

Preparation of hydride complexes of ruthenium with bidentate phosphite ligands

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Abstract

Hydride complex $\text{RuH}_2(\text{PFFP})_2$ (**1**) [$\text{PFFP} = (\text{CF}_3\text{CH}_2\text{O})_2\text{PN}(\text{CH}_3)\text{N}(\text{CH}_3)\text{P}(\text{OCH}_2\text{CF}_3)_2$] was prepared by allowing the compound $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ ($\text{bpy} = 1,2$ -bipyridine) to react first with the phosphite PFFP and then with NaBH_4 . Chloro-complex $\text{RuCl}_2(\text{PFFP})_2$ (**2**) was also prepared, either by reacting $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ with PFFP and zinc dust or by substituting triphenylphosphine with PFFP in the precursor complex $\text{RuCl}_2(\text{PPh}_3)_3$. Hydride derivative $\text{RuH}_2(\text{POOP})_2$ (**3**) ($\text{POOP} = \text{Ph}_2\text{POCH}_2\text{CH}_2\text{OPPh}_2$) was prepared by reacting compound $\text{RuCl}_3(\text{AsPh}_3)_2(\text{CH}_3\text{OH})$ first with the phosphite POOP and then with NaBH_4 . Depending on experimental conditions, treatment of carbonylated solutions of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with POOP yields either the *cis*- or *trans*- $\text{RuCl}_2(\text{CO})(\text{PPh}_2)(\text{POOP})$ (**4**) derivative. Reaction of both *cis*- and *trans*-**4** with LiAlH_4 in thf affords dihydride complex $\text{RuH}_2(\text{CO})(\text{PPh}_2)(\text{POOP})$ (**5**). Chloro-complex *all-trans*- $\text{RuCl}_2(\text{CO})_2(\text{PPh}_2\text{OMe})_2$ (**6**) was obtained by reacting carbonylated solutions of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in methanol with POOP. Treatment of chloro-complex **6** with NaBH_4 in ethanol yielded hydride derivative *all-trans*- $\text{RuH}_2(\text{CO})_2(\text{PPh}_2\text{OMe})_2$ (**7**). The complexes were characterised spectroscopically and the X-ray crystal structures of complexes **1**, **3**, *cis*-**4** and **6** were determined. © 2007 Elsevier B.V. All rights reserved.

Keywords: Ruthenium; Carbonyl complexes; Hydride complexes; Bidentate phosphites

1. Introduction

Numerous studies over the past 30 years have acknowledged the important role played by hydride complexes of ruthenium in catalysing many reactions [1–3]. Among these, the catalytic hydrogenation of unsaturated organic molecules is important in both academic and industrial research, and has proven particularly useful for many syntheses [4,5].

Non-classical hydride complexes $[\text{Ru}]\text{-}\eta^2\text{-H}_2$ have also been comprehensively investigated [6], both from a funda-

mental point of view and in an attempt to activate molecular hydrogen by coordination with an appropriate Ru fragment.

Mono- and bidentate phosphine ligands have been widely used as ancillary ligands [1–3,6] in ruthenium hydride chemistry, and systematic studies have shown how both the electronic and steric properties of the phosphine ligand are important in determining the properties of the hydride derivatives [1–7]. In this context, although a large number of phosphines have been used to prepare hydride complexes of ruthenium, we have found no examples containing bidentate phosphite $(\text{RO})_2\text{P}(\text{R}_1\text{-R}_1)\text{P}(\text{OR})_2$ or $\text{R}_2\text{PO}(\text{CH}_2)_n\text{OPR}_2$ ligands [R , $\text{R}_2 = \text{alkyl}$ or aryl ; $\text{R}_1 = \text{CH}_2$, NCH_3 ; $n = 2, 3$].

We are interested in the chemistry of classical and non-classical hydride complexes of transition metals, and have

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reported [8] the synthesis and reactivity of hydride complexes containing both mono- and bidentate phosphite as ancillary ligands. Now we have extended our studies to include ruthenium as a central metal, and report here the synthesis of some new hydride complexes stabilised by bidentate phosphite ligands.

2. Experimental

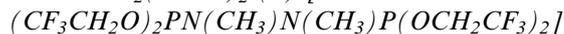
2.1. General comments

All experimental manipulations were carried out under argon using standard Schlenk techniques. All solvents were dried over appropriate drying agents [9], degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was an Aldrich product, used as received. The ligands 1,2-bis(diphenylphosphanyloxy)ethane [10] (POOP) and 1,2-bis[di(2,2,2-trifluoroethoxy)phosphino]-1,2-dimethylhydrazine [11] (PFFP) were prepared using published methods. ^1H and ^{31}P NMR spectra were recorded in CDCl_3 or CD_2Cl_2 on Bruker ARX-400 or Bruker AVANCE 300 spectrometers, using the solvent as internal lock. ^1H signals were referred to internal TMS, while $^{31}\text{P}\{^1\text{H}\}$ were referred to 85% H_3PO_4 with downfield considered positive. Spin-lattice relaxation times T_1 were determined at various temperatures in deuterated dichloromethane by the inversion-recovery method using a standard $180^\circ\text{-}\tau\text{-}90^\circ$ pulse sequence and 16 different values of τ at each temperature. The HMBC NMR experiments were performed using its standard program. The gNMR [12] and INMR [13] software packages were used to treat NMR data. IR spectra of samples in KBr pellets were obtained on Bruker Vector IFS28 or Perkin–Elmer Spectrum One FT spectrometers. Mass spectra were recorded on a Micromass Autospec M LSIMS (FAB^+) system with 3-nitrobenzyl alcohol as matrix. Microanalyses were carried out on a Fisons EA-1108 apparatus.

2.2. Synthesis of complexes

The complexes $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ ($\text{bpy} = 2,2'$ -bipyridine), $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuCl}_3(\text{AsPh}_3)_2(\text{CH}_3\text{OH})$ were prepared following the method previously reported [14–16].

2.2.1. $\text{RuH}_2(\text{PFFP})_2$ (1) [PFFP =



An excess of PFFP (1.5 g, 2.9 mmol) was added to a solution of $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ (1.10 mmol, 0.46 g) in 5 mL of toluene and the resulting solution was stirred for 1 h. An excess of NaBH_4 (10 mmol, 0.38 g) in 20 mL of ethanol was added and the reaction mixture was stirred at 0°C for 4 h. The solvent was removed under reduced pressure to give an oil from which the hydride complex was extracted with three 10-mL portions of CH_2Cl_2 . The extracts were evaporated to dryness to give an oil from which the hydride complex was extracted again with three 10-mL portions of petroleum ether ($40\text{--}60^\circ\text{C}$). The extracts were evaporated

to dryness to give an oil which was triturated with ethanol (3 mL). By slow cooling of the resulting solution to -25°C , pale yellow crystals separated out, which were collected by filtration and dried under vacuum; yield $\geq 25\%$. Anal. Calc. for $\text{C}_{20}\text{H}_{30}\text{F}_{24}\text{N}_4\text{O}_8\text{P}_4\text{Ru}$: C, 21.16; H, 2.66; N, 4.93. Found: C, 21.02; H, 2.75; N, 4.90%. ^1H NMR (CD_2Cl_2 , 300 MHz) δ (ppm): -9.67 (dt, 2H, $J_{\text{HP}} = 23$ Hz, RuH), 2.45 (m), 2.83 (d) (12H, CH_3), 3.80–5.00 (m, 16H, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121.5 MHz) δ (ppm): A_2B_2 spin system, δ_{A} 203.6, δ_{B} 189.4, $J_{\text{AB}} = 39.3$ Hz.

2.2.2. $\text{RuCl}_2(\text{PFFP})_2$ (2)

Method 1: An excess of zinc dust (10 mmol, 0.65 g) was added to a solution of $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ (1 mmol, 0.42 g) in 20 mL of toluene containing a slight excess of the phosphine PFFP (2.1 mmol, 1.08 g). The reaction mixture was stirred for 3 h, ethanol (20 mL) was added and the suspension was stirred for 20 h. The solvent was removed by evaporation under reduced pressure to give an oil from which the chloro-complex was extracted with three 5-mL portions of toluene. The extracts were evaporated to dryness to give an oil which was triturated with ethanol (3 mL). An orange solid slowly separated out, which was filtered and dried under vacuum; yield $\geq 20\%$.

Method 2: A slight excess of the phosphine PFFP (1 mmol, 0.42 g) was added to a solution of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.48 mmol, 0.46 g) in 15 mL of toluene and the reaction mixture was stirred for 3 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 mL). A yellow-orange solid slowly separated out, which was filtered. By fractional crystallisation from CH_2Cl_2 and ethanol, orange microcrystals of the complex were obtained; yield $\geq 45\%$.

Anal. Calc. for $\text{C}_{20}\text{H}_{28}\text{Cl}_2\text{F}_{24}\text{N}_4\text{O}_8\text{P}_4\text{Ru}$: C, 19.95; H, 2.34; Cl, 5.89; N, 4.65. Found: C, 19.78; H, 2.45; Cl, 5.70; N, 4.59%. ^1H NMR (CD_2Cl_2 , 300 MHz) δ (ppm): 3.10 (t, 12H, $J_{\text{HP}} = 2$ Hz, CH_3), 4.60 (m, 16H, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121.5 MHz) δ (ppm): 157.8 (s).

2.2.3. $\text{RuH}_2(\text{POOP})_2$ (3)



An excess of the phosphite POOP (0.76 g, 1.76 mmol) in toluene (6 mL) was added to a solution of $\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeOH})$ (0.50 g, 0.59 mmol) in 20 mL of toluene and the reaction mixture was stirred at room temperature for 1 h. The orange-red solution obtained was filtered and 0.058 g (1.53 mmol) of NaBH_4 dissolved in 5 mL of ethanol were added. The yellow mixture was stirred for 1 h and then filtered. The solvent was evaporated off under vacuum and the solid obtained dissolved in CH_2Cl_2 . The solution was stirred for 10 min and precipitation was induced by the addition of 5 mL of diethylether. The white solid obtained was filtered off and recrystallised from ethanol giving suitable crystals for an X-ray diffraction study; yield $\geq 44\%$. Anal. Calc. for $\text{C}_{52}\text{H}_{50}\text{O}_4\text{P}_4\text{Ru}$: C, 64.79; H, 5.23. Found: C, 63.99; H, 5.18%. IR (cm^{-1}): 1910 (m), 1879 (m) $\nu(\text{Ru-H})$. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): -8.30 (m, 2H,

Ru–H), 2.40 (m, 2H, CH₂), 3.09 (m, 2H, CH₂), 3.29 (m, 2H, CH₂), 3.42 (m, 2H, CH₂), 6.60–8.00 (m, 40H, Ph). ³¹P{¹H} NMR (CDCl₃, 161 MHz) δ (ppm): A₂B₂ spin system, δ_A 155.4, δ_B 157.7, J_{AB} = 27.1 Hz. FAB MS: *m/z* (referred to the most abundant isotopes) 962 [M–2H].

2.2.4. *trans*-RuCl₂(CO)(PPh₂)(POOP) (*trans*-4)

A solution of RuCl₃ · 3H₂O (0.150 g, 0.57 mmol) in thf (20 mL) was allowed to stand under a CO atmosphere (1 atm) and refluxed for 1 h. The resulting orange solution was cooled to room temperature and a toluene solution of POOP (2.460 mmol, 1.06 g in 8 mL) was added. The mixture was stirred for 24 h and then the solvent was removed under vacuum. The resulting oily residue was treated with methanol (2 mL) obtaining a yellow solid that was filtered off and crystallised from methanol; yield ≥34%. Anal. Calc. for C₃₉H₃₅Cl₂O₃P₃Ru: C, 57.36; H, 4.32. Found: C, 57.26; H, 4.32%. IR (cm⁻¹): 320 (m) ν(Ru–Cl), 1994 (s) ν(CO), 2380 (w) ν(P–H). ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 4.10 (m, 4H, CH₂), 5.65 (dm, 1H, PPh₂, J_{HP} = 369 Hz), 7.00–7.80 (m, 30H, Ph). ³¹P{¹H} NMR (CDCl₃, 161 MHz) δ (ppm): 15.4 (dd, 1P, PPh₂, J_{trans} = 334, J_{cis} = 35 Hz), 118.6 (dd, 1P, J_{cis} = 43 and 35 Hz), 134.2 (dd, 1P, J_{cis} = 43, J_{trans} = 334 Hz). FAB MS: *m/z* (referred to the most abundant isotopes) 816 [M], 781 [M–Cl].

2.2.5. *cis*-RuCl₂(CO)(PPh₂)(POOP) (*cis*-4)

The complex was obtained following the same method used for *trans*-4 but adding the phosphine POOP to a boiling carbonylated solution of RuCl₃ · 3H₂O in thf. Recrystallization from a CH₂Cl₂ solution of the solid obtained gave suitable crystals for an X-ray diffraction study; yield ≥48%. Anal. Calc. for C₃₉H₃₅Cl₂O₃P₃Ru: C, 57.36; H, 4.32. Found: C, 58.28; H, 4.32%. IR (cm⁻¹): 270 (w) ν_s(Ru–Cl), 299 (w) ν_{as}(Ru–Cl), 1981 (s) ν(CO), 2350 (w) ν(P–H). ¹H NMR (CD₂Cl₂, 400 MHz) δ (ppm): 4.00 (m, 1H, CH₂), 4.20 (m, 2H, CH₂), 5.20 [ddd, 1H (PPh₂), J_{HP} = 363, ³J_{HP} = 3 and 6 Hz], 5.40 [m, 1H, CH₂ (L)], 7.20–8.40 (m, 30H, Ph). ³¹P{¹H} NMR (CD₂Cl₂, 161 MHz) δ (ppm): 15.8 [dd, 1P(PPh₂), J_{trans} = 375, J_{cis} = 21 Hz], 115.0 (dd, 1P, J_{trans} = 375, J_{cis} = 32 Hz), 139.9 (dd, 1P, J_{cis} = 32, J_{cis} = 21 Hz). FAB MS: *m/z* (referred to the most abundant isotopes) 781 [M–Cl].

2.2.6. *cis*-RuH₂(CO)(PPh₂)(POOP) (5)

To a solution of complex *trans*-RuCl₂(CO)(PPh₂)(POOP) (*trans*-4) (0.150 g, 0.183 mmol) in thf (20 mL), an excess of LiAlH₄ (0.070 g, 1.83 mmol) was added. The reaction mixture was stirred for 5 h at room temperature, filtered through celite and then evaporated to dryness. After adding CH₂Cl₂ to the solid obtained, the mixture was filtered again and the resulting yellow solution was evaporated to dryness. Addition of methanol and stirring for a whole night resulted in the formation of a white precipitate, which was filtered off, washed with methanol and crystallised from methanol; yield ≥40%. Anal. Calc. for

C₃₉H₃₇O₃P₃Ru: C, 62.65; H, 4.99. Found: C, 62.15; H, 5.10%. IR (cm⁻¹): 2360 (w) ν(PH), 1963 (s) ν(CO), 1832 (m) ν(Ru–H). ¹H NMR (CD₂Cl₂, 400 MHz) δ (ppm): –7.80 (ddd, 1H, Ru–H), –7.40 (dtd, 1H, Ru–H, J_{cis} = 25, J_{trans} = 76, J_{HH} = 3 Hz), 4.06 (m, 3H, CH₂), 4.28 (m, 1H, CH₂), 5.44 [dm, 1H (PPh₂), J_{HP} = 336 Hz], 7.00–8.20 (m, 30H, Ph). ³¹P{¹H} NMR (CD₂Cl₂, 161 MHz) δ (ppm): ABM spin system, δ_M 38.7 (PPh₂), δ_A 154.9, δ_B 156.9, J_{AB} = 29.7, J_{AM} = 15.8, J_{BM} = 254.6 Hz. FAB MS: *m/z* (referred to the most abundant isotopes) 746 [M], 718 [M–CO].

2.2.7. *all-trans*-RuCl₂(CO)₂(PPh₂OMe)₂ (6)

CO was bubbled for 30 min through a refluxing solution of RuCl₃ · 3H₂O (0.150 g, 0.723 mmol) in MeOH (20 mL). A colour change from orange to dark blue was observed. The solution was then cooled to room temperature, an excess of POOP (0.93 g, 2.180 mmol) was added and the mixture was stirred for 24 h. The resulting yellow precipitate was filtered off and crystallised from methanol. From the mother liquor, yellow crystals suitable for X-ray crystallography were isolated, yield ≥23%. Anal. Calc. for C₂₈H₂₆Cl₂O₄P₂Ru: C, 50.91; H, 3.97. Found: C, 51.31; H, 3.83%. IR (cm⁻¹): 330 (w) ν_{as}(Ru–Cl), 2015 (s) ν(CO). ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 3.55 (vt, 6H, CH₃, J_{vt} = 6.4 Hz), 7.40 (m, 12H, Ph), 7.80 (m, 8H, Ph). ³¹P{¹H} NMR (CDCl₃, 161 MHz) δ (ppm): 120.1 [s, 2P, PPh₂(OMe)]. FAB MS: *m/z* (referred to the most abundant isotopes) 660 [M], 604 [M–2CO], 597 [M–{CO, Cl}].

2.2.8. *all-trans*-RuH₂(CO)₂(PPh₂OMe)₂ (7)

To a solution of complex RuCl₂(CO)₂(PPh₂OMe)₂ (6) (0.100 g, 0.151 mmol) in toluene (15 mL) an excess of NaBH₄ (0.180 g, 4.75 mmol) in ethanol (10 mL) was added. The mixture was stirred at room temperature for 12 h and then the solution was evaporated to dryness. From the residue obtained the hydride was extracted with three 5-mL portions of CH₂Cl₂. The extracts were evaporated to dryness and the oil obtained was triturated with ethanol (5 mL). An orange solid slowly separated out which was filtered and crystallised from ethanol; yield ≥44%. Anal. Calc. for C₂₈H₂₈O₄P₂Ru: C, 56.85; H, 4.77. Found: C, 56.69; H, 4.70%. IR (cm⁻¹): 1972 (vs) ν(CO), 2023 (s) ν(Ru–H). ¹H NMR (CDCl₃, 400 MHz) δ (ppm): –7.63 (t, 2H, Ru–H, J_{HP} = 23 Hz), 3.53 (vt, 6H, CH₃, J_{vt} = 7 Hz), 7.31 (m, 12H, Ph), 7.71 (m, 8H, Ph). ³¹P{¹H} NMR (CDCl₃, 161 MHz) δ (ppm): 155.3 [s, 2P, P(OMe)Ph₂]. FAB MS: *m/z* (referred to the most abundant isotopes) 591 [M–H], 562 [M–{CO, 2H}], 534 [M–{2CO, 2H}].

2.2.9. X-ray crystallography of compounds 1, 3, *cis*-4 and 6

Single crystals of compounds 1, 3, *cis*-4 and 6 were mounted on a glass fibre and studied in a SIEMENS Smart CCD area-detector diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). For compounds 1, *cis*-4 and 6 the studies were carried out at

room temperature but, for compound **3**, the data collection was made at $-100\text{ }^{\circ}\text{C}$, in order to avoid the disorder expected for dihydride complexes. Absorption corrections were carried out using SADABS [17]. The crystallographic calculations were performed with the OSCAIL program [18]. All the structures were solved by direct methods and refined by full-matrix least-squares based on F^2 [19]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The SQUEEZE program was used with the data from **3** to correct the reflection data for the diffuse scattering due to disordered solvent [20]. In all cases the hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters, except for the hydride ligand in **3** and that of the phosphine ligand in **6** which were located on a difference electron density map but no refined. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography [21].

3. Results and discussion

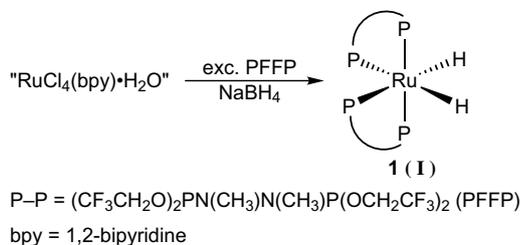
3.1. Hydride complexes with bidentate phosphites

The synthesis of dihydride complex $\text{RuH}_2(\text{PFFP})_2$ (**1**), with 1,2-bis(ditrifluoroethoxyphosphine)-1,2-dimethylhydrazine (PFFP) as supporting ligand, was achieved by reacting chloro-complex $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ [14a,14b] with an excess of phosphite, followed by treatment with NaBH_4 in ethanol, as shown in Scheme 1.

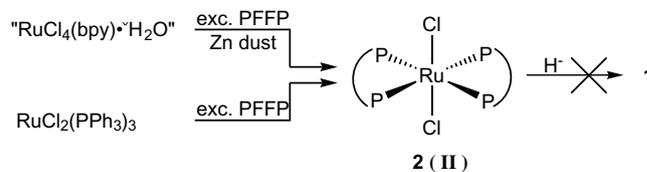
The use of $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ as a precursor seems to be crucial for successful synthesis, because the reaction of dichloro-complex $\text{RuCl}_2(\text{PFFP})_2$ (**2**) with NaBH_4 , or other hydrating agents, did not give the expected dihydride **1**. Not even the Grubbs method [22] can be used owing to the decomposition of the phosphite.

Ru(II) dichloro-complex $\text{RuCl}_2(\text{PFFP})_2$ (**2**) was prepared following two different methods, involving either reaction of $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ with the diphosphine PFFP in the presence of zinc dust, or substitution of PPh_3 in the $\text{RuCl}_2(\text{PPh}_3)_3$ precursor, as shown in Scheme 2.

Zinc dust is needed for reducing the ruthenium central metal to give $\text{RuCl}_2(\text{PFFP})_2$ (**2**) using $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ as a precursor. Instead, substitution of PPh_3 in $\text{RuCl}_2(\text{PPh}_3)_3$ is easy with PFFP and gives **2** in reasonable yields.



Scheme 1.



Scheme 2.

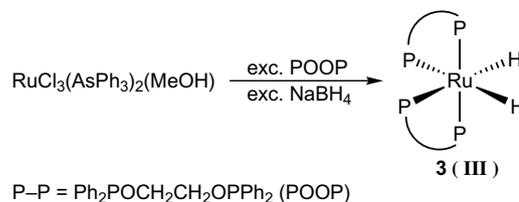
Treatment of dichloro-complexes **2** with NaBH_4 or LiAlH_4 in different conditions did not give the related dihydride **1**. Also the reaction of $\text{RuCl}_2(\text{PFFP})_2$ (**2**) with H_2 in the presence of base (LiOH or NEt_3) did not give the dihydride, and the starting dichloro-complex **2** was the only isolated product. Any other attempt to obtain **1** from the dichloro-species **2** failed, and it therefore seems that only the direct reaction of $\text{RuCl}_4(\text{bpy}) \cdot \text{H}_2\text{O}$ first with PFFP and then with NaBH_4 (Scheme 1) does allow the preparation of the dihydride complex of ruthenium **1** with 1,2-bis(alkoxyphosphine)-1,2-dimethylhydrazine (PFFP) ligand.

A different precursor was instead used to prepare the dihydride complex $\text{RuH}_2(\text{POOP})_2$ (**3**), containing the 1,2-bis(diphenylphosphanyloxy)ethane (POOP) as supporting ligand (Scheme 3).

Treatment of the arsine complex $\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeOH})$ [16], first with an excess of POOP and then with NaBH_4 in ethanol, gives dihydride **3** as white microcrystals in moderate yield. It therefore seems that the synthesis of dihydrides with bidentate phosphites like **1** and **3** requires the use of precursors in a high oxidation state [Ru(III)] whose reduction, in the presence of NaBH_4 , allows coordination of the H^- ligand, to yield the final hydride complexes.

Both dihydrides $\text{RuH}_2(\text{PFFP})_2$ (**1**) and $\text{RuH}_2(\text{POOP})_2$ (**3**) are crystalline, pale orange (**1**) or white (**3**) solids, stable in air and in solution of common organic solvents, where they behave as non-electrolytes. Analytical and spectroscopic data support the proposed formulation, which was further confirmed by X-ray crystal structure determination (Figs. 1 and 2).

Compound **1** consists of a ruthenium atom site on a symmetry centre, coordinated by two P,P' -donor bidentate ligands and two hydride ligands, which do not appear in the X-ray solution, probably due to the well known limitations of this technique for light atoms in the vicinity of heavy transition metals, the poor quality of the crystal obtained, and the number of disordered atoms. However, the spectroscopic data and coordination polyhedron fit



Scheme 3.

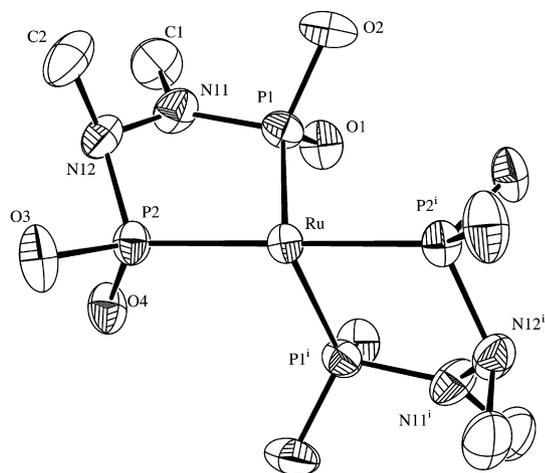


Fig. 1. Molecular structure of $\text{RuH}_2(\text{PFFP})_2$ (**1**). The atoms are drawn at 30% probability level. The trifluoroethyl groups and the hydrogen atoms of the methyl groups have not been drawn.

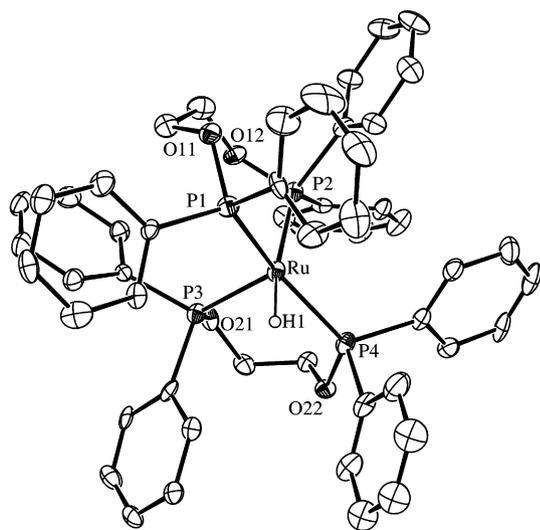


Fig. 2. Molecular structure of compound $\text{RuH}_2(\text{POOP})_2$ (**3**) with 30% probability ellipsoids.

the proposed formulation. In this sense, the polyhedron may be considered as an octahedron, with the *P,P'*-bidentate ligands occupying four coordinating sites, and the hydride atoms two mutually *cis* positions, on the coordination sphere. Both chelate angles (symmetry related) are $80.26(10)^\circ$, more acute than the theoretical 90° for an octahedral coordinating sphere and an important source of distortion. Only other two *cis* angles (apart from the chelate ones) are known, and range from $101.2(1)^\circ$ to $103.6(1)^\circ$, not far from the theoretical 90° . Only one *trans* angles is known, $174.04(14)^\circ$, not far from the theoretical 180° .

The Ru–P bond distances, 2.238(2) and 2.248(3) Å, are similar to those found for other phosphite or phosphonite Ru(II) complexes [23,24] and, as expected, they are shorter than those found for other ruthenium(0) complexes with

P,P-dimethyldiphosphinehydrazine ligands [25], partly due to the oxidation state of the metal and partly to the different type of phosphorus ligand (see Table 2).

The P–N bond distances in the hydrazine ligand are 1.684(9) and 1.736(9) Å, and are similar to those found for other Ru(II) complexes [24]. The shorter one corresponds to longer Ru–P bond lengths and N(11) atom. Angles around N(11) total 360° , and this fits the sp^2 character for this atom, due to the important double bond nature of the P–N bond. A different environment is found around the N(12) atom, since the sum of angles is 334.0° , and the N(12)–P bond should be considered as single. Another consequence of those features is the planarity of the chelate ring, essentially planar except for the N(12) atom, 0.52(1) Å out of the plane [r.m.s. = 0.0454, if N(12) is not considered]. These facts have been already reported for tungsten(0) complexes [26] in a different way from that which occurs with Pd and Pt complexes, in which the whole chelate is essentially planar [26,27]. The N–N bond length 1.36(1) is, however, shorter than that found for Ru(II) complexes with similar ligands [24].

The molecular structure of $\text{RuH}_2(\text{POOP})_2$ (**3**), including the atom-numbering scheme of the complex, is shown in Fig. 2. Table 3 lists some selected bond lengths and angles. The compound consists of molecular units without intramolecular interactions other than weak, non-classic, hydrogen bonds. Four phosphorus atoms and one hydride ligand coordinate the Ru atom in a square pyramidal fashion. The basal plane, formed of three phosphorus atoms and the hydride ligand, has an r.m.s. of 0.0668, with a maximum deviation of 0.08(3) Å. The ruthenium atom is 0.30(2) Å out of plane in the direction of the other phosphorus atom. However, ^1H NMR spectroscopy indicates the presence of a second hydride ligand, but its position was not determined by X-ray diffraction. This second hydride ligand should be in a *cis* position with respect to the other hydride ligand, and the geometrical parameters are in good agreement with these statements, since the four Ru–P distances are grouped in two pairs. Ru–P(4) and Ru–P(1) are around 2.27 Å [2.276(2) and 2.277(2) Å], and are in *trans* position to each other, but Ru–P(2) and Ru–P(3) are around 2.31 Å [2.305(2) and 2.313(2) Å], reflecting the *trans* influence of the hydride ligands. These Ru–P distances are well within the expected range for dihydride Ru^{2+} complexes (see Table 1) [7b,28].

The IR spectra of $\text{RuH}_2(\text{PFFP})_2$ (**1**) show the band characteristic of the phosphine PFFP but none attributable to the ν_{RuH} of the hydride ligand. However, the presence of this ligand is confirmed by the ^1H NMR spectra, which show one doublet of triplets at -9.67 ppm, characteristic of hydride ligands, coupled to the phosphorus nuclei of the phosphites, which are two-by-two magnetically equivalent. The ^{31}P spectrum, in fact, is an A_2B_2 multiplet, simulated with the parameters reported in Experimental. On the basis of these data, a *cis* geometry **1** like that observed in the solid state (Fig. 1) may be proposed for hydride complex **1**.

Table 1
Crystal data and structure refinement for compounds **1**, **3**, *cis*-**4** and **6**

Identification code	1	3	<i>cis</i> - 4	6
Empirical formula	C ₂₀ H ₃₀ F ₂₄ N ₄ O ₈ P ₄ Ru	C ₅₂ H ₄₈ O ₄ P ₄ Ru	C ₃₉ H ₃₄ Cl ₂ O ₃ P ₃ Ru	C ₂₈ H ₂₆ Cl ₂ O ₄ P ₂ Ru
Formula weight	1135.43	961.85	815.54	660.40
Temperature (K)	293(2)	173(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c	P $\bar{1}$	P21/c	C2/c
<i>Unit cell dimensions</i>				
<i>a</i> (Å)	12.0730(12)	12.903(3)	10.3012(9)	16.191(2)
<i>b</i> (Å)	18.6061(18)	13.133(3)	27.296(2)	9.0599(13)
<i>c</i> (Å)	18.8583(19)	17.171(4)	12.9737(11)	20.132(3)
α (°)	90	80.969(4)	90	90
β (°)	93.483(2)	70.198(4)	100.676(2)	102.836(3)
γ (°)	90	84.765(5)	90	90
Volume (Å ³)	4228.3(7)	2701.3(10)	3584.8(5)	2879.3(7)
<i>Z</i>	4	2	4	4
<i>D</i> _{calc} (Mg/m ³)	1.784	1.183	1.511	1.523
Absorption coefficient (mm ⁻¹)	0.672	0.447	0.758	0.873
<i>F</i> (000)	2248	992	1660	1336
Crystal size	0.33 × 0.23 × 0.20 mm	0.28 × 0.24 × 0.08 mm	0.50 × 0.40 × 0.20 mm	0.40 × 0.35 × 0.29 mm
θ Range for data collection	2.01–28.01°	1.27–28.20°	1.49–28.02°	2.08–28.00°
Index ranges	–12 ≤ <i>h</i> ≤ 15; –22 ≤ <i>k</i> ≤ 24; –24 ≤ <i>l</i> ≤ 24	–16 ≤ <i>h</i> ≤ 17; –17 ≤ <i>k</i> ≤ 16; –21 ≤ <i>l</i> ≤ 22	–12 ≤ <i>h</i> ≤ 13; –33 ≤ <i>k</i> ≤ 35; –17 ≤ <i>l</i> ≤ 17	–16 ≤ <i>h</i> ≤ 21; –11 ≤ <i>k</i> ≤ 9; –26 ≤ <i>l</i> ≤ 24
Reflections collected	11 884	15 129	20 862	8568
Independent reflections	4779 [<i>R</i> (int) = 0.0748]	10 679 [<i>R</i> (int) = 0.0816]	8156 [<i>R</i> (int) = 0.0637]	3330 [<i>R</i> (int) = 0.0278]
Reflections observed (>2 σ)	2201	3597	4114	2696
Data completeness	0.933	0.802	0.941	0.959
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.714	1.000 and 0.663	1.000 and 0.904	1.000 and 0.841
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4779/19/231	10 679/0/540	8156/0/433	3330/0/170
Goodness-of-fit on <i>F</i> ²	0.987	0.734	0.803	1.000
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.1089 <i>wR</i> ₂ = 0.2954	<i>R</i> ₁ = 0.0687 <i>wR</i> ₂ = 0.1376	<i>R</i> ₁ = 0.0450 <i>wR</i> ₂ = 0.0632	<i>R</i> ₁ = 0.0305 <i>wR</i> ₂ = 0.0759
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1830 <i>wR</i> ₂ = 0.3330	<i>R</i> ₁ = 0.1805 <i>wR</i> ₂ = 0.1595	<i>R</i> ₁ = 0.1271 <i>wR</i> ₂ = 0.0741	<i>R</i> ₁ = 0.0420 <i>wR</i> ₂ = 0.0790
Largest diffraction peak and hole (e Å ⁻³)	1.433 and –0.913	0.873 and –0.549	0.810 and –0.357	0.369 and –0.332

Table 2
Bond lengths (Å) and angles (°) for RuH₂(PFFP)₂ (**1**)

<i>Lengths</i>			
Ru–P(2)	2.238(2)	Ru–P(2 ⁱ)	2.238(2)
Ru–P(1)	2.248(3)	Ru–P(1 ⁱ)	2.248(3)
P(1)–O(2)	1.620(8)	P(1)–O(1)	1.635(7)
P(1)–N(11)	1.684(9)	P(2)–N(12)	1.736(9)
N(11)–N(12)	1.358(12)		
<i>Angles</i>			
P(2)–Ru–P(2 ⁱ)	174.04(14)	P(2)–Ru–P(1 ⁱ)	103.61(10)
P(2)–Ru–P(1)	80.26(10)	P(1 ⁱ)–Ru–P(1)	101.25(15)
O(2)–P(1)–O(1)	95.6(5)	O(2)–P(1)–N(11)	106.1(5)
O(1)–P(1)–N(11)	97.9(4)	O(2)–P(1)–Ru	122.1(4)
O(1)–P(1)–Ru	123.2(3)	O(3)–P(2)–O(4)	101.5(5)
O(4)–P(2)–N(12)	101.1(4)	O(3)–P(2)–N(12)	98.5(5)
N(12)–N(11)–C(1)	116.9(9)	C(2)–N(12)–P(2)	117.3(9)
N(12)–N(11)–P(1)	121.1(6)	N(11)–N(12)–P(2)	106.3(6)
C(1)–N(11)–P(1)	122.0(8)	N(11)–N(12)–C(2)	110.4(10)

Symmetry transformations used to generate equivalent atoms: ⁱ 1 – *x*, *y*, 3/2 – *z*.

The ³¹P{¹H} NMR spectrum of RuH₂(POOP)₂ (**3**) also shows an A₂B₂ pattern, indicating the *cis* arrangement of

Table 3
Bond lengths (Å) and angles (°) for compound **3**

<i>Lengths</i>			
Ru–H(1)	1.68(7)	Ru–P(4)	2.276(2)
Ru–P(1)	2.277(2)	Ru–P(2)	2.305(2)
Ru–P(3)	2.313(2)		
<i>Angles</i>			
H(1)–Ru–P(4)	79(2)	H(1)–Ru–P(1)	80(2)
P(4)–Ru–P(1)	153.92(8)	H(1)–Ru–P(2)	165(2)
P(4)–Ru–P(2)	103.14(8)	P(1)–Ru–P(2)	92.76(8)
H(1)–Ru–P(3)	98(2)	P(4)–Ru–P(3)	93.95(8)
P(1)–Ru–P(3)	104.80(8)	P(2)–Ru–P(3)	96.42(8)

the dihydride ligands. At room temperature, the proton spectrum displays a hydride multiplet at –8.30 ppm, which broadens on lowering the sample temperature and gives *T*_{1(min)} values of 194 ms at 253 K (400 MHz), fitting the classical nature [7a] of H[–] ligands.

The IR spectrum shows two ν_{RuH} bands at 1910 and 1879 cm⁻¹, characteristic of the *cis* position [29] of the

hydride ligands in a geometry **III**, like that observed in the solid state (Fig. 2).

Good analytical data were obtained for the chloro-complex $\text{RuCl}_2(\text{PFFP})_2$ (**2**), which is an orange solid, stable in air and in solution of common organic solvents. The IR spectra show the bands characteristic of the phosphite ligand PFFP, whose presence is confirmed by the ^1H NMR spectrum, showing a triplet at 3.10 ppm of the NCH_3 protons and a multiplet at 4.60 ppm of the methylene $\text{CF}_3\text{CH}_2\text{O}$ hydrogen atoms. In the temperature range between +20 and -80°C , the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** is a sharp singlet, suggesting the magnetic equivalence of the four phosphorus nuclei of the two bidentate phosphite ligands. On the basis of these data, a *trans* geometry **II** may be proposed for dichloro-complex **2**.

3.2. Hydride-carbonyl complexes

Treatment of a carbonylated solution (CO , 1 atm) of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in thf with an excess of the diphosphinite $\text{Ph}_2\text{POCH}_2\text{CH}_2\text{OPPh}_2$ (POOP) gave, after workup, a yellow solid characterised as the chloro-carbonyl complex *trans*- $\text{RuCl}_2(\text{CO})(\text{PPhPh}_2)(\text{POOP})$ (*trans*-**4**) (Scheme 4). The carbonylated solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ probably contains $\text{RuCl}_2(\text{CO})_3(\text{solvent})$ or $[\text{RuCl}_2(\text{CO})_2]_n$ species [1a,30], which react with the bidentate phosphite to give the final monocarbonyl complex **4**.

Surprisingly, the reaction proceeds not only with the coordination of POOP but also with the formation of the secondary phosphine PPhPh_2 , probably obtained by disruption of the POOP ligand. Metal-mediated disruption of the $\text{Ph}_2\text{POCH}_2\text{CH}_2\text{OPPh}_2$ ligand to give a diphosphoxane (POP) complex has been previously reported [8j,31] but, in any case, the formation of a secondary phosphine had been observed.

Complex **4** is stable in solution but slowly isomerises both at room temperature and in refluxing thf, to give the *cis* isomer (*cis*-**4**) which was isolated as a pale yellow solid in high yield. The *cis* isomer can also be obtained by reacting the carbonylated solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with phosphite POOP in refluxing thf.

Both the *cis* and *trans* isomers of complex $\text{RuCl}_2(\text{CO})(\text{PPhPh}_2)(\text{POOP})$ (**4**) are stable yellow (*trans*-**4**) or pale yellow (*cis*-**4**) solids, soluble in common organic solvents and non-electrolytes. Their formulation is supported by

analytical and spectroscopic (IR, NMR) data, and by the X-ray crystal structure determination of *cis*- $\text{RuCl}_2(\text{CO})(\text{PPhPh}_2)(\text{POOP})$ (*cis*-**4**).

The molecular structure, including the atom-numbering scheme, of the complex is shown in Fig. 3. Table 4 lists some selected bond lengths and angles, and Table 5 some intramolecular hydrogen interactions. There are no important interactions between discrete molecules. The ruthenium atom is coordinated by two phosphorus atoms of the chelating bidentate phosphinite ligand, one phosphorus atom of the diphenylphosphine ligand, two chloride ions and one carbon atom of the carbonyl ligand, giving a core $[\text{RuP}_3\text{C}_1\text{Cl}_2]$. The chlorine ligands are in relative *cis* positions $[\text{Cl}(1)-\text{Ru}-\text{Cl}(2)] = 90.88(4)^\circ$. The $\text{Ru}-\text{Cl}$ bond lengths do not show the expected differences, owing to the different *trans* effect of the phosphinite and carbonyl ligands, the distances being 2.4532(11) and 2.4563(11) Å, respectively. The *cis* angles around the Ru atom vary from $84.93(4)^\circ$ to $97.99(13)^\circ$, and the *trans* angles are $175.55(4)^\circ$, $174.38(12)^\circ$ and $171.14(4)^\circ$. The major deviation from regularity seems to arise from repulsion between the H atom of the phosphine and the π cloud of the neighbouring phenyl ring (shown in Fig. 3 with dotted lines) [32]. The three equatorial orthorhombic planes [dihedral angles of $89.93(4)^\circ$, $88.85(4)^\circ$ and $85.55(4)^\circ$] contain the Ru atom

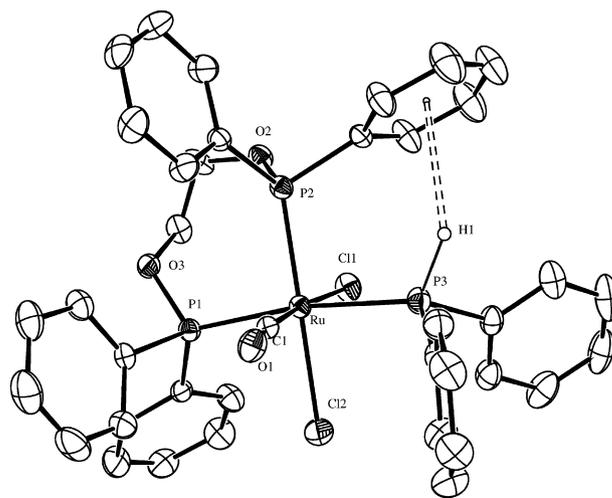
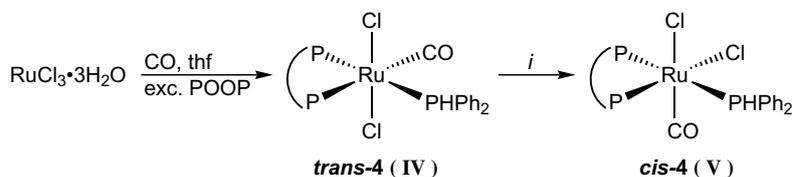


Fig. 3. Molecular structure of *cis*- $\text{RuCl}_2(\text{CO})(\text{PPhPh}_2)(\text{POOP})$ (*cis*-**4**). The atoms are drawn at 30% probability level.



P-P = $\text{Ph}_2\text{POCH}_2\text{CH}_2\text{OPPh}_2$ (POOP)

i = either in CH_2Cl_2 solution at 25°C for 6 days, or in refluxing thf for 1 hour

Table 4
Bond lengths (Å) and angles (°) for *cis-4*

Lengths			
Cl(1)–Ru	2.4563(11)	Cl(2)–Ru	2.4532(11)
Ru–C(1)	1.885(5)	Ru–P(2)	2.3158(11)
Ru–P(1)	2.3456(11)	Ru–P(3)	2.4059(11)
Angles			
C(1)–Ru–P(2)	97.99(13)	C(1)–Ru–P(1)	89.60(12)
P(2)–Ru–P(1)	93.27(4)	C(1)–Ru–P(3)	86.33(12)
P(2)–Ru–P(3)	95.09(4)	C(1)–Ru–Cl(2)	86.08(13)
P(1)–Ru–Cl(2)	84.93(4)	P(3)–Ru–Cl(2)	86.94(4)
P(2)–Ru–Cl(1)	85.21(4)	P(1)–Ru–Cl(1)	94.85(4)
P(3)–Ru–Cl(1)	88.79(4)	Cl(2)–Ru–Cl(1)	90.88(4)
P(2)–Ru–Cl(2)	175.55(4)	C(1)–Ru–Cl(1)	174.38(12)
P(1)–Ru–P(3)	171.14(4)		

Table 5
Hydrogen bonds parameters for *cis-4* (Å, °)

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
P(3)–H(1)...Cg	1.42(3)	2.79(3)	3.8254(11)	127.5(14)
C(12)–H(12)...Cl(1)	0.93	2.58	3.436(4)	153.9
C(26)–H(26)...O(3)	0.93	2.40	2.829(5)	107.7
C(36)–H(36)...O(2)	0.93	2.60	2.971(5)	104.5
C(46)–H(46)...Cl(1)	0.93	2.80	3.475(4)	130.5
C(66)–H(66)...Cl(2)	0.93	2.75	3.574(4)	147.6

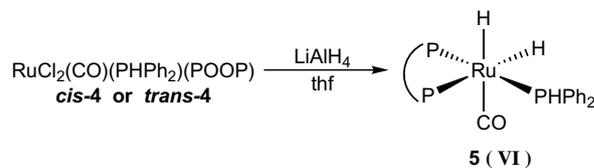
Cg stands for the centroid of the phenyl ring.

[max. deviation of 0.021(1) Å], except in the case of the plane formed by atoms C(1), Cl(1), P(1) and P(3). The Ru atom lies 0.113(1) Å out of the best plane as a consequence of the lack of regularity in the octahedron.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of *trans*-RuCl₂(CO)(PPh₂)(POOP) (*trans-4*) shows three doublets of doublets at 15.4, 118.6 and 134.2 ppm, with coupling constants $^2J_{\text{PP}}$ of 334, 35 and 43 Hz, fitting the *mer* position of the phosphorus ligands. The ^1H NMR spectrum displays a doublet of multiplets at 5.65 ppm, with a coupling constant of 369 Hz attributed to the H atom of the PPh₂ ligand; the methylene protons of the POOP ligand appear as a multiplet centred at 4.10 ppm. The IR spectrum shows a strong band at 1994 cm⁻¹ attributed to ν_{CO} and, in the far region, a medium-intensity band at 320 cm⁻¹, due to the ν_{RuCl} of the two Cl⁻ ligands in a mutually *trans* position. On the basis of these data, a *mer-trans* geometry **IV** may be proposed for the *trans-4* compound.

Instead, the IR spectra of the related *cis* isomers *cis-4* show two ν_{RuCl} bands at 299 and 270 cm⁻¹, fitting the mutually *cis* position of the two chloride ligands. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra display three doublets of doublets, with J_{PP} values of 21, 32 and 375 Hz, in agreement with the *mer* arrangement of the three phosphorus nuclei of the phosphine. On the basis of these data, a *mer-cis* geometry **V**, like that observed in the solid state, may be proposed in solution for the *cis-4* derivative.

Both *cis* and *trans* dichloro-complexes RuCl₂(CO)(PPh₂)(POOP) (**4**) react with LiAlH₄ in thf to give the related dihydride complex *cis*-RuH₂(CO)(PPh₂)(POOP)



Scheme 5.

(**5**), which was isolated as a white solid and characterised (Scheme 5) [33].

The IR spectrum of **5** shows one strong band at 1963 cm⁻¹, due to ν_{CO} , and one at 1832 cm⁻¹, attributable to the stretching vibrations of the Ru–H bonds. Weak absorption at 2360 cm⁻¹, due to the ν_{PH} of the secondary phosphine PPh₂ [34], was also observed.

In the high field of the proton NMR spectrum of **5**, two multiplets appear at –7.80 and –7.40 ppm, each integrating by one proton, and were attributed to two chemically non-equivalent hydride ligands. As the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum corresponds to that of an ABM system of the *mer* arrangement of the three phosphorus nuclei, the hydride pattern may be simulated [12] with an ABMXY model ($X, Y = ^1\text{H}$), with the parameters reported in Experimental. The good fit between the calculated and experimental spectra (Fig. 4) supports the proposed *cis* attribution [29,35]. The classical hydridic nature of the complex was also confirmed by T_1 measurements, which gave values of $T_{1(\text{min})}$ of 373 and 419 ms, in agreement with the proposed formulation [7a,36]. In the ^1H NMR spectra of **5**, two multiplets at 4.06 and 4.28 ppm also appear, due to the methylene protons of the POOP ligand. The doublet of multiplets at 5.44 ppm was attributed to the H proton of the PPh₂ phosphine group. On the basis of these data, a *mer-cis* geometry **VI** may reasonably be proposed for dihydride complex **5**.

The reaction on carbonylated solutions of RuCl₃ · 3H₂O with bidentate phosphite POOP was also carried out in

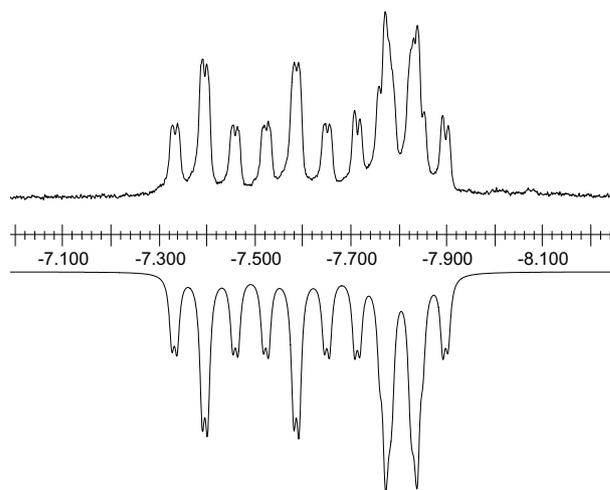
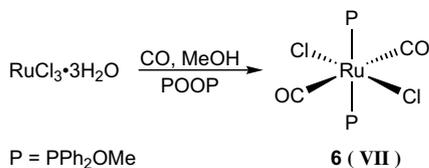


Fig. 4. ^1H NMR spectrum (experimental top, simulated bottom) between –7.0 and –8.2 ppm of compound *cis*-RuH₂(CO)(PPh₂)(POOP) (**5**).



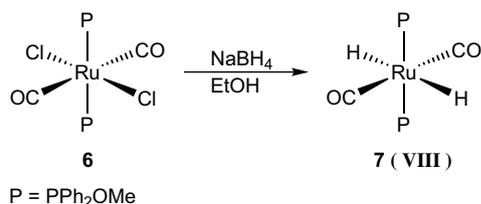
Scheme 6.

methanol instead of thf. In this case, the transesterification reaction of Ph₂POCH₂CH₂OPPh₂ with MeOH, giving PPh₂OMe, is faster than the coordination reaction of POOP, and yields complex RuCl₂(CO)₂(PPh₂OMe)₂ (**6**) as final product (Scheme 6).

The carbonylated methanol solution probably contains chloro-carbonyl ruthenium complexes [RuCl₂(CO)₂]_n or RuCl₂(CO)₃(MeOH), which react with the PPh₂OMe forming in solution to give the known dicarbonyl RuCl₂(CO)₂P₂ (**6**) derivative [37]. The use of boiling methanol, instead of 2-methoxyethanol, as a solvent yielded the *all-trans* isomer instead of the *cis-cis-trans* one [37]. The thermodynamically less stable *all-trans* isomer **6**, due to the mutual competition of both CO ligands for the electronic charge of the metal [38], can therefore be obtained using methanol as solvent.

Treatment of chloro-complex RuCl₂(CO)₂(PPh₂OMe)₂ (**6**) with NaBH₄ in ethanol afforded dihydride derivative RuH₂(CO)₂(PPh₂OMe)₂ (**7**), which was isolated in moderate yield (Scheme 7).

Both chloro-RuCl₂(CO)₂P₂ (**6**) and hydride RuH₂(CO)₂P₂ (**7**) complexes are stable yellow (**6**) or orange (**7**) solids, soluble in common organic solvents and non-electrolytes. Their formulation is supported by analytical and spectroscopic data and by X-ray single-crystal structure determination of RuCl₂(CO)₂(PPh₂OMe)₂ (**6**). The molecular structure of the complex, including the atom-numbering scheme, is shown in Fig. 5. Table 6 lists some selected bond lengths and angles. The compound crystallises in monoclinic spatial group *C2/c* in such a way that the metal atom is located at the inversion centre of the molecule. The geometry around the Ru atom is a slightly distorted octahedron with three pairs of symmetry-related ligands in an *all-trans* environment. Bond distances Ru–Cl, Ru–C and Ru–P have values of 2.4091(6), 1.943(3) and 2.3844(6) Å, respectively, at the expected range for bonds between Ru(II) and the corresponding ligands, and of the same magnitude as those reported for similar compounds, com-



Scheme 7.

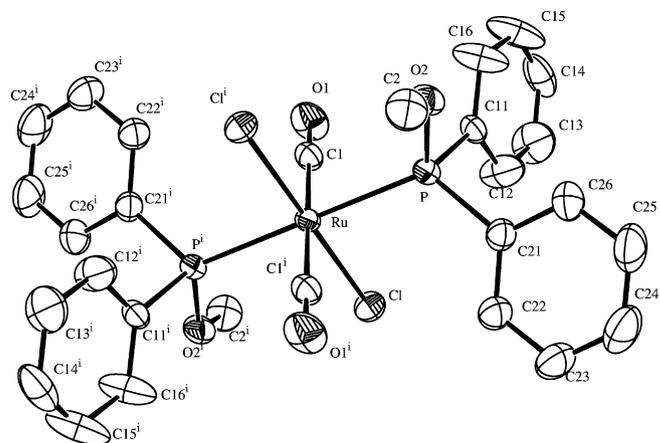


Fig. 5. Molecular structure of compound RuCl₂(CO)₂(PPh₂OMe)₂ (**6**). The atoms are drawn at 30% probability level.

Table 6
Bond lengths (Å) and angles (°) for **6**

Lengths			
Ru–C(1 ⁱ)	1.943(3)	Ru–C(1)	1.943(3)
Ru–P ⁱ	2.3844(6)	Ru–P	2.3844(6)
Ru–Cl ⁱ	2.4091(6)	Ru–Cl	2.4091(6)
Angles			
C(1)–Ru–P ⁱ	90.74(7)	C(1 ⁱ)–Ru–P	90.74(7)
C(1)–Ru–P	89.26(7)	P ⁱ –Ru–P	180.0
C(1 ⁱ)–Ru–C(1)	180.0	C(1 ⁱ)–Ru–P ⁱ	89.26(7)
C(1 ⁱ)–Ru–Cl ⁱ	88.87(8)	C(1)–Ru–Cl ⁱ	91.13(8)
P ⁱ –Ru–Cl ⁱ	88.54(2)	P–Ru–Cl ⁱ	91.46(2)
C(1 ⁱ)–Ru–Cl	91.13(8)	C(1)–Ru–Cl	88.87(8)
P ⁱ –Ru–Cl	91.46(2)	P–Ru–Cl	88.54(2)
Cl ⁱ –Ru–Cl	180.0	O(2)–P–C(11)	98.72(11)

Symmetry transformations used to generate equivalent atoms: ⁱ 1/2 – x, 1/2 – y, 1 – z.

plexes like [RuCl₂(CO)₂(PPh₃)₂] [39] or [RuCl₂(CO)₂(PBz₃)₂] [40].

The IR spectrum of chloro-complex RuCl₂(CO)₂(PPh₂OMe)₂ (**6**) shows only one ν_{CO} band at 2015 cm⁻¹, fitting the mutually *trans* position of the two carbonyl ligands. In addition, in the far region, only one weak band at 330 cm⁻¹ is observed, attributable to the ν_{Ru–Cl} of two Cl⁻ ligands in a mutually *trans* position. In the temperature range between +20 and –80 °C, the ³¹P NMR spectra show only one singlet at 120.1 ppm, fitting the presence of two magnetically equivalent phosphite ligands. The ¹H NMR spectra also show the methoxy signals of the PPh₂OMe as a virtual triplet at 3.55 ppm (*J*_{virtual} = ³*J*_{PH} + ⁵*J*_{PH} = 6.4 Hz), fitting the mutually *trans* position of the two phosphite ligands. On the basis of these data, an *all-trans* geometry **VII**, like that found in the solid state, may be proposed for chloro-complex **6**.

The IR spectrum of dihydride complex RuH₂(CO)₂(PPh₂OMe)₂ (**7**) shows one strong absorption at 1972 cm⁻¹, attributed to the ν_{CO} of two carbonyls in a mutually *trans* position, and another strong one at 2023 cm⁻¹, due to the ν_{Ru–H} of two *trans* hydride ligands. However, the presence

of the H^- ligand is confirmed by the 1H NMR spectra, which show a sharp singlet at -7.63 ppm. T_1 measurements on this signal gave a $T_{1(\min)}$ value of 467 ms (at 400 MHz), fitting the classical nature of dihydride complex **7**. The 1H NMR spectra of **7** also show a sharp triplet at 3.53 ppm ($J_{vt} = 7$ Hz), due to the methoxy resonance of the two PPh_2OMe phosphite ligands in a mutually *trans* position. In the temperature range between $+20$ and -80 °C, the $^{31}P\{^1H\}$ NMR spectra appear as a sharp singlet, confirming the magnetic equivalence of the two phosphite ligands. On the basis of these data, an *all-trans* geometry **VIII**, like that of chloro-precursors **6**, may be proposed for dihydride complex **7**.

4. Conclusions

This report describes new routes for preparing dihydride complexes of ruthenium with bidentate phosphite ligands, giving rise to unprecedented dihydrides $RuH_2(PFFP)_2$, $RuH_2(POOP)_2$ and $RuH_2(CO)(PPh_2)(POOP)$. An unexpected example of metal-mediated fragmentation of the bidentate phosphite POOP, yielding the secondary phosphine PPh_2 , is observed. The spectroscopic data and structural parameters of both dichloro- and dihydride complexes are also reported.

5. Supplementary material

CCDC 652770, 639443, 639141 and 639142 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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