Dihydrogen and Hydrido Complexes *via* Hydrogen Addition to d^6 Five-co-ordinate Complexes of Ruthenium and Osmium with 1,2-Bis(dicyclohexylphosphino)ethane

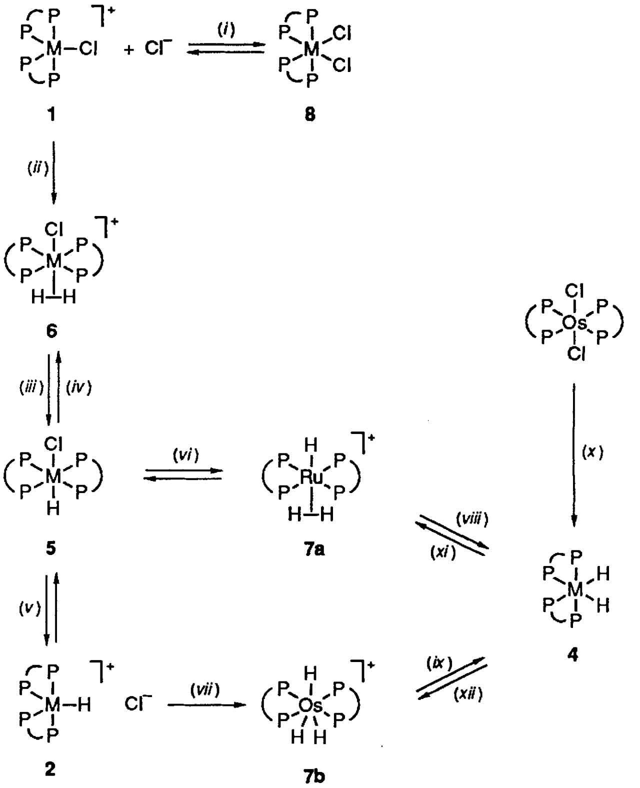
Antonio Mezzetti,[a] **Alessandro Del Zotto,**[a] **Pierluigi Rigo***[,a] **and Erica Farnetti**[b]
[a] *Istituto di Chimica, Università di Udine, Viale Ungheria 43, 33100 Udine, Italy*
[b] *Dipartimento di Scienze Chimiche, Università di Trieste, Via A. Valerio 22, 34127 Trieste, Italy*

The dihydrogen complexes $[MX(\eta^2\text{-}H_2)(dcpe)_2]BPh_4$ [dcpe = 1,2-bis(dicyclohexylphosphino)ethane; M = Ru, X = H or Cl; M = Os, X = Cl] were prepared by reaction of molecular hydrogen with the five-co-ordinate complexes $[MX(dcpe)_2]BPh_4$, or by protonation of the hydrides $[MH(X)(dcpe)_2]$. The same synthetic procedures yielded $[OsH_3(dcpe)_2]BPh_4$, for which a classical trihydride seven-co-ordinate structure is proposed. The compounds have been characterized by variable-temperature ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra and T_1 measurements. The reaction of molecular hydrogen with the complexes *cis*-$[MCl_2(dcpe)_2]$ to yield *trans*-$[MH(Cl)(dcpe)_2]$ and *cis*-$[MH_2(dcpe)_2]$ is also discussed.

Recent developments in the co-ordination chemistry of molecular hydrogen have led to the discovery of an increasing number of transition-metal complexes containing an intact co-ordinated dihydrogen molecule.[1,2] Most compounds reported involve a d^6 ML_5 fragment interacting with molecular hydrogen to give the so-called 'non-classical' $M(\eta^2\text{-}H_2)L_5$ adducts. On the other hand, the interaction of hydrogen with a d^6 ML_5 fragment can also give the classical d^4 dihydride MH_2L_5, in which the oxidation number of the metal is increased by two. In an effort to understand the factors determining the formation either of $\eta^2\text{-}H_2$ or dihydrido complexes, a variety of phosphorus ligands containing different substituents has been used to prepare compounds of the type $[MH(\eta^2\text{-}H_2)L_4]^+$ and $[MH_3L_4]^+$ (M = Fe, Ru or Os) with a P_4 donor set formed by phosphites,[3] phosphines,[4] di(tertiary phosphines)[5] or by a tetradentate phosphine.[6] Recently, the complexes $[MCl(\eta^2\text{-}H_2)(L_2)_2]^+$ (M = Fe, Ru or Os; L_2 = diphosphine) have been identified by Morris and co-workers[5g] as intermediates in the synthesis of the dihydrides $[MH_2(L_2)_2]$ from *cis*-$[MCl_2(L_2)_2]$ and hydrogen. Two successive $\eta^2\text{-}H_2$ species are suggested to be formed by addition of molecular hydrogen to the five-co-ordinate intermediates $[MX(L_2)_2]^+$ (X = Cl or H).

Though six-co-ordination predominates in the case of phosphine complexes of ruthenium(II)[7] and osmium(II),[8] five-co-ordinate, unsaturated species can be obtained with bulky phosphorus ligands.[9,10] In particular, we have prepared the trigonal-bipyramidal derivatives $[MX(dcpe)_2]BPh_4$ (M = Ru[9d] or Os,[10b] X = Cl or H) with the sterically demanding ligand 1,2-bis(dicyclohexylphosphino)ethane (dcpe). We now report on the reactions of these compounds with molecular hydrogen to give either classical hydrides or non-classical $\eta^2\text{-}H_2$ derivatives, depending on the nature of M and X. The properties of the products formed are compared to those of the analogous species containing the diphosphines $R_2PCH_2CH_2PR'_2$ [R,R' = Ph (dppe);[5a] R,R' = Et (depe);[5b] R = Ph, R' = Et (dedppe)[5c]] and $Ph_2P(CH_2)_nPPh_2$ [n = 3 (dppp) or 4 (dppb)].[5i,j] The interaction of hydrogen with the complexes *cis*-$[MCl_2(dcpe)_2]$ to give *trans*-$[MH(Cl)(dcpe)_2]$ and *cis*-$[MH_2(dcpe)_2]$ has also been examined, and found to proceed according to Scheme 1 as suggested by Morris and co-workers[5g] for other *cis*-$[MCl_2(L_2)_2]$.

With regard to the dynamics and mechanism of addition of H_2, the compounds $[MX(dcpe)_2]^+$ provide the opportunity of studying the direct addition of molecular hydrogen to trigonal-bipyramidal d^6 complexes. It should be noted that theoretical studies on the interaction of molecular hydrogen with metal centres are carried out by assuming a square-pyramidal geometry for the ML_5 fragment.[11]



Scheme 1 $\widehat{PP}$ = dcpe, M = Ru or Os. (*i*) Equilibrium in CH_2Cl_2; (*ii*) H_2 in CH_2Cl_2; (*iii*), Na(OEt) (1:1 ratio) in acetone; (*iv*) $HBF_4\cdot Et_2O$ in CH_2Cl_2 (M = Ru) or C_6H_6 (M = Os); (*v*) equilibrium in CH_2Cl_2; (*vi*) H_2 in CH_2Cl_2 at −60 °C; (*vii*) as (*vi*) but at room temperature (r.t.); (*viii*) Na(OEt) in acetone at −60 °C; (*ix*) as (*viii*) but at r.t.; (*x*) H_2 and Na(OEt) (excess) in boiling 2-methoxyethanol; (*xi*) $HBF_4\cdot Et_2O$ in CH_2Cl_2 at −60 °C; (*xii*) as (*xi*) but at r.t.

Table 1 NMR data[a]

		^{1}H NMR			
Complex	^{31}P NMR (δ)	δ	^2J(P–H)/Hz	T_1 (min)[b]/ms	T/K
2b $[OsH(dcpe)_2]BPh_4$	53.5 (s)	−40.6 (qnt)	14.4		305
	53.9 (br)	−40.4 (br)			193
	51 (br), 60 (br)				153
3b *trans*-$[OsH(CO)(dcpe)_2]BPh_4$	30.6 (s)	−10.1 (qnt)	19.8		305
4a *cis*-$[RuH_2(dcpe)_2]$[c]	65.8 (t), 90.2 (t)[d]	−12.3 (m)	*e*		305
4b *cis*-$[OsH_2(dcpe)_2]$[c]	34.2 (t), 56.9 (t)[f]	−14.5 (m)	*e*		305
5b *trans*-$[OsH(Cl)(dcpe)_2]\cdot 0.5C_6H_6$[c]	31.7 (s)	−24.0 (qnt)	15.3	63[g]	305
6a *trans*-$[RuCl(\eta^2\text{-}H_2)(dcpe)_2]BPh_4$	57.8 (s)	−14.3 (br)			305
		−14.4 (br)		4	213
	48.6, 55.3, 61.9, 64.4[h,i]				153
6b *trans*-$[OsCl(\eta^2\text{-}H^2)(dcpe)_2]BPh_4$	27.2 (s)	−14.0 (qnt, br)	12.8		305
		−14.1 (br)		10	213
	16.4, 23.9, 34.2, 35.9[h,j]				153
7a *trans*-$[RuH(\eta^2\text{-}H_2)(dcpe)_2]BPh_4$	76.1 (s)	−6.6 (br)			305
		−6.4 (br), −11.2 (qnt)	17.7		253
		−6.4 (br), −11.2 (br)		3, 56	213
7b $[OsH_3(dcpe)_2]BPh_4$	44.9 (s)	−10.4 (qnt)	10.4		305
	44 (br)	−10.6 (br)		35	213

[a] In CD_2Cl_2 solution, unless otherwise stated. Multiplicity given in parentheses by s = singlet, t = triplet, qnt = quintet, m = multiplet or br = broad. [b] Determined by the inversion-recovery method at 80 MHz on a Bruker WP 80 SY spectrometer. [c] In benzene solution. [d] ^2J(P–P′) = 13.0 Hz. [e] Multiplet (XX′ part of AA′BB′XX′ spectrum) not analysed. [f] ^2J(P–P′) = 4.6 Hz. [g] In [$^2H_8$]toluene solution at −60 °C. [h] In CD_2Cl_2–$CHFCl_2$ solution. Simulations performed assuming positive *trans*-^2J(L–L) and negative *cis*-^2J(L–L) constants; refined parameters in the order: δ(A), δ(B), δ(C), δ(D); *J*(AB), *J*(AC), *J*(AD), *J*(BC), *J*(BD), *J*(CD) (atom labels in order of increasing positive chemical shift, assignment not attempted). Experimental and calculated spectra for compound **6a** shown in Fig. 1. [i] Refined ^2J(P–P′) values are 237.6, 16.8, 19.1, 17.3, 18.1 and 218.9 Hz. [j] Refined ^2J(P–P′) values are 218.9, 10.7, 12.2, 9.1, 8.2 and 201.4 Hz.

Table 2 Infrared, conductivity and analytical data

			Analysis (%)[c]	
Complex	ν(M–H)[a]/cm^{-1}	Λ_M[b]/S cm^2 mol^{-1}	C	H
2b	—	77	66.70 (67.35)	8.75 (8.70)
3b	1972s, 1875s[d]	79	66.40 (66.85)	8.45 (8.50)
4a	1985m, 1960s	*e*	65.45 (65.85)	10.30 (10.40)
4b	2075m, 2050s	*e*	59.85 (60.20)	9.45 (9.50)
5b	2103s	*e*	59.35 (59.40)	9.05 (9.05)
6a	*f*	76	69.40 (70.05)	9.10 (9.15)
6b	2215vw, 2165w[f]	76	65.10 (65.55)	8.50 (8.55)
7b	2067vw, 2005w	77	66.55 (67.25)	8.85 (8.90)

[a] In Nujol mull. [b] In acetone at 22 °C, for 10^{-3} mol dm^{-3} solutions. [c] Required values are given in parentheses. [d] ν(CO). [e] Insoluble in acetone. [f] See text.

Results and Discussion

The five-co-ordinate complexes $[MX(dcpe)_2]BPh_4$ (M = Ru, X = Cl, **1a**; or H, **2a**; M = Os, X = Cl, **1b**) were obtained as reported previously.[9d,10b] The novel complex $[OsH(dcpe)_2]BPh_4$ **2b** was prepared by refluxing *trans*-$[OsCl_2(dcpe)_2]$ in 2-methoxyethanol in the presence of an excess of $NaBPh_4$. A deep red solution is slowly formed, from which dark red crystals of **2b** precipitate upon cooling. Complex **2b** was characterized by means of analytical data and ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy (Tables 1 and 2). Similarly to its ruthenium analogue **2a**, the cation $[OsH(dcpe)_2]^+$ is assigned a trigonal-bipyramidal geometry with the hydride in the equatorial plane and the diphosphines spanning axial and equatorial positions.[9d] The compound is stereochemically non-rigid at room temperature on the NMR time-scale, its ^{31}P-{^{1}H} spectrum in dichloromethane showing a single resonance at δ 53.5. When the temperature is lowered below −80 °C, the singlet broadens and at −120 °C (CD_2Cl_2–CHF_2Cl solution) separates into two broad resonances of intensity ratio 1:1 at *ca.* δ 51 and 60, respectively. At room temperature in CD_2Cl_2 the high-field ^{1}H NMR spectrum shows a quintet, which broadens upon cooling below −80 °C. Neither ^{31}P nor ^{1}H NMR slow-exchange spectra were obtained.

In agreement with their co-ordinatively unsaturated nature, complexes **1a** and **1b** have been reported to react with neutral ligands such as CO to form stereoselectively the *cis*-$[MCl(CO)(dcpe)_2]^+$ cations. These are thermally converted into the thermodynamically stable *trans* isomers.[10b] The hydrides **2a** and **2b**, however, behave differently: the ruthenium complex **2a** does not react with carbon monoxide, while the osmium analogue **2b** readily forms *trans*-$[OsH(CO)(dcpe)_2]BPh_4$ **3b**. The latter is the only product formed also at low temperature (−60 °C), thus appearing both kinetically and thermodynamically favoured. The *trans* configuration is suggested by the ^{31}P-{^{1}H} NMR spectrum, which shows a sharp singlet at δ 30.6, and by the appearance of a binomial quintet at δ −10.1 in the ^{1}H NMR spectrum. The IR spectrum exhibits ν(Os–H) and ν(CO) at 1972 and 1875 cm^{-1}, respectively (Table 2).

In order to make chemical and structural comparisons, we have also prepared *cis*-$[MH_2(dcpe)_2]$ (M = Ru, **4a**; or Os, **4b**) and *trans*-$[OsH(Cl)(dcpe)_2]$ **5b**; the ruthenium analogue *trans*-$[RuH(Cl)(dcpe)_2]$ **5a** has been reported previously.[9d] The dihydride **4a** was made by reaction of $[RuH_2(PPh_3)_4]$ with dcpe in a 1:2 molar ratio, while the osmium analogue **4b** was initially prepared by $LiAlH_4$ reduction of *cis*-$[OsCl_2(dcpe)_2]$ in tetrahydrofuran. However, **4b** is more conveniently prepared by treating *trans*-$[OsCl_2(dcpe)_2]$ with hydrogen in the presence of

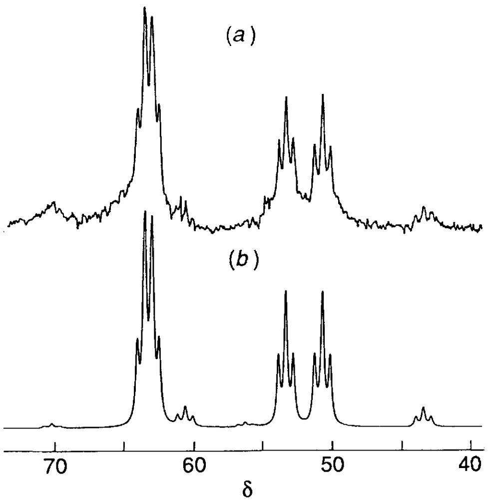


Fig. 1 Experimental (*a*) and simulated ($W_{\frac{1}{2}}$ = 9.0 Hz) (*b*) ^{31}P NMR spectra of *trans*-$[RuCl(H_2)(dcpe)_2]BPh_4$ **6a** at 153 K

sodium ethoxide (1:2 molar ratio) at 140 °C in 2-methoxyethanol. Probably this reaction proceeds *via* the five-co-ordinate intermediate **1b** (Scheme 1). The dihydrides **4a** and **4b** are white, diamagnetic solids, whose geometry was established by ^1H and $^{31}P-\{^1H\}$ NMR spectra (Table 1). The latter show clear AA′BB′ pseudo-triplets, typical of *cis* octahedral diphosphine complexes of C_2 symmetry.[12] The metal hydride resonance in the ^1H NMR spectrum appears as a symmetrical second-order pattern containing six resolved lines (XX′ part of an AA′XX′ multiplet), which is consistent with a *cis* arrangement of the hydride ligands. The IR spectra of both compounds **4a** and **4b** show two bands in the ν(M–H) region (Table 2).

The chlorohydride **5b** was prepared by addition of hydrogen to *cis*-$[OsCl_2(dcpe)_2]$ and successive deprotonation of the η^2-H_2 ligand with sodium ethoxide (Scheme 1). A white product was obtained, whose IR spectrum shows an intense Os–H absorption at 2103 cm^{-1}. The hydride region of the ^1H NMR spectrum of **5b** (C_6D_6 solution) shows a quintet pattern consistent with coupling to four equivalent phosphorus atoms. The *trans* geometry is also confirmed by the $^{31}P-\{^1H\}$ NMR spectrum in the same solvent, which shows a single signal at δ 31.7. Complex **5b** dissociates in dichloromethane yielding the five-co-ordinate hydride **2b**, as shown by conductivity and NMR data.

Hydrogen Addition to Five-co-ordinate $[MX(dcpe)_2]^+$.—When hydrogen gas is bubbled through a dichloromethane solution of chloro derivatives **1a** and **1b** the red colour immediately disappears and the dihydrogen adducts *trans*-$[MCl(\eta^2\text{-}H_2)(dcpe)_2]BPh_4$ (M = Ru, **6a**; or Os, **6b**) are isolated from the resulting solution. The same products can be obtained by protonation of **5a** and **5b** with stoichiometric amounts of $HBF_4 \cdot Et_2O$ in dichloromethane (M = Ru) or benzene (M = Os). Compounds **6a** and **6b** are white products, stable under argon both in the solid state and in solution. Loss of hydrogen does not take place, also under vacuum at room temperature. By heating under vacuum at 140 °C, **6a** evolves hydrogen and hydrogen chloride with formation of a mixture of **1a** and **2a**; under the same conditions, **6b** is stable for several hours. Both complexes are diamagnetic and 1:1 electrolytes in acetone solution (Table 2). The IR spectrum of the ruthenium complex **6a** shows no bands which can be attributed either to H–H or to M–H stretching vibrations, while **6b** displays two weak bands at 2165 and 2215 cm^{-1} both in the solid state and in solution. The ν(η^2-H_2) vibration has been generally observed in the range 2300–2700 cm^{-1}.[2,13]

The high-field ^1H NMR spectrum of compound **6a** at room temperature shows a broad, featureless signal at δ −14.3, which becomes even broader below −40 °C. No resolved coupling to phosphorus is observed between room temperature and −90 °C. In the case of **6b**, the hydride signal is a quintet [δ −14.0, ^2J(P–H) = 12.8 Hz] at room temperature, but becomes broad and featureless below −20 °C. The broadening of the η^2-H_2 resonance at low temperature has been reported for other dihydrogen complexes. Several factors have been suggested to account for this, such as slowing of the molecular motions of the H_2 ligand and dipolar interactions betweeen the hydrogen atoms.[5a,13] The relaxation time T_1 of the hydrido signals was measured at 80 MHz by the inversion-recovery method at different temperatures, and the minimum values of 4 and 10 ms are obtained at −60 °C for **6a** and **6b**, respectively. These values strongly implicate the presence of an η^2-H_2 ligand according to the criterion suggested by Crabtree and co-workers.[14,15]

To support the non-classical structures of **6a** and **6b**, we recorded the ^1H NMR spectra of the isotopomers *trans*-$[MCl(\eta^2\text{-}HD)(dcpe)_2]^+$, which were prepared by protonation of chlorohydrides **5a** and **5b** with stoichiometric amounts of D_2SO_4 in CD_2Cl_2 (M = Ru) or C_6D_6 (M = Os). The signals of the η^2-HD protons appear as partially resolved multiplets which can be simulated assuming ^1J(H–D) and ^2J(P–H) values of 16 and 8 Hz for **6a**, and 10.5 and 12.8 Hz for **6b**, respectively. These ^1J(H–D) values, although smaller than those reported for other η^2-H_2 complexes,[1–6] are much larger than expected for classical MHD complexes. On the contrary, the ^2J(P–H) coupling constants of **6a** and **6b** are somewhat high when compared to the values of 0–6 Hz reported for similar dihydrogen derivatives.[5b] However, a value as high as 19 Hz is reported for $[ReCl(\eta^2\text{-}H_2)(PMePh_2)_4]$.[16] The combination of low ^1J(H–D) and rather high ^2J(P–H) values indicates strong interaction between the dihydrogen ligand and the metal centre, with corresponding weakening of the H–H bond. On the basis of similar NMR data, Morris and co-workers[5g] suggested that the analogous complexes $[MCl(\eta^2\text{-}H_2)(depe)_2]^+$ exist in rapid equilibrium with a significant amount of a dihydride isomer, while the dppe derivatives are predominantly in the dihydrido form. The complexes **6a** and **6b** are remarkably resistant toward loss of hydrogen, and stable in acetonitrile solution. Moreover, complex **6b** does not react with carbon monoxide in refluxing acetone, while the ruthenium analogue **6a** is converted into *trans*-$[RuCl(CO)(dcpe)_2]^+$ in dichloromethane solution under CO in about 24 h at room temperature.

The *trans* geometry of complexes **6a** and **6b** is suggested by the $^{31}P-\{^1H\}$ NMR data. The room-temperature spectra consist of sharp signals at δ 57.8 and 27.2, respectively, in keeping with the presence of four equivalent phosphorus atoms. The singlets broaden when the temperature is lowered, and seven broad signals are observed below −100 °C, which eventually sharpen up into seven resolved multiplets. This behaviour is entirely reversible with temperature. The no-exchange limit spectra can be reproduced by computer simulation assuming an ABXY spin system; the observed and calculated spectra of **6a** at −120 °C are shown in Fig. 1. The values found for two of the ^2J(P–P′) constants (237.6 and 218.9 Hz) indicate the presence of two pairs of mutually *trans* P atoms. A similar low-temperature ^{31}P NMR behaviour has been observed for *trans*-$[RuX(L)(dcpe)_2]^+$ (X = Cl or Br, L = CO or MeCN), and attributed to the slowing of ligand motions at very low temperature due to steric interations among the bulky cyclohexyl groups.[9d]

The monohydrides **2a** and **2b** behave differently towards molecular hydrogen: while the ruthenium species **2a** does not react either at room temperature or at −60 °C, the osmium analogue **2b** readily adds H_2 at ambient temperature and pressure to form $[OsH_3(dcpe)_2]BPh_4$ **7b**. The ruthenium derivative *trans*-$[RuH(\eta^2\text{-}H_2)(dcpe)_2]BF_4$ **7a**, however, can be prepared by reaction of dihydride **4a** with $HBF_4 \cdot Et_2O$ (1:1 molar ratio) at −40 °C in dichloromethane (or CD_2Cl_2)

under hydrogen. Complex **7a** is thermally unstable and loses H_2 at room temperature also in the solid state: its characterization was therefore carried out in solution by ^1H and ^{31}P-$\{^1H\}$ NMR methods. By contrast, the osmium compound **7b** is an air-stable, white solid which is quite resistant toward loss of hydrogen: *e.g.* it remains intact after storage at 1 Torr (*ca* 133 Pa) and 140 °C for several hours.

The high-field ^1H NMR spectrum of compound **7a** at -20 °C shows a broad signal (δ -6.4) and a quintet (δ -11.2), integrating in a 2:1 ratio. The T_1 measurements at 80 MHz show that minimum values of 3 and 56 ms are reached at -60 °C for the signals at δ -6.4 and -11.2, respectively. The short T_1 value for the latter signal is in the range observed for η^2-H_2 complexes, while the resonance with the higher relaxation time can be assigned to a classical Ru–H bond. Further support to a $[RuH(\eta^2\text{-}H_2)(L_2)_2]^+$ species comes from the isotopomer $[RuH(\eta^2\text{-}HD)(dcpe)_2]^+$ obtained by addition of D^+ to **4a** at -40 °C in CD_2Cl_2 solution: its ^1H NMR spectrum at -20 °C shows a broad triplet at δ -6.4, with a ^1J(H–D) value of 31.5 Hz, which is close to those reported for other η^2-HD complexes.[1–6]

The ^1H NMR spectrum of compound **7a** shows a temperature dependence which is similar to that observed for other *trans*-$[MH(\eta^2\text{-}H_2)(L_2)_2]^+$ complexes: as the temperature is raised above -20 °C, the two resonances broaden and eventually coalesce near room temperature. This can be interpreted in terms of an intramolecular exchange process between the hydride and the hydrogen atoms of the η^2-H_2 ligand.[5a,b,j] In the ruthenium derivatives $[RuH(\eta^2\text{-}H_2)(L_2)_2]^+$ [$L_2 = R_2P(CH_2)_nPR_2$] examined so far, this behaviour has been observed only with dppp and dppb (n = 3 or 4), while the complexes containing dppe and depe (n = 2) are rigid at room temperature. Though this has been discussed in terms of chelate ring size,[5j] the fast hydride–(η^2-H_2) exchange observed in **7a** indicates that also the bulkiness of the substituents at phosphorus affects the dynamic behaviour of these species. When the sample temperature is lowered below -60 °C the signal at δ -6.4 broadens further and merges into the spectrum baseline, probably because rotation of the η^2-H_2 ligand slows down.

The *trans* geometry of compound **7a** is supported by the presence of a single, sharp signal in its ^{31}P-$\{^1H\}$ NMR spectrum. The singlet broadens when the temperature is lowered below -60 °C in contrast to the behaviour of the $[MCl(\eta^2\text{-}H_2)(dcpe)_2]^+$ analogues **6a** and **6b** for which the limiting spectrum is not reached even at -130 °C.

Complex **7b** is diamagnetic and a 1:1 electrolyte in acetone solution, and its IR spectrum reveals two weak absorptions at 2067 and 2005 cm^{-1} which can be attributed to terminal Os–H stretchings. The room-temperature ^1H NMR spectrum shows a binomial quintet centred at δ -10.4 [^2J(P–H) = 10.4 Hz], indicating the presence of three equivalent hydride ligands. The quintet broadens at about -60 °C, but the sample freezes before any multiplet structure is re-established (-120 °C in CD_2Cl_2–CF_3Cl). The T_1 relaxation time of this signal decreases as the temperature is lowered, reaches a minimum at -60 °C, and then increases. The minimum T_1 value of 35 ms (80 MHz) is consistent with a formulation of **7b** as a trihydride rather than as a $MH(\eta^2\text{-}H_2)$ derivative, and can be compared with the T_1 value of 63 ms found for the hydride **5b** at the same temperature. There is no evidence of an equilibrium between classical and η^2-H_2 structures. Complex **7b** can be prepared also by protonation of dihydride **4b** with strong acids. In the ^1H NMR spectrum of the deuterio derivative $[OsH_2D(dcpe)_2]^+$, formed by reaction of **4b** with D_2SO_4, the high-field quintet is in the same position as for **7b** and integrates as two protons. No ^1J(H–D) coupling was observed, as expected for a classical hydride complex.

The room-temperature ^{31}P-$\{^1H\}$ NMR spectrum of compound **7b** in CD_2Cl_2 shows a sharp signal at δ 44.9. As the temperature is lowered this signal broadens giving rise to a six-line multiplet at -120 °C. Apparently the limiting spectrum is not reached even at -130 °C (CD_2Cl_2–CHF_2Cl), the lowest available temperature. It is possible that **7b** possesses a seven-co-ordinate structure similar to that reported for $[OsH_3(PPh_3)_4]^+$.[4b]

Reaction of H_2 *with* cis-$[MCl_2(dcpe)_2]$.—Starting from Morris's observation on some $[MCl_2(L_2)_2]$ derivatives,[5g] we have studied the reaction between molecular hydrogen and *cis*-$[MCl_2(dcpe)_2]$ (M = Ru, **8a**; or Os, **8b**. When **8a** and **8b** are dissolved in dichloromethane under a hydrogen atmosphere the cations $[MCl(\eta^2\text{-}H_2)(dcpe)_2]^+$ are immediately formed, as detected by ^{31}P-$\{^1H\}$ NMR spectroscopy (Scheme 1). Compounds **6a** and **6b** can be recovered from the reaction mixture by addition of $NaBPh_4$ in ethanol. This is in accord with the observation that **8a** and **8b** dissociate in dichloromethane giving the five-co-ordinate **1a** and **1b**,[10b] while the more inert *trans* isomers react only at high temperature. ^{31}P-$\{^1H\}$ NMR measurements show that a stoichiometric amount of sodium ethoxide quantitatively deprotonates complexes **6a** and **6b** in acetone solution yielding the chlorohydrides **5a** and **5b**. The latter are dissociatively unstable in dichloromethane solution, wherein they form the five-co-ordinate cations **2a** and **2b**.[9d,10b] Accordingly, the osmium derivative **5b** reacts with H_2 in dichloromethane to give the trihydride **7b**. The ruthenium chlorohydride **5a** forms the dihydrogen adduct **7a** only at -40 °C in dichloromethane solution, which is rather surprising since the five-co-ordinate **2a** does not add molecular hydrogen even at low temperature. Moreover, both complexes **7a** and **7b** are deprotonated by ethoxide ion in acetone solution to yield the dihydrides **4a** and **4b** (Scheme 1). Taken together, these observations show that the reaction of the *cis* complexes **8a** and **8b** with hydrogen in the presence of sodium ethoxide can be used for the synthesis either of the *trans*-chlorohydrides **5a** and **5b** or of the *cis*-dihydrides **4a** and **4b**, depending on the metal-to-base molar ratio.

Conclusion

The electronic effects of changing metal and ancillary ligand X in the complexes $[MXH_2(dcpe)_2]^+$ can be evaluated on the basis of the T_1 and ^1J(H–D) data. These indicate that the M–(η^2-H_2) bond interactions vary widely along the series $[MX(\eta^2\text{-}H_2)(dcpe)_2]^+$, increasing in the order **7a** < **6a** < **6b**, where the osmium derivative **7b** can be considered a classical trihydride. The weakening of the H–H bond appears to parallel the increasing electron richness at the metal centre in the $[MX(dcpe)_2]^+$ moiety, which follows the order **1a** < **1b** < **2b**, as shown by the ν(CO) stretching frequencies of *trans*-$[MX(CO)(dcpe)_2]^+$ (1940, 1917 and 1875 cm^{-1}, respectively; **2a** does not add CO).[9d,10b] Since none of complexes **1a** and **1b** and **2a** and **2b** reacts with dinitrogen, Morris' criterion for the stability of η^2-H_2 complexes, based on the N≡N stretching frequency, cannot be applied.[17] With regard to the influence of the ancillary ligand X, both ruthenium and osmium form η^2-H_2 complexes when X is chloride. When X is hydride the ruthenium derivative **7a** is non-classical, but in the osmium species **7b** the high σ-donor ability of the hydride ligand promotes oxidative addition, with cleavage of the H–H bond. In the case of ruthenium the dihydrogen ligand is more labile in **7a** than in **6a** as a consequence of the higher *trans* effect of the hydride. The role of the metal is revealed by the comparison between the η^2-H_2 species **7a** and the classical trihydride **7b**.

The properties of the dcpe derivatives can also be compared to those of their analogues containing the diphosphines dppe[5a] and depe.[5b]. The ruthenium dihydrogen adducts $[RuH(\eta^2\text{-}H_2)(L_2)_2]^+$ are formed with all three ligands, essentially with retention of the H–H bond. In the case of osmium the $[OsH(L_2)_2]^+$ fragments interact with H_2 to give a η^2-H_2 complex when L_2 is depe, but a classical dihydride when L_2 is dcpe: this shows that the electronic influences can be more important than steric effects in stabilizing H_2 co-ordination.

Experimental

All manipulations were performed under argon with use of Schlenk-line techniques. Solvents were purified by standard methods. All chemicals used were of reagent grade or comparable purity. The salt $[NH_4][OsCl_6]$ was purchased from Aldrich, dcpe from Strem. The complexes $[RuCl_2(PPh_3)_3]$,[18] $[RuH_2(PPh_3)_4]$,[19] *trans*- and *cis*-$[OsCl_2(dcpe)_2]$,[10b] $[OsCl(dcpe)_2]BPh_4$[10b] and $[RuH(Cl)(dcpe)_2]$[9d] were prepared as reported previously. Yields are based on the metal. Infrared and ultraviolet–visible spectra were recorded on DS 702 G and Uvidec 505 JASCO spectrophotometers, respectively, ^1H and ^{31}P NMR spectra on a Bruker WP 80 SY spectrometer. At temperatures lower than 173 K, CD_2Cl_2–CHF_2Cl and CD_2Cl_2–CF_3Cl solutions were used for ^{31}P and ^1H NMR spectra, respectively. Positive ^{31}P chemical shifts are downfield from 85% H_3PO_4 as external standard. The T_1 data were obtained with standard pulse sequences by the inversion-recovery method. The NMR spectral simulations were performed on an Aspect 2000 computer using PANIC (Bruker Spectrospin). Conductance data were measured on a Metrohm E 518 conductivity bridge. Microanalyses were performed by the Microanalytical Laboratory of our Institute.

Selected ^1H and ^{31}P-$\{^1H\}$ NMR spectroscopic data are given in Table 1, while IR, analytical and physical data are collected in Table 2.

$[OsH(dcpe)_2]BPh_4$ **2b**.—The complex *trans*-$[OsCl_2(dcpe)_2]$ (0.55 g, 0.50 mmol) was suspended in a solution of $NaBPh_4$ (1.70 g, 5.0 mmol) in 2-methoxyethanol (40 cm^3) and the slurry was refluxed for 1.5 h, during which time the complex slowly dissolved giving a deep red solution. Dark red crystals separated upon cooling and were filtered off, washed twice with 2-methoxyethanol and ethanol and dried *in vacuo*. Yield: 0.52 g, 75%.

trans-$[OsH(CO)(dcpe)_2]BPh_4$ **3b**.—A dichloromethane solution (20 cm^3) of $[OsH(dcpe)_2]BPh_4$ (0.40 g, 0.30 mmol) was saturated with carbon monoxide. The initially red solution turned colourless within 1 min. Addition of propan-2-ol (20 cm^3) and evaporation of dichloromethane yielded a white precipitate, which was filtered off, washed with propan-2-ol and dried *in vacuo*. Yield: 0.27 g, 65%.

cis-$[RuH_2(dcpe)_2]$ **4a**.—A slurry of $[RuH_2(PPh_3)_4]$ (1.15 g, 1.0 mmol), dcpe (0.84 g, 2.0 mmol) and propan-2-ol (30 cm^3) was refluxed for 2 h, during which time the mustard-yellow solid slowly turned off-white. After cooling, the solid was filtered off, washed with propan-2-ol and dried *in vacuo*. A white product was obtained by recrystallization from benzene–propan-2-ol. Yield: 0.58 g, 61%.

cis-$[OsH_2(dcpe)_2]$ **4b**.—(*a*) The complex *trans*-$[OsCl_2(dcpe)_2]$ (0.55 g, 0.5 mmol) and a 1 mol dm^{-3} solution of Na(OEt) in ethanol (1.5 cm^3, 1.5 mmol) were mixed in 2-methoxyethanol (20 cm^3), and heated to reflux for 2 h under hydrogen. After cooling, the white precipitate which had formed was filtered off, washed with ethanol and dried *in vacuo*. Recrystallization from benzene–propan-2-ol. Yield: 0.40 g, 78%.

(*b*) The complex *cis*-$[OsCl_2(dcpe)_2]$ (0.55 g, 0.50 mmol) was dissolved in tetrahydrofuran (20 cm^3), and an excess of $LiAlH_4$ (0.40 g, 1.0 mmol) was added. Upon refluxing (30 min), the pale yellow solid dissolved giving a colourless solution. After cooling, ethanol (20 cm^3) was added to destroy the excess of $LiAlH_4$ and the solution was evaporated to dryness. The solid was extracted with benzene (20 cm^3) and the resulting solution was filtered. Addition of propan-2-ol and evaporation of benzene yielded a white solid, which was filtered off, washed with propan-2-ol and dried *in vacuo*. Yield: 0.18 g, 35%.

$[OsH(Cl)(dcpe)_2]\cdot 0.5C_6H_6$ **5b**.—The complex $[OsCl_2(dcpe)_2]$ (0.55 g, 0.5 mmol) was shaken in acetone–dichloromethane (20 cm^3, 1:1) under hydrogen until dissolution was complete. After pumping off dichloromethane, a 1 mol dm^{-3} solution of Na(OEt) in ethanol (0.5 cm^3, 0.5 mmol) was added, and the solution was shaken for 30 min. The resulting white precipitate was filtered off, dried *in vacuo* and recrystallized from benzene–hexane. Analytical and ^1H NMR data indicate that compound **5b** crystallizes as a 2:1 benzene solvate. Yield: 0.38 g, 70%.

trans-$[RuCl(\eta^2\text{-}H_2)(dcpe)_2]BPh_4$ **6a**.—A slurry of $[RuCl_2(PPh_3)_3]$ (0.48 g, 0.5 mmol), dcpe (0.42 g, 1.0 mmol), $NaBPh_4$ (1.71 g, 5.0 mmol) and ethanol (20 cm^3) was refluxed for 10 min, during which time the colour changed from brown to purple-red. The reaction vessel was then filled with hydrogen, and during further heating (10 min) a white precipitate formed, which was filtered off, dried *in vacuo* and recrystallized from dichloromethane–ethanol. Yield: 0.35 g, 55%.

$[OsCl(\eta^2\text{-}H_2)(dcpe)_2BPh_4$ **6b**.—(*a*) An acetone solution (20 cm^3) of $[OsCl(dcpe)_2]BPh_4$ (0.70 g, 0.50 mmol) was saturated with H_2. The resulting colourless solution was filtered and propan-2-ol was added. Elimination of the acetone *in vacuo* yielded a white precipitate, which was filtered off and dried *in vacuo*. Yield: 0.59 g, 85%.

(*b*) The complex *cis*-$[OsCl_2(dcpe)_2]$ (0.28 g, 0.25 mmol) was dissolved in dichloromethane under a hydrogen atmosphere, and a propan-2-ol solution (20 cm^3) of $NaBPh_4$ (0.17 g, 0.50 mmol) was added dropwise. Upon elimination of dichloromethane, a white solid formed, which was filtred off, washed with propan-2-ol and dried *in vacuo*. Recrystallization was from dichloromethane–propan-2-ol. Yield: 0.23 g, 67%.

$[OsH_3(dcpe)_2]BPh_4$ **7b**.—Upon saturating with H_2 a dichloromethane solution (15 cm^3) of $[OsH(dcpe)_2]BPh_4$ (0.49 g, 0.36 mmol) the initially dark red colour disappeared within 1 min. After filtering, propan-2-ol was added, and elimination of dichloromethane *in vacuo* gave a white precipitate, which was filtered off, washed with propan-2-ol and dried *in vacuo*. Yield: 0.46 g, 94%.

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