability of $[MX(\eta^2\text{-}H_2)P_4]^+$ under different conditions, and we observed that the compounds were quite stable in solution, even under H_2, but the addition of even a small amount of $HBF_4{\cdot}Et_2O$ gave rise to the transformation of all the starting complexes into the $[MH(\eta^2\text{-}H_2)P_4]^+$ cations (Scheme 6). The presence of acid seems to be crucial for the formation of hydride–dihydrogen complexes and, also in this case, interaction of the Brønsted acid with ligand X of $[MX(\eta^2\text{-}H_2)P_4]^+$ may be invoked to explain its formation, according to the path shown in Scheme 7. The substitution of ligand X labilised by interaction with acid (H^+) gives the bis(dihydrogen) dicationic complex $[M(\eta^2\text{-}H_2)_2P_4]^{2+}$, which must be very acidic and can easily lose H^+ to give the final $[MH(\eta^2\text{-}H_2)P_4]^+$ derivative. Therefore, both the mechanisms of Schemes 5 and 7 may operate to give the final hydride–dihydrogen complexes, by protonation of $MHXP_4$ under H_2. However, the experimental data do not distinguish the two paths, which may also be concurrent.



Scheme 6



Scheme 7 [M] = RuP_4 or OsP_4.

In order to obtain further information on these reactions and to support the mechanism proposed in Schemes 5 and 7, we studied the reactions by ^1H and ^{31}P NMR spectra, but no new species, apart from the starting $MHXP_4$ or $[MX(\eta^2\text{-}H_2)P_4]^+$, were observed in the spectra of the reaction mixture, and even the use of deuteriated species such as D_2 and CF_3SO_3D did not give any further information on the possible mechanism. However, the formation of $[MH(\eta^2\text{-}H_2)P_4]^+$ by protonation of both $MHXP_4$ and $[MX(\eta^2\text{-}H_2)P_4]^+$ under H_2 may reasonably be explained on the basis of Schemes 5 and 7: although other mechanisms may be operating, the proposed labilisation of ligand X by interaction with Brønsted acid is plausible and fits experimental data.

Characterisation of complexes

The spectroscopic data of new classical and non-classical complexes **6–10** are listed in Tables 1 and 2. Some complexes were obtained as pale yellow solids (**6**), stable in air and in solution of polar organic solvents, where they behave as 1 : 1 electrolytes;[17] the others (**7–10**) are thermally unstable and were characterised only in solution. However, the presence of $\eta^2\text{-}H_2$ ligand in $[MX(\eta^2\text{-}H_2)P_4]^+$ and of H^- in $[MH_2(N_3)P_4]^+$ derivatives was confirmed by ^1H NMR spectra and variable-temperature T_1 measurements: in the low-frequency region of the proton spectra of all the $\eta^2\text{-}H_2$ complexes a slightly broad quintet at δ −9.11 to −10.75 is present, due to the H_2 ligand coupled with four equivalent phosphorus atoms (Fig. 1). The

Table 2 ^{1}H NMR data at 200 MHz in the hydride region for some osmium and ruthenium complexes

Compound		T/K	δ(M–H$_2$)	δ(M–H)	T_1/ms	r(H–H)^a/Å fast rotation
1b	$OsHBr[PPh(OEt)_2]_4$	210		−16.75 (qnt)	191 ± 20	
3b	$OsHBr(PPh_2OEt)_4$	208		−11.9 (br)	161 ± 16	
6b	$[OsBr(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$	206	−10.37 (qnt)		22 ± 2	1.01 ± 0.02
6c	$[OsI(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$	209	−10.33 (qnt)		21 ± 2	1.00 ± 0.02
6d	$[Os(SEt)(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$	206	−10.30 (qnt)		22 ± 2	1.01 ± 0.02
6e	$[OsH_2(N_3)\{PPh(OEt)_2\}_4]^+$	203		−15.6 (br)	233 ± 20	
8b	$[OsBr(\eta^2\text{-}H_2)(PPh_2OEt)_4]^+$	203	−9.2 (br)		28 ± 3	1.05 ± 0.02
9b	$[RuBr(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$	209	−10.8 (br)		9 ± 1	0.87 ± 0.02
9c	$[RuI(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$	203	−9.7 (br)		9 ± 1	0.87 ± 0.02
9e	$[RuH_2(N_3)\{PPh(OEt)_2\}_4]^+$	203		−14.8 (br)	449 ± 40	
	$[OsH(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^{+\,b}$	209	−7.0 (br)		32 ± 3	1.07 ± 0.02
	$[OsH(\eta^2\text{-}H_2)(PPh_2OEt)_4]^{+\,b}$	215	−4.7 (br)		10 ± 1	0.89 ± 0.02
	$[RuH(\eta^2\text{-}H_2)\{PPh_2(OEt)_2\}_4]^+$	200	−3.8 (br)		4 ± 0.5	0.76 ± 0.02

^{a} For calculations, see ref. 19. ^{b} See ref. 8(*b*).

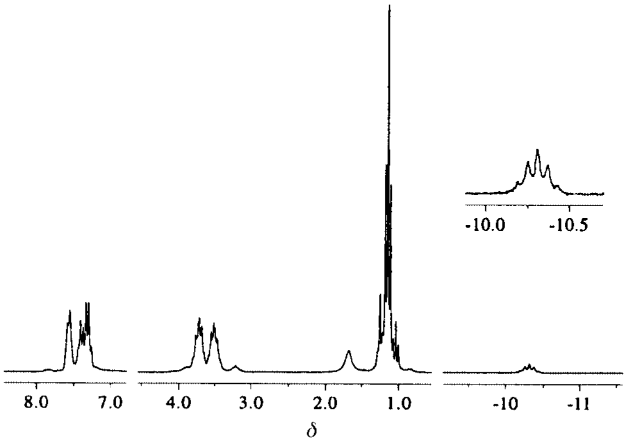


Fig. 1 Proton NMR spectrum of $[OsCl(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$ **6a** (in CD_2Cl_2 at 295 K).

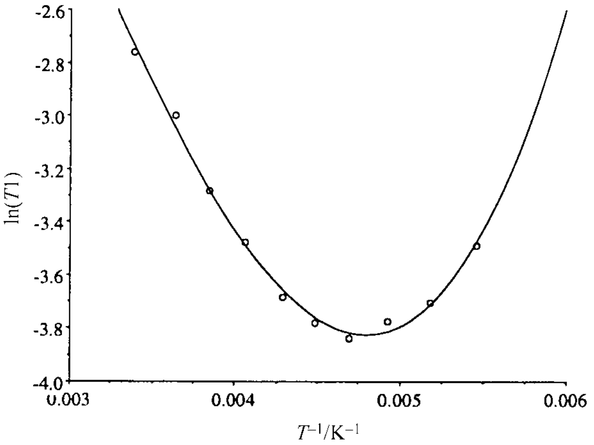


Fig. 2 Plot of ln(T_1) *vs* 1/K for $[OsI(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$ **6c**.

presence of a quintet for the signal of the η^2-H_2 ligand, which also determines the J_{PH} value of 12 Hz, is rather surprising, because a broad signal is always observed for dihydrogen complexes[1–4] of the iron triad and a well resolved signal is often associated with the classical hydride. However, variable-temperature T_1 measurements (Fig. 2) gave T_1(min.) values of 9–28 ms (Table 2), consistent with the non-classical nature of the H_2 ligand.[18] Hydride precursors $MHXP_4$ **1b** and **3b** give T_1(min.) values of 191 and 161 ms, respectively. We also attempted to support the attribution further by determining the J_{HD} values of isotopomers $[MX(\eta^2\text{-}HD)P_4]^+$, prepared either by treating $MHXP_4$ with CF_3CO_2D or $[MX(\eta^2\text{-}H_2)P_4]^+$ in solution with gaseous HD. Unfortunately, the proton spectra of the isotopomers could not unambiguously determine the J_{HD} values for these compounds. However, T_1(min.) values and comparisons with values obtained for the $MHXP_4$ precursors support the non-classical nature of these $[MX(\eta^2\text{-}H_2)P_4]^+$ species. It may be noted that the ^{1}H NMR spectra of osmium complexes $[OsX(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]^+$ **7** containing $P(OEt)_3$ ligands do not show any signal between +20 and −80 °C, easily attributable to η^2-H_2 resonance. This absence may be due to the loss of H_2, with formation of an unsaturated complex $[MXP_4]^+$, but treatment of **7** with NEt_3 gave the starting $MHXP_4$ complexes, thus confirming the presence of the η^2-H_2 ligand (Scheme 8). A similar deprotonation reaction was observed for all the new dihydrogen complexes. Therefore, the absence of the η^2-H_2 ^{1}H NMR signal of **7** may be attributed to fluxionality of the molecule, which even at −80 °C does not give a low-exchange spectrum, or to a very short T_1 value of the η^2-H_2 proton, giving a very broadened signal difficult to observe.

$$[MX(\eta^2\text{-}H_2)P_4]^+ \xrightarrow{\text{excess } NEt_3} MHXP_4$$

Scheme 8 M = Ru or Os; P = $P(OEt)_3$, $PPh(OEt)_2$ or PPh_2OEt.

In the temperature range between +30 and −70 °C, the ^{31}P-{^{1}H} NMR spectra of all η^2-H_2 complexes **6**–**10** show sharp singlets (Table 1), suggesting *trans* geometry **III**. In some cases, however, the ^{31}P-{^{1}H} NMR spectra at temperatures below −70 °C begin to broaden and resolve (about at −90 °C) into multiplets which, for some compounds, are of A_2B_2, or A_2BC type. The magnetic inequivalence of the phosphine ligands at very low temperatures may be explained, as proposed for the related $MHXP_4$ **1**–**5** precursors, on the basis of restricted rotation of the phosphite ligand around the M–P bond. However, the A_2B_2 spectra observed for $[OsX(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]^+$ **7** may also be explained on the basis of a distorted *trans* octahedral geometry of type **IV** and previously proposed for the related hydride–dihydrogen $[MH(\eta^2\text{-}H_2)P_4]^+$ derivatives.[8] In every case, the A_2B_2-type ^{31}P spectra observed for **7** do not seem to be consistent with *cis* geometry, for which an AB_2C or A_2BC spectrum is expected, but rather with *trans* which, at very low temperatures, displays two-by-two equivalent phosphorus nuclei (geometry **IV**).

III **IV**

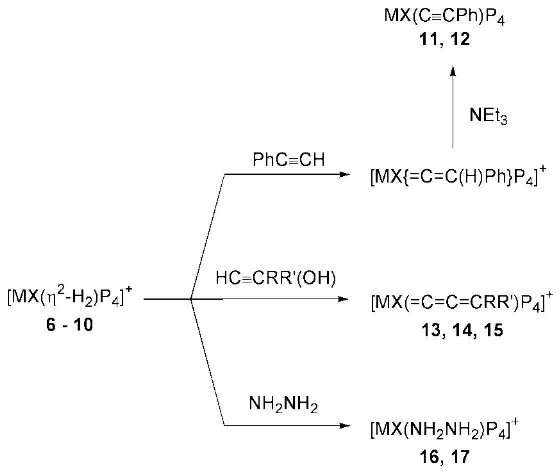
Both azido derivatives $[MH_2(N_3)P_4]^+$ **6e** and **9e** are thermally unstable and could not be obtained in the solid state owing to their decomposition above 0 °C. However, NMR data in solution support their formulation and suggest, in contrast with related complexes **6**–**9**, the presence of a classical dihydride with the central metal in the formal oxidation state of +4 [M^{IV}]. The ^1H NMR spectra, in the hydride region, do show a broad signal at δ −15.6 for osmium **6e** and at δ −14.8 for ruthenium **9e**, the T_1 measurements of which, at variable temperatures, give T_1(min.) of 232 (**6e**) and 449 ms (**9e**), consistent[18] with the classical nature of H_2 ligands. The protonation reaction of the azido derivative $MH(N_3)P_4$ thus proceeds through oxidative addition of H^+, giving a dihydride species $[MH_2(N_3)P_4]^+$ of M^{IV}.

For further structural information in solution of these seven-co-ordinate complexes $[MH_2(N_3)P_4]^+$ **6e** and **9e**, we recorded ^{31}P-{^1H} NMR spectra in the temperature range between +30 and −90 °C. Unfortunately, the spectra appear as broad signals which do not resolve, even at −100 °C.

The results obtained on the protonation reaction of $MHXP_4$ complexes indicate the influence that ligand X has, not only on the reaction course, but also on the H–H distance and stability to the loss of H_2 from $[MX(\eta^2\text{-}H_2)P_4]^+$ derivatives. First of all, protonation gives an η^2-H_2 complex for all the halogenide Cl^-, Br^- and I^- and thiol SEt^- species, whereas a classical dihydride $[MH_2(N_3)P_4]^+$ was obtained only in the case of the azide derivative. Instead, stability to the loss of H_2 in the dihydrogen complexes does not depend on the nature of ligand X, but on the central metal and the nature of the phosphite ligands, as only osmium complexes **6** containing the $PPh(OEt)_2$ ligand are stable and capable of being isolated. Furthermore, all the η^2-H_2 complexes are stable in solution in an H_2 atmosphere, but give hydride–dihydrogen $[MH(\eta^2\text{-}H_2)P_4]^+$ derivatives even in the presence of small amounts of Brønsted acids.

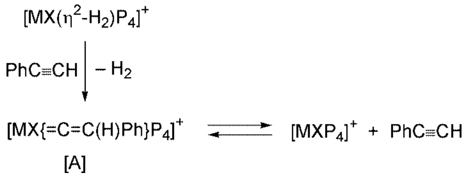
T_1 measurements allow H–H distances to be calculated,[19] and values are listed in Table 2. Although these values can be considered as an estimate of the H–H distance, a comparison among similar compounds such as our $[MX(\eta^2\text{-}H_2)P_4]^+$ cations can reasonably be made. This shows that the H–H distances are not influenced by the nature of the halogenide ligand and that, in the case of osmium bound to $PPh(OEt)_2$ ligand, the same value of 1.01 Å (fast rotation) was found for both halogenide and thiol derivatives. A longer distance of 1.07 Å was calculated for the related hydride $[OsH(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$, indicating that the effect of *trans* halogenide or thiol ligands is to shorten the H–H bonds relative to hydride *trans* ligands. These results contrast those of the related ruthenium complexes $[RuX(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$ **9**, which have a longer H–H distance (0.87 Å) than the hydride–hydrogen $[RuH(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$ derivatives (0.76 Å). In our ruthenium complexes, therefore, the effect of *trans* halogenide ligands is to lengthen the H–H bond relative to *trans* hydride ligands, in agreement with similar results[5a] obtained on other η^2-H_2 ruthenium complexes of the type $[RuCl(\eta^2\text{-}H_2)(dppe)]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane]. However, this lengthening does not seem to be a general trend in η^2-H_2 complexes, but only concerns ruthenium complexes. In related osmium derivatives $[OsX(\eta^2\text{-}H_2)P_4]^+$ the opposite trend was observed, which may suggest that it is the nature of the central metal which determines the influence of the *trans* ligand X in η^2-H_2 complexes, although only a few complexes have been studied so far.

Reactivity



Scheme 9 M = Os **11**, **13**, **14**, **16** or Ru **12**, **15**, **17**; X = Br^-; P = $PPh(OEt)_2$ or $P(OEt)_3$; R = R′ = Ph; R = Me, R′ = Ph.

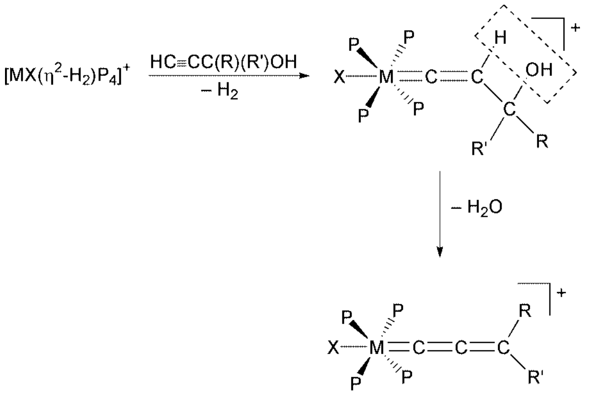
Some reactivity studies of new η^2-H_2 complexes **6**–**10** are summarised in Scheme 9. The η^2-H_2 ligand is rather labile in all complexes and may easily be substituted by several ligands, affording new derivatives. However, we focused attention on particular molecules such as alkynes and hydrazine, which require the use of appropriate precursors for synthesis of their related complexes.[20–22] Thus, the reaction with an excess of phenylacetylene gives a pink solution from which, in the case of ruthenium, known vinylidene $[RuX\{=C=C(H)Ph\}P_4]BPh_4$ complexes[23] can be isolated. In the case of osmium, we were not able to separate any vinylidene species, probably owing to the existence of equilibrium of the type shown in Scheme 10.



Scheme 10 M = Ru or Os.

In every case, the addition of an excess of NEt_3 to the pink solution gives acetylides $MX(C{\equiv}CPh)P_4$ **11** and **12**, which were isolated in high yield and characterised. This reaction and the separation of $[RuX\{=C=C(H)Ph\}P_4]BPh_4$ strongly suggest, for osmium too, the formation of a vinylidene intermediate [**A**], which is probably rather unstable towards dissociation of the =C=C(H)Ph ligand,[24] thus preventing separation of vinylidene derivatives.

Treatment of $[MX(\eta^2\text{-}H_2)P_4]^+$ with propargylic alcohol gives a dark red solution from which propadienylidene complexes $[MX(=C=C=CRR')P_4]BPh_4$ **13**–**15** were isolated in high yield and characterised. The reaction probably proceeds with evolution of H_2 and tautomerisation of the alkyne HC≡CC(R)(R′)OH on the metal centre to give a vinylidene intermediate $[MX\{=C=C(H)C(R)(R')OH\}P_4]^+$ which, by spontaneous loss of H_2O, gives the final propadienylidene[20] derivative (Scheme 11). Propadienylidene complexes of ruthenium and osmium are



V

13 - 15

Scheme 11 M = Os **13**, **14** or Ru **15**; P = $PPh(OEt)_2$; R = R′ = Ph **13**, **15** or R = Ph, R′ = Me **14**.

Table 3 $^{13}C\text{-}\{^1H\}$ NMR data of some osmium and ruthenium complexes

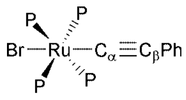
Compound	δ (*J*/Hz)[a]	Assignment
11b	122.3 (s, br)	C_β
	107.9 (dm)	C_α
	64.7 (m)	CH_2
	16.7 (m)	CH_3
13b	302.6 (dm)	C_α
	201.4 (dm)	C_β
	167.2 (s)	C_γ
	66.6 (t)	CH_2
	65.2 (d)	
	63.4 (t)	
	63.1 (d)	
	16.0 (m)	CH_3
14b	301.1 (m)	C_α
	197.2 (m)	C_β
	168.7 (s)	C_γ
	66.4–63.1 (m)	CH_2
	16.2 (m)	CH_3
15b	309.9 (qnt)	C_α
	$J_{CP} = 17$	
	199.9 (qnt, br)	C_β
	166.5 (s)	C_γ
	63.9 (br)	CH_2
	16.3 (s, br)	CH_3

[a] In CD_2Cl_2 at 25 °C. Phenyl carbon resonances are omitted.

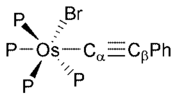
reported to contain mainly cyclopentadienyl or arene rings as well as bidentate phosphines as ancillary ligands.[20] The use of $[MX(\eta^2\text{-}H_2)P_4]^+$ as a precursor allows the preparation of the first propadienylidene derivatives stabilised by phosphite coligands. Hydrazine NH_2NH_2 also substitutes the H_2 ligand in $[MX(\eta^2\text{-}H_2)P_4]^+$, giving the related $[MX(NH_2NH_2)P_4]BPh_4$ derivatives **16**, **17**.

All the new complexes **11**–**17** are air-stable solids and soluble in polar organic solvents. Propadienylidene **13**–**15** and hydrazine **16**, **17** derivatives behave as 1 : 1 electrolytes.[17] Their analytical and spectroscopic data (Tables 1 and 3) support the proposed formulation.

The infrared spectra of acetylide complexes **11**, **12** show medium-intensity $\nu(C{\equiv}C)$ bands at 2083 (**11**) and 2091 cm^{-1} (**12**). The $^{13}C\text{-}\{^1H\}$ NMR spectra (Table 3) are also consistent with the presence of the acetylide ligand, showing the characteristic signals of C_α and C_β carbon atoms. Lastly, in the temperature range between +30 and −80 °C the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the $RuBr(C{\equiv}CPh)P_4$ **12b** complex shows a sharp singlet, suggesting, as in geometry **VI**, a mutually *trans* position



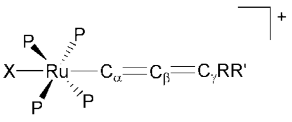
VI



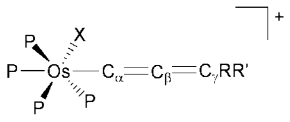
VII

of the acetylide and the Br^- ligand. Instead, the ^{31}P spectrum of the related $OsBr(C{\equiv}CPh)P_4$ **11b** derivative is an AB_2C multiplet, consistent with *cis* geometry **VII**.

The infrared spectra of propadienylidene complexes **13**–**15** show strong bands attributed to ν(CCC) of the =C=C=CRR′ ligand at 1973–1952 cm^{-1}. However, diagnostic for the presence of the propadienylidene group[20] are the $^{13}C\text{-}\{^1H\}$ NMR spectra, which show the characteristic highly deshielded C_α carbon atom at δ 309.9–301.1 and C_β and C_γ at δ 201.4–197.2 and 168.7–166.5, respectively. Furthermore, like related acetylides **11**, **12**, the $^{31}P\text{-}\{^1H\}$ NMR spectra indicate *trans* geometry **VIII** for ruthenium **15** and *cis* **IX** for osmium complexes **13**, **14**, respectively, showing a singlet for the former and an AB_2C multiplet for the latter.

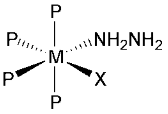


VIII



IX

The infrared spectra of hydrazine complexes **16**, **17** show the characteristic[25] ν(NH) of the NH_2NH_2 ligand at 3344–3263 cm^{-1} and δ(NH) at 1595 cm^{-1}. However, further support for the presence of the hydrazine ligand comes from the ^1H NMR spectra, which show the NH_2 signals as two broad multiplets at δ 4.48–4.41 and 3.25–2.93, respectively, consistent with the proposed formulation. Furthermore, some structural information can be detected from the $^{31}P\text{-}\{^1H\}$ NMR spectra of **16** and **17** which show the presence of a complicated multiplet in both cases. These patterns may be simulated using an A_2BC model in case **16b**, and an ABC_2 model in **17b**, suggesting a mutually *cis* position of the NH_2NH_2 and Br^- ligands, as in geometry **X**. We



X

studied the reactivity of the hydrazine complexes towards oxidation with $Pb(OAc)_4$ at low temperature, and preliminary results indicate the formation of the 1,2-diazene $[MBr(NH{=}NH)P_4]^+$ derivative. However, the reaction needs further investigation and will be the subject of a forthcoming paper.

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