New rhenium complexes with phosphinite PPh_2OR or phosphonite $PPh(OR)_2$ (R = Me, Et or Pr^i) ligands: synthesis and protonation of various polyhydrides †

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The rhenium complexes $[ReOCl_3L_2]$ and $[ReCl_3L_3]$ [L = PPh_2OMe, PPh_2OEt, PPh_2OPr^i, $PPh(OEt)_2$ or $PPh(OPr^i)_2$] were prepared by allowing $[ReOCl_3(AsPh_3)_2]$ to react with the appropriate amount of phosphinite or phosphonite. Treatment of $[ReCl_3L_3]$ with CO and p-MeC_6H_4NC afforded the *mer-trans*-$[ReCl(CO)_3L_2]$ and $[ReCl_2(p\text{-}MeC_6H_4NC)_4L]BPh_4$ complexes, respectively. Treatment of $[ReOCl_3L_2]$ with $NaBH_4$ gave $[Re_2H_8L_4]$, but in the presence of phosphinite or phosphonite the trihydrides $[ReH_3L_4]$ were obtained. Treatment of $[ReCl_3L_3]$ with $NaBH_4$ gave instead pentahydride complexes $[ReH_5L_3]$. All the multihydrides were characterised as 'classical' species by variable-temperature NMR spectroscopy (^1H and ^{31}P) and T_1 measurements. Protonation of $[Re_2H_8L_4]$ and $[ReH_3L_4]$ with $HBF_4 \cdot Et_2O$ gave the classical hydride cations $[Re_2H_9L_4]^+$ and $[ReH_4L_4]^+$, respectively, while similar treatment of $[ReH_5L_3]$ gave a species formulated as containing an η^2-H_2 ligand, $[ReH_4(\eta^2\text{-}H_2)L_3]^+$ on the basis of $T_{1(min)}$ evidence.

A number of studies on the synthesis and properties of rhenium complexes containing tertiary phosphine ligands have been reported in recent years [1] and, among them, particular attention has been devoted to the multihydride compounds.[2] This interest is due to different factors including the ability of rhenium polyhydrides to activate the C–H bond [2a,3] in both aromatic and aliphatic hydrocarbons and the relationship between multihydride and dihydrogen complexes.[4] It has, in fact, been reported that some rhenium polyhydrides contain both hydride and η^2-H_2 ligands in the molecule and that protonation of these hydride species can give dihydrogen derivatives.[2,4,5]

Despite the number of studies reported with mono- and di-tertiary phosphine ligands, relatively little data are available on the corresponding phosphite complexes.[6] As ligands, phosphites are generally more electron withdrawing and sterically less bulky than phosphines [7] and their use as ancillary ligands may have interesting effects on both the structure and reactivity of the resulting complexes, as a result of different steric and electronic properties. Therefore we thought it would be of interest to develop a systematic investigation on the synthesis and reactivity of rhenium complexes with phosphinite and phosphonite ligands,[8] in particular with 'mixed phosphines' of the type $PPh(OR)_2$ and PPh_2OR in which the steric and electronic properties can be changed extensively. The results of these studies including T_1 measurements on the new polyhydrides are reported here.

Experimental

All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. Reactions were carried out in an atmosphere of argon or dinitrogen, using standard Schlenk techniques or a vacuum atmosphere dry-box. Once isolated, the air-stable complexes were stored at −25 °C. Phosphinites $PPh_2(OR)$ and phosphonites $PPh(OR)_2$ (R = Me, Et or Pr^i) were prepared by the method of Rabinowitz and Pellon,[9] whereas p-tolyl isocyanide was prepared by the method of Ziehn and co-workers.[10] Other reagents were obtained from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna-IR 750 FT spectrophotometer, NMR spectra (^1H and ^{31}P) on a Bruker AC 200 spectrometer at temperatures between −90 and +30 °C, unless otherwise noted. The ^1H spectra are referred to internal tetramethylsilane; ^{31}P-{^1H} chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. Values of T_1 (± 10%) were determined by the inversion recovery method between −90 and +30 °C in CD_2Cl_2 with a standard 180°-τ-90° pulse sequence. Conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in nitromethane at 25 °C were measured on a Radiometer CDM 83 instrument.

Preparation of complexes

The perrhenate salt $KReO_4$ was prepared by dissolving rhenium powder in 30% hydrogen peroxide and, after concentration, by adding KCl to precipitate the salt. The arsine complex $[ReOCl_3(AsPh_3)_2]$ was prepared by the method previously reported.[2e]

$[ReOCl_3L_2]$ 1 [L = PPh_2OMe a, PPh_2OEt b, PPh_2OPr^i c, $PPh(OEt)_2$ d or $PPh(OPr^i)_2$ e]. To a suspension of $[ReOCl_3(AsPh_3)_2]$ (1.63 mmol, 1.5 g) in tetrahydrofuran(thf) (40 cm^3) was added the appropriate phosphinite or phosphonite (3.26 mmol) and the reaction mixture stirred for 3–4 h. The solvent was then removed under reduced pressure giving an oil which was triturated with ethanol (10–15 cm^3). A blue solid slowly separated which was filtered off, washed with ethanol and crystallised from thf–ethanol (5:15 cm^3); yield ⩾70% (Found: C, 42.35; H, 3.45. $C_{26}H_{26}Cl_3O_3P_2Re$ **1a** requires C, 42.15; H, 3.55. Found: C, 43.60; H, 3.80. $C_{28}H_{30}Cl_3O_3P_2Re$ **1b** requires C, 43.75; H, 3.95. Found: C, 44.95; H, 4.15. $C_{30}H_{34}Cl_3O_3P_2Re$ **1c** requires C, 45.20; H, 4.30. Found: C, 33.80; H, 4.30. $C_{20}H_{30}Cl_3O_5P_2Re$ **1d** requires C, 34.10; H, 4.30. Found: C, 38.00; H, 4.95. $C_{24}H_{38}Cl_3O_5P_2Re$ **1e** requires C, 37.90; H, 5.05%).

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† *Non-SI unit employed:* atm = 101 325 Pa.

$[ReCl_3L_3]$ 2 [L = PPh_2OMe a, PPh_2OEt b, PPh_2OPr^i c or $PPh(OEt)_2$ d]. An excess of the appropriate phosphinite or phosphonite (16 mmol) was added to a suspension of $[ReOCl_3(AsPh_3)_2]$ (1.63 mmol, 1.5 g) in thf (30 cm^3) and the reaction mixture stirred for about 5 h. The resulting solution was concentrated under reduced pressure to about 5 cm^3 and the slow addition of ethanol (10–15 cm^3) resulted in the precipitation of a yellow solid which was filtered off, washed with ethanol and crystallised from thf–ethanol (5:15 cm^3); yield ⩾60% (Found: C, 49.65; H, 4.15. $C_{39}H_{39}Cl_3O_3P_3Re$ **2a** requires C, 49.75; H, 4.20. Found: C, 51.00; H, 4.50. $C_{42}H_{45}Cl_3O_3P_3Re$ **2b** requires C, 51.30; H, 4.60. Found: C, 52.50; H, 5.00. $C_{45}H_{51}Cl_3O_3P_3Re$ **2c** requires C, 52.70; H, 5.0. Found: C, 40.40; H, 5.00. $C_{30}H_{45}Cl_3O_6P_3Re$ **2d** requires C, 40.60; H, 5.10%).

$[ReCl(CO)_3L_2]$ 3 [L = PPh_2OMe a, PPh_2OEt b or $PPh(OEt)_2$ d]. A solution of $[ReCl_3L_3]$ (0.5 mmol) in thf (40 cm^3) was refluxed under a CO atmosphere (1 atm) for 1 h and then the volume of the mixture was reduced to about 5 cm^3. Slow addition of hexane (5–10 cm^3) resulted in precipitation of the complexes, which was completed by cooling the mixture to −25 °C; yield ⩾60% (Found: C, 47.10; H, 3.70. $C_{29}H_{26}ClO_5P_2Re$ **3a** requires C, 47.20; H, 3.55. Found: C, 48.45; H, 4.10. $C_{31}H_{30}ClO_5P_2Re$ **3b** requires C, 48.60; H, 3.95. Found: C, 39.25; H, 4.20. $C_{23}H_{30}ClO_7P_2Re$ **3d** requires C, 39.35; H, 4.30%).

$[ReCl_2(p\text{-}MeC_6H_4NC)_4L]BPh_4$ 4 [L = $PPh_2(OEt)$ b or $PPh(OEt)_2$ d]. An excess of *p*-tolyl isocyanide (2.5 mmol, 0.29 µl) was added to a solution of $[ReCl_3L_3]$ (0.5 mmol) in 1,2-dichloroethane (20 cm^3) and the reaction mixture refluxed for 90 min. The solvent was removed under reduced pressure giving an oil which was triturated with ethanol (10 cm^3). The addition of $NaBPh_4$ (0.5 mmol, 0.17 g) in ethanol (5 cm^3) to the resulting solution gave a brown solid which was filtered off and crystallised from ethanol; yield ⩾70%; Λ_M = 54.6 for **4b**, 50.9 S cm^2 mol^{-1} for **4d** (Found: C, 65.70; H, 5.30; N, 4.25. $C_{70}H_{63}BCl_2N_4OPRe$ **4b** requires C, 65.95; H, 5.00; N, 4.40. Found: C, 63.50; H, 5.30; N, 4.35. $C_{66}H_{63}BCl_2N_4O_2PRe$ **4d** requires C, 63.75; H, 5.10; N, 4.50%).

$[Re_2H_8L_4]$ 5 [L = PPh_2OEt b or $PPh(OEt)_2$ d]. An excess of $NaBH_4$ (25 mmol, 0.95 g) in ethanol (10 cm^3) was added to a suspension of $[ReOCl_3L_2]$ (0.5 mmol) in ethanol (10 cm^3) and the mixture stirred at room temperature for 6 h. The solvent was removed under reduced pressure giving a pale yellow solid. From this solid the hydride was extracted first with three portions (20 cm^3) of light petroleum (b.p. 40–70 °C) and then with two portions (10 cm^3) of benzene. The extracts were mixed and the solvent removed under reduced pressure giving a brown oil which was triturated with ethanol (3–5 cm^3). By cooling the resulting solution to −25 °C a red-brown solid separated which was filtered off and dried under vacuum; yield ⩾40% (Found: C, 51.55; H, 5.15. $C_{56}H_{68}O_4P_4Re_2$ **5b** requires C, 51.70; H, 5.25. Found: C, 41.10; H, 5.60. $C_{40}H_{68}O_8P_4Re_2$ **5d** requires C, 40.95; H, 5.85%).

$[ReH_3L_4]$ 6 [L = PPh_2OEt b or $PPh(OEt)_2$ d]. To a suspension of $[ReOCl_3L_2]$ (1 mmol) in ethanol (10 cm^3) was added a solution of $NaBH_4$ (10 mmol, 0.38 g) in ethanol (10 cm^3) containing an excess (10 mmol) of the appropriate phosphite and the reaction mixture was refluxed for 4 h. The resulting suspension was filtered and the solvent removed under reduced pressure giving a white solid. From this solid the hydride was extracted with three portions (15 cm^3) of benzene and the resulting solution evaporated to dryness. The oil obtained was treated with ethanol (5 cm^3) and the resulting solution cooled to −25 °C giving white crystals of the product; yield ⩾60% (Found: C, 60.40; H, 5.65. $C_{56}H_{63}O_4P_4Re$ **6b** requires C, 60.60; H, 5.70. Found: C, 48.70; H, 6.50. $C_{40}H_{63}O_8P_4Re$ **6d** requires C, 48.90; H, 6.45%). These crystals are stable below 0 °C, but in the case of **6b** increase in temperature slowly caused the crystals to transform into an oil.

$[ReH_5L_3]$ 7 [L = PPh_2OMe a, PPh_2OEt b or $PPh(OEt)_2$ d]. A suspension of $[ReCl_3L_3]$ (1 mmol) in 10 cm^3 of ethanol was treated with an excess of $NaBH_4$ (50 mmol, 1.9 g) in ethanol (40 cm^3) and the reaction mixture refluxed for 2 h. The solvent was removed under reduced pressure giving a solid from which the hydride was extracted with three portions (15 cm^3) of benzene. The resulting solution was evaporated to dryness giving an oil which was treated with ethanol (5 cm^3). By slowly cooling the resulting solution to −25 °C, white microcrystals gradually formed which were filtered off and dried under vacuum; yield ⩾60% (Found: C, 55.60; H, 5.45. $C_{39}H_{44}O_3P_3Re$ **7a** requires C, 55.75; H, 5.30. Found: C, 56.80; H, 5.90. $C_{42}H_{50}O_3P_3Re$ **7b** requires C, 57.20; H, 5.70. Found: C, 45.95; H, 6.25. $C_{30}H_{50}O_3P_3Re$ **7d** requires C, 45.85; H, 6.40%).

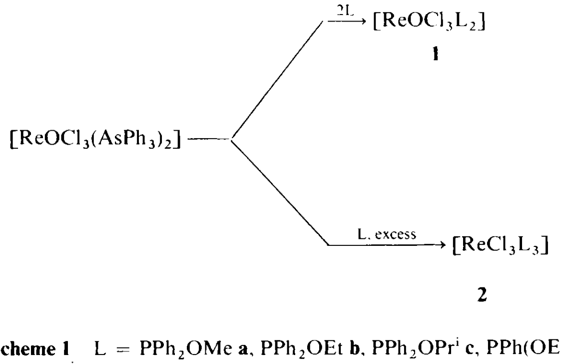
Protonation reactions

The hydrides **5b**, **5d**, **6d** and **7b** were protonated by adding an equimolar amount of $HBF_4\cdot Et_2O$ to a degassed dichlorodeuteriomethane solution of the appropriate complex placed in a NMR tube sealed with screw septum cap and cooled to −80 °C. A typical experiment involved the addition by syringe of a slight excess of $HBF_4\cdot Et_2O$ (13.2 µmol, 1.9 µl of *ca.* 54% solution in Et_2O) to a cooled (−80 °C) solution of $[ReH_5(PPh_2OEt)_3]$ (12.4 µmol, 10.9 mg) in dry CD_2Cl_2 (0.5 cm^3) prepared in a dry-box and placed in a 5 mm NMR tube. After transferring the tube to the spectrometer probe the ^1H and ^{31}P NMR spectra were recorded in the temperature range −90 to +25 °C and T_1 values were measured.

Results and Discussion

The new rhenium complexes $[ReOCl_3L_2]$ **1** and $[ReCl_3L_3]$ **2** have been synthesised by treating the arsine derivatives $[ReOCl_3(AsPh_3)_2]$ with 2 equivalents or with an excess of the appropriate phosphinite or phosphonite, as shown in Scheme 1. The complexes are blue (**1**) or yellow (**2**) solids, stable in air, soluble in non-polar solvents and non-electrolytes. Some spectroscopic properties are reported in Table 1.

The $[ReOCl_3L_2]$ **1** derivatives are diamagnetic and in the infrared spectra the ν(ReO) band[1a,11] appears at 977–990 cm^{-1}. The $^{31}P\text{-}\{^1H\}$ NMR spectra of **1b–1e** show only one sharp singlet at δ 66.8–88.7, while the spectrum of $[ReOCl_3(PPh_2OMe)_2]$ **1a** consists of one singlet at δ 68.7 and one AB quartet with δ_A 80.7, δ_B 40.4 and J_{AB} = 9.4 Hz. Furthermore, in the ^1H NMR spectrum of **1a** the methyl protons of the PPh_2OMe ligands appear as two doublets excluding the presence of phosphinites in the mutually *trans* position. In this case a triplet may be expected due to coupling of the methyl protons with two phosphorus atoms.



Scheme 1 L = PPh_2OMe **a**, PPh_2OEt **b**, PPh_2OPr^i **c**, $PPh(OEt)_2$ **d** or $PPh(OPr^i)_2$ **e**

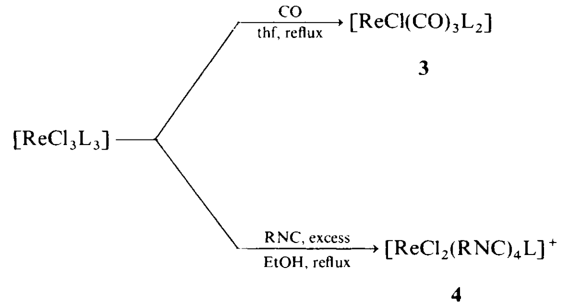
Table 1 Infrared and phosphorus-31 NMR data for the rhenium complexes

	IR[a]		^{1}H NMR[b,c]			^{31}P-{^{1}H} NMR[b,d]
Compound	$\tilde{\nu}$/cm^{-1}	Assignment	Solvent	δ (*J*/Hz)	Assignment	δ
1a $[ReOCl_3(PPh_2OMe)_2]$	988s	ν(ReO)	$CDCl_3$	3.78 (d) (J_{PH} = 12)	CH_3	68.7 (s)
				3.51 (d) (J_{PH} = 12)		60.5 (q)[e]
1b $[ReOCl_3(PPh_2OEt)_2]$	982s	ν(ReO)	CD_2Cl_2	3.75 (m), 3.60 (m)	CH_2	68.4 (s)
				1.13 (t)	CH_3	
1c $[ReOCl_3(PPh_2OPr^i)_2]$	990s	ν(ReO)	$CDCl_3$	5.23 (m)	CH	66.8 (s)
				1.20 (d) (J_{PH} = 6)	CH_3	
1d $[ReOCl_3\{PPh(OEt)_2\}_2]$	977s	ν(ReO)	$CDCl_3$	4.30 (m), 4.11 (m)	CH_2	88.7 (s)
				1.42 (t)	CH_3	
1e $[ReOCl_3\{PPh(OPr^i)_2\}_2]$			$CDCl_3$	4.97 (m), 4.84 (m)	CH	82.2 (s)
				1.38 (d), 1.36 (d)	CH_3	
				1.25 (d), 1.21 (d) (J_{PH} = 6)		
2a $[ReCl_3(PPh_2OMe)_3]$			$CDCl_3$	8.58 (m), 8.05 (m)	CH_3	
2b $[ReCl_3(PPh_2OEt)_3]$			$CDCl_3$	9.64 (m), 8.06 (m)	CH_2	
				3.03 (t), 1.63 (t)	CH_3	
2c $[ReCl_3(PPh_2OPr^i)_3]$			$CDCl_3$	7.87–7.24 (m)	CH	
				2.74 (d), 1.35 (d)	CH_3	
2d $[ReCl_3\{PPh(OEt)_2\}_3]$			$CDCl_3$	11.20 (m), 9.92 (m)	CH_2	
				3.66 (t), 2.62 (t)	CH_3	
3a $[ReCl(CO)_3(PPh_2OMe)_2]$	2062m, 1967s, 1888s	ν(CO)	$CDCl_3$	3.59 (t)	CH_3	105.3 (s)
	(2062m), (1963s), (1912s)					
3b $[ReCl(CO)_3(PPh_2OEt)_2]$	2065m, 1956s, 1916s	ν(CO)	$CDCl_3$	3.86 (m)	CH_2	100.7 (s)
	(2066m), (1961s), (1911s)			1.28 (t)	CH_3	
3d $[ReCl(CO)_3\{PPh(OEt)_2\}_2]$	2056m, 1948s, 1914s	ν(CO)	CD_2Cl_2	4.10 (m), 3.90 (m)	CH_2	125.7 (s)
				1.28 (t)	CH_3	
4b $[ReCl_2(p\text{-}MeC_6H_4NC)_4(PPh_2OEt)]^{+f}$	2143m, 2073s, 2038s	ν(CN)	$CDCl_3$	3.71 (qnt)	CH_2	106.0 (s)
	(2143m), (2072s), (2037s)			2.36 (s), 2.34 (s), 2.32 (s)	CH_3 of RNC	
				1.04 (t)	CH_3 of L	
4d $[ReCl_2(p\text{-}MeC_6H_4NC)_4\{PPh(OEt)_2\}]^{+f}$	2144m, 2062s, 2030s	ν(CN)	$CDCl_3$	3.83 (m), 3.67 (m)	CH_2	135.3 (s)
	(2128m), (2067s), (2036s)			2.37 (s), 2.32 (s), 2.30 (s)	CH_3 of RCN	
				1.31 (t), 1.09 (t)	CH_3 of L	
5b $[Re_2H_8(PPh_2OEt)_4]$	2004w, 1967w	ν(ReH)	C_6D_6	3.79 (qnt)	CH_2	126.9 (s)
				1.06 (t)	CH_3	
				−5.41 (qnt) (J_{PH} = 8)	Hydride	
5d $[Re_2H_8\{PPh(OEt)_2\}_4]$	1988w, 1963w	ν(ReH)	$CD_3C_6D_5$	3.87 (m), 3.64 (m)	CH_2	153.2 (s)
				1.09 (t)	CH_3	
				−6.18 (qnt) (J_{PH} = 8)	Hydride	
6b $[ReH_3(PPh_2OEt)_4]$	1893w, 1816m	ν(ReH)	C_6D_6	3.75 (m)	CH_2	121.0 (s)
				1.09 (t)	CH_3	
				−5.29 (qnt) (J_{PH} = 18)	Hydride	
6d $[ReH_3\{PPh(OEt)_2\}_4]$	1801m	ν(ReH)	C_6D_6	3.75 (m), 3.43 (m)	CH_2	151.7 (s)[g]
				1.08 (t)	CH_3	
				−6.57 (qnt) (J_{PH} = 18)[h]	Hydride	
7a $[ReH_5(PPh_2OMe)_3]$	1937w, 1882w	ν(ReH)	C_6D_6	3.36 (d)	CH_3	134.5 (s)
				−5.83 (q) (J_{PH} = 17)	Hydride	
7b $[ReH_5(PPh_2OEt)_3]$	1958sh, 1936w, 1872w	ν(ReH)	C_6D_6	3.86 (m)	CH_2	129.3 (s)
				1.09 (t)	CH_3	
				−5.78 (q) (J_{PH} = 17)	Hydride	
7d $[ReH_5\{PPh(OEt)_2\}_3]$	1932w, 1970w	ν(ReH)	CD_2Cl_2	3.79 (m), 3.50 (m)	CH_2	151.4 (s)
				1.13 (t)	CH_3	
				−6.94 (q) (J_{PH} = 17)	Hydride	
5b* $[Re_2H_9(PPh_2OEt)_4]^+$			CD_2Cl_2	3.42 (qnt)	CH_2	116.1 (s)[i]
				1.15 (t)	CH_3	
				−4.28 (qnt) (J_{PH} = 8)	Hydride	
5d* $[Re_2H_9\{PPh(OEt)_2\}_4]^+$			$CD_3C_6D_5$	3.68 (m), 3.48 (m)	CH_2	137.4 (s)
				1.07 (t)	CH_3	
				−4.48 (qnt) (J_{PH} = 8)	Hydride	
6d* $[ReH_4\{PPh(OEt)_2\}_4]^+$			CD_2Cl_2	3.68 (m), 3.47 (m)	CH_2	134.2 (s)[i]
				1.17 (m)	CH_3	
				−4.51 (qnt) (J_{PH} = 18)[j]	Hydride	
7b* $[ReH_4(\eta^2\text{-}H_2)(PPh_2OEt)_3]^+$			CD_2Cl_2	3.44 (qnt)	CH_2	109.1 (s)
				1.15 (t)	CH_3	
				−4.12 (q) (J_{PH} = 14)[k]	Hydride	

[a] In KBr pellets or CH_2Cl_2 solutions (in parentheses). [b] At room temperature. [c] Phenyl-proton resonances are omitted. [d] Positive shift downfield from 85% H_3PO_4. [e] Spin system AB, δ_A 80.7, δ_B 40.4, J_{AB} = 9.4 Hz. [f] BPh_4^- salt. [g] At −90 °C in CD_2Cl_2: δ 155.2 (br s) and 148.9 (br s). [h] At −90 °C in CD_2Cl_2: δ −7.01 (br) and −7.51 (br). [i] At −90 °C. [j] At −90 °C: δ −4.65 (br). [k] At −90 °C: δ −4.2 (br).

The structure of these complexes can be discussed in terms of the three geometries **I**–**III** and our results may be interpreted on the basis of the existence in solution for compound **1a** of two isomers, one with geometry **II** (singlet in the ^{31}P NMR spectrum) and the other with geometry **III** for which an AB ^{31}P NMR spectrum is expected. Indeed, for the related compounds **1b**–**1e** with only one singlet in the ^{31}P spectra we cannot decide between geometry **I** and **II**.

The rhenium(III) complexes $[ReCl_3L_3]$ **2**, which contain a d^4 centre in an octahedral environment,[12] show second-order paramagnetism with some of the proton resonances in the NMR spectra at unusual chemical shifts, as reported in Table 1. Furthermore, the signals of the Me, Et and Pr^i substituents show inequivalence of the phosphinite or phosphonite ligands (2:1 ratio) and, although the ^{31}P resonances are too broad (owing to rapid relaxation) to be observed, a *mer* geometry **IV** may be proposed for these complexes on the basis of the ^{1}H NMR spectra. A similar structure has been previously observed for related compounds containing tertiary and ditertiary phosphine ligands.[1a,5f,11]

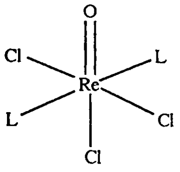


Scheme 2 L = PPh_2OMe **a**, PPh_2OEt **b**, or $PPh(OEt)_2$ **d**; R = *p*-tolyl

The reactivity of these rhenium-(v) and -(III) complexes toward CO and isocyanide has been investigated and while $[ReOCl_3L_2]$ often give intractable mixtures, $[ReCl_3L_3]$ quickly react with CO (1 atm) or *p*-tolyl isocyanide to give $[ReCl(CO)_3L_2]$ **3** and $[ReCl_2(p\text{-}MeC_6H_4NC)_4L]BPh_4$ **4** derivatives as shown in Scheme 2. The carbonylation reaction of the $[ReCl_3L_3]$ compounds proceeds under reflux conditions with reduction to Re^I and the formation of tricarbonyl complexes **3** which can be isolated as white or pale yellow solids and characterised (Table 1). The compounds are diamagnetic, non-electrolytes and their IR spectra show in the ν(CO) region three bands at 2065–1888 cm^{-1}, two strong and one weak, indicating the presence of three carbonyl groups in a *mer* arrangement.[13] In the temperature range between +30 and −80 °C the $^{31}P\text{-}\{^1H\}$ NMR spectra show, for all the carbonyl compounds **3**, only one sharp singlet indicating the magnetic equivalence of the two phosphine ligands. Furthermore, the ^1H NMR spectra also suggest the mutually *trans* position of the two phosphinite or phosphonite groups showing, for example, a triplet for the methyl protons of the PPh_2OMe groups of **3a**. On this basis a *mer-trans* geometry of type **V** can reasonably be proposed for these complexes in solution. A similar structure has been suggested for previously reported tricarbonyl compounds prepared by substitution of rhenium(I) pentacarbonyl complexes $[ReX(CO)_5]$ (X = Cl or Br)[14] or by carbonylation of tertiary phosphine complexes.[14]

Treatment of $[ReCl_3L_3]$ with an excess of *p*-tolyl isocyanide affords seven-co-ordinate tetrakis(isocyanide) compounds $[ReCl_2(p\text{-}MeC_6H_4NC)_4L]BPh_4$ **4** which are diamagnetic 1 : 1 electrolytes.[15] However, only **4b** (L = PPh_2OEt) and **4d** [L = $PPh(OEt)_2$] can be obtained as solids, the others being oils. The IR spectra show three ν(NC) bands between 2144 and 2030 cm^{-1}, while the ^1H NMR spectra show the presence of the isocyanide and of the phosphinite or phosphonite ligands in a 4 : 1 ratio (Table 1), in agreement with the proposed formulation. Isocyanide complexes of Re are known mainly as rhenium(I) derivatives[1b,c] and only one example of a mixed phosphine–isocyanide complex, $[ReCl_2(Bu^tNC)_4(PPh_2Et)]PF_6$, has been reported.[16]

We have also studied the reactivity of both the rhenium-(v) and -(III) complexes toward $NaBH_4$ under different conditions and the results obtained are reported in Scheme 3. Treatment of $[ReOCl_3L_2]$ **1** with $NaBH_4$ in ethanol at room temperature gave, in the case of L = $PPh(OEt)_2$ and PPh_2OEt, the $[Re_2H_8L_4]$ **5** derivatives as orange microcrystalline solids. With the other phosphinites or phosphonites intractable oils were always obtained. The formation of the dimeric complexes **5** is rather unexpected because the reaction of rhenium(v) complexes of the type $[ReOCl_3L_2]$ is reported to give heptahydride derivatives $[ReH_7L_2]$.[2a,e,g,o] These compounds, however, are often thermally unstable and can give, by loss of H_2 and dimerisation, the $[Re_2H_8L_4]$ derivatives. However, some studies on the reaction course seem to indicate that also in our case the reaction of **1** with $NaBH_4$ probably proceeds with the formation of $[ReH_7L_2]$ which easily dimerises to produce **5** as the final compound. In fact, from the reaction of $[ReOCl_3\{P\text{-}Ph(OEt)_2\}_2]$ with $NaBH_4$ at 0 °C we isolated a product containing, before crystallisation, a small amount of a new hydride (ratio 1 : 10 with respect to **5d**) attributable to a $[ReH_7L_2]$ intermediate on the basis of the presence in the ^1H NMR spectrum of a triplet at δ −6.11 beside the quintet at δ −6.18 of **5d**.



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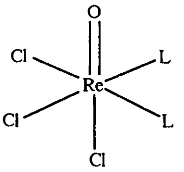

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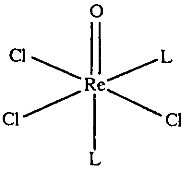

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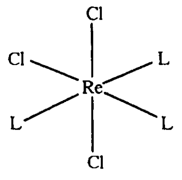

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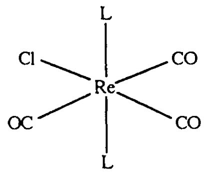

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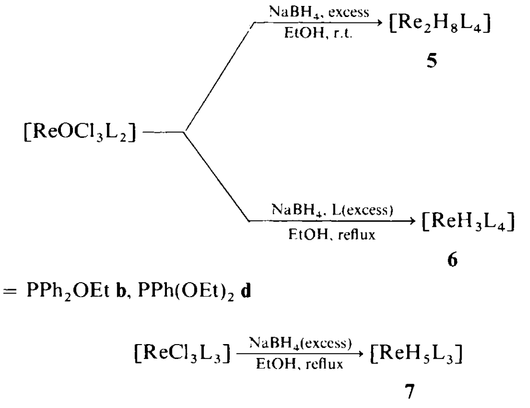


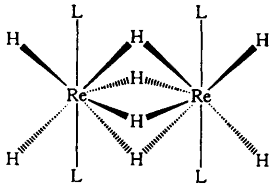
L = PPh_2OEt **b**, $PPh(OEt)_2$ **d**

L = PPh_2OMe **a**, PPh_2OEt **b**, $PPh(OEt)_2$ **d**

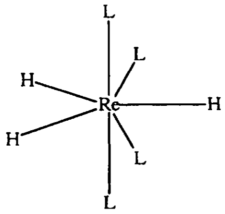
Scheme 3

The formulation of complex **5** as dimeric $[Re_2H_8L_4]$ comes from the analytical and spectroscopic data in Table 1. The complexes are diamagnetic, non-electrolytes and their infrared spectra show, in the 2004–1963 cm^{-1} region, well defined ν(ReH) modes which agree with those previously reported for related tertiary phosphine complexes.[2a,c,o] In the range between −90 and +30 °C the $^{31}P\text{-}\{^1H\}$ NMR spectra are sharp singlets for each compound. At room temperature the ^1H NMR spectra show, apart from the signals of the phosphine ligands, a sharp quintet at δ −5.41 to −6.18 with J_{PH} 8 Hz. Lowering of the sample temperature does not cause spectral variation and also at −90 °C all the hydrides appear equivalent on the NMR timescale. Careful integration of the ^1H NMR spectra seems to indicate the presence of approximately eight hydride ligands. A ^{31}P NMR spectrum with selective decoupling of the methyl or ethyl groups of the phosphinite or phosphonite was also recorded, in order to determine exactly the number of hydride ligands in the molecule, but the expected nine lines were not clearly observed owing to the broad nature of the spectra and the small value of J_{PH}. However, all the results seem to support the formulation of **5** as dirhenium octahydride complexes with a geometry (**VI**) of the type found in the related $[Re_2H_8(PR_3)_4]$ derivatives.[2]

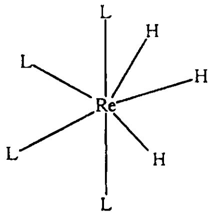
When the reaction of $[ReOCl_3L_2]$ with $NaBH_4$ is carried out in the presence of an excess of the appropriate free phosphinite or phosphonite the trihydride $[ReH_3L_4]$ complexes **6** can be



VI



A



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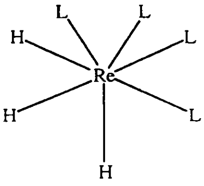


C

isolated as white solids in some cases and as oils in others. The infrared spectra show the ν(ReH) bands in the 1893–1816 cm^{-1} region (Table 1) while in the ^1H NMR spectra the hydride resonance appears as a well defined quintet at δ −5.29 to −6.57 (J_{PH} = 18 Hz) indicating that the hydrides are coupled to four equivalent phosphite ligands. However, strong support for the formulation of **6** as a trihydride comes from the selective proton-decoupled ^{31}P NMR spectra which display a quartet with J_{PH} about 18 Hz when decoupling all the organic protons only, indicating coupling of the ^{31}P nuclei with three hydride ligands. The ^1H and ^{31}P NMR spectra of trihydrides **6** are temperature dependent and were studied between +30 and −90 °C with the complex $[ReH_3\{PPh(OEt)_2\}_4]$ **6d**. At room temperature the ^1H NMR spectrum shows in the hydride region a sharp quintet which broadens as the temperature is lowered and splits into two broad humps of intensity ratio 1:2 at −50 °C and remains unchanged until −90 °C. Also the sharp singlet at room temperature in the ^{31}P-$\{^1H\}$ NMR spectrum is split into two broad signals of intensity ratio 1:1 as the temperature is lowered, in agreement with the presence of two by two magnetically equivalent phosphine ligands. However, also at −90 °C the spectra do not resolve into a well defined pattern remaining as two rather broad signals. The structure of seven-co-ordinate rhenium polyhydrides has been discussed in terms[2a,f] of a pentagonal bipyramidal (**A**), a monocapped octahedral (**B**) or a capped trigonal-prismatic (**C**) geometry, but our spectroscopic data do not allow us to distinguish between these possible structures. However, it is worth noting that crystal structure determinations of rhenium trihydrides show either a pentagonal bipyramid in $[ReH_3(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) and $[ReH_3(PMePh_2)_4]$[17] or a monocapped octahedron in the $[ReH_3(dppe)(PPh_3)_2]$.[18]

Treatment of the rhenium(III) complexes $[ReCl_3L_3]$ with an excess of $NaBH_4$ in refluxing ethanol gives the pentahydrides $[ReH_5L_3]$ **7** which can be isolated as white solids with the methoxy- and ethoxy-phosphine ligands, while only an intractable oil is obtained with related isopropoxyphosphine. The compounds are diamagnetic, non-electrolytes and show the ν(ReH) absorption at 1958–1870 cm^{-1}. The elemental analyses and the NMR spectra (Table 1) support the proposed formulation. In particular, the ^1H NMR spectra show the hydride resonance as a quartet at δ −5.78 to −6.94 indicating the presence of three phosphine ligands, while selective decoupling ^{31}P spectra show the expected six lines when decoupling all the organic protons only, thus confirming that the ^{31}P nuclei are coupled to five equivalent hydrides. In the range between +30 and −90 °C the ^1H and the ^{31}P NMR spectra show that the pentahydride complexes are fluxional. The quartet due to the hydride resonance broadens as the temperature is lowered, being only a broad hump at −90 °C. Also the ^{31}P signals do not change in profile with the sample temperature, showing even at −90 °C only one slightly broad signal and so preventing any discussion on the geometry of the complexes.

When the synthesis of these complexes was carried out by treating $[ReCl_3L_3]$ with an excess of $NaBH_4$ at room temperature the white solid obtained contained another compound besides **7** in variable amounts (40–60%). This compound is a hydride containing three equivalent phosphine ligands (singlet near δ 125 between −90 and +30 °C in the ^{31}P NMR spectrum of the PPh_2OEt derivative) as deduced by the presence of a well defined quartet at δ −5.60 (J_{PH} = 18 Hz) in the ^1H NMR spectra. Furthermore, selective proton-decoupling ^{31}P spectra indicated the presence of five equivalent hydride ligands showing a pattern of six lines with J_{PH} about 18 Hz. The compound is a non-electrolyte and the NMR spectra strongly suggest a $[ReH_5L_3]$ formulation. In order to elucidate the properties of this new hydride we have measured the $T_{1(min)}$ of the hydride protons (see below) of the mixture and found similar values for **7b** (68 ms) and for the new hydride (66 ms), thus suggesting a classical structure for both. Unfortunately we are not able to separate the new species in pure form and therefore, in the absence of other data, don't feel able to propose a complete formulation or geometry for it.

Pentahydride complexes $[ReH_5L_3]$ {L = PPh_3, $PPhMe_2$, PPh_2Me, $P(OCH_2)_3CEt$, $Ph_2PCH_2PPh_2$, $Ph_2PCHCHPPh_2$, $PPh[CH_2CH_2P(C_6H_{11})_2]_2$, *etc.*} are known both with mono- and poly-dentate phosphine ligands[2a,g,h,k,q,6g,19a] and although T_1 measurements on the $[ReH_5(PPh_3)_3]$ derivatives have given rise to debatable assignment,[2j,k] a classical structure seems to be certain for all the derivatives, as we have proposed for our phosphinite and phosphonite pentahydride compounds.

Since the preparation of the first η^2-H_2 complexes by Kubas *et al.*[20] many studies in this field have demonstrated that rhenium polyhydride may contain classical (H–M–H) or non-classical $[M(\eta^2\text{-}H_2)]$ hydride ligands and that the η^2-hydrogen ligand can be generated by a simple protonation of the same polyhydride.[2a–h,4] We have therefore studied our polyhydrides containing phosphinite or phosphonite ligands **5**–**7** by measuring the $T_{1(min)}$ values in order to establish the classical or non-classical nature of the hydride ligand in these complexes.[19] In Table 2 the values of $T_{1(min)}$ (determined in CD_2Cl_2 at 200 MHz) for some hydrides and the related protonated species are reported. In all cases plots of ln T_1/s *vs.* 1/T show well defined V-shaped curves of the type shown in Fig. 1, from which $T_{1(min)}$ can easily be determined. The $T_{1(min)}$ values for the hydrides **5b**, **6d** and **7b** are 70, 87 and 68 ms, respectively, and strongly suggest, by comparison with literature values,[4,19] a classical structure for all the complexes.

Addition of 1 equivalent of $HBF_4\cdot Et_2O$ to a CD_2Cl_2 solution of the dimer $[Re_2H_8L_4]$ **5** at −80 °C caused the disappearance in the NMR spectra of the signals of $[Re_2H_8L_4]$ and the appearance of a new quintet in the ^1H NMR hydride region at δ −4.28 (**5b***) and at −4.48 (**5d***) (J_{PH} = 8 Hz) and new singlets in the ^{31}P spectra at δ 116.1 and 137.4. No gas evolution was observed and further addition of an excess of NEt_3 regenerated the starting $[Re_2H_8L_4]$ derivative. Although the protonated complexes were not isolated, the protonation probably gives the new species $[Re_2H_9L_4]^+$ **5***, the relaxation time of the hydride

Table 2 Proton NMR data in the hydride region for some rhenium complexes

Compound	T/K	δ(MH)	$T_{1(\min)}$/ms
5b	213	−5.92 (br)	70
5b*	208	−4.14 (br)	63
6d	202	−6.98 (br), −7.47 (br)	87
6d*	198	−4.64 (br)	71
7b	200	−6.64 (br)	68
7b*	207	−4.30 (br)	12

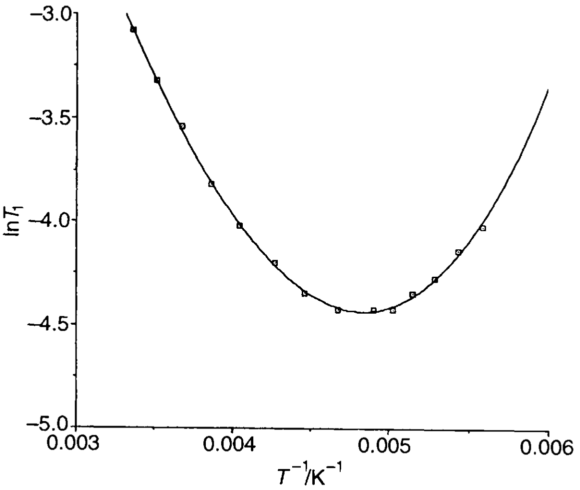
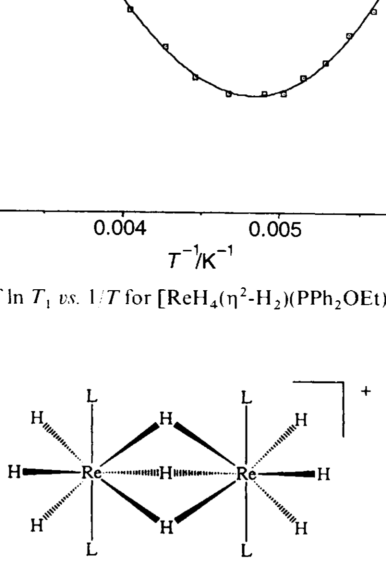


Fig. 1 Plot of ln T_1 *vs.* 1/T for $[ReH_4(\eta^2\text{-}H_2)(PPh_2OEt)_3]^+$



VII

Table 3 Variable-temperature T_1 data for the hydride–η^2-dihydrogen resonance of the cation $[ReH_4(\eta^2\text{-}H_2)(PPh_2OEt)_3]^+$ **7b***

T/K	T_1/s	T/K	T_1/s
179	0.018	224	0.013
184	0.016	234	0.015
189	0.014	247	0.018
194	0.013	259	0.022
199	0.012	272	0.029
204	0.012	285	0.036
214	0.012	298	0.046

Measurements were carried out in CD_2Cl_2 solution at 200 MHz.

protons being measured between −90 and +30 °C. Surprisingly, a $T_{1(\min)}$ value of 63 ms was found (**5b***), which suggests[19] a classical structure for the protonated complexes too, thus excluding that protonation gives rise to the formation of an η^2-H_2 ligand in the molecule. A likely explanation of these results may involve one of the hydride bridges of **5** as protonation site, giving a $(\mu\text{-}H)_3$ $[Re_2H_9L_4]^+$ cation of the type **VII**. Unfortunately, the molecule is fluxional and also at −90 °C the ^1H and ^{31}P NMR spectra show both the hydrides and the phosphine ligands to be magnetically equivalent, so preventing any structural information from being obtained for this protonated derivative. It may also be noted that despite the number of studies[2,4] (T_1 measurements and protonation reactions) on rhenium polyhydrides, none is related to dimeric species of the type $[Re_2H_8L_4]$ and therefore no comparison can be made with previously reported derivatives.

Trihydrides $[ReH_3L_4]$ **6** can also be easily protonated by addition of 1 equivalent of $HBF_4{\cdot}Et_2O$ to give new cationic hydride species as shown by the ^1H and ^{31}P NMR spectra. In particular, by protonation of **6d** a sharp quintet at δ −4.51 is observed in the proton spectrum, while a sharp singlet at δ 134.2 appears in the ^{31}P spectrum. The T_1 measurements of this protonated species give a $T_{1(\min)}$ value of 71 ms (**6d***) suggesting, in this case too, a classical structure for the complex.[19] On this basis it can be hypothesised that the protonation of **6** does not proceed *via* protonation of a Re–H bond affording an η^2-H_2 ligand, but involves oxidative addition of H^+ giving a formal rhenium(v) $[ReH_4L_4]^+$ **6*** derivative. These protonation reactions are reversible and the addition of an excess of triethylamine to a solution of **6b*** gave back the trihydride $[ReH_3L_4]$ species, as seen by ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra. Previously reported[2b] tetrahydride derivatives $[ReH_4(PPhMe_2)_4]^+$ with monodentate tertiary phosphine ligands have also been formulated as classical species, while protonation of the trihydride carbonyl complex $[ReH_3(CO)(PPhMe_2)_3]$[2f] gives an equilibrium mixture of $[ReH_4(CO)(PPhMe_2)_3]^+$ and its non-classical tautomer $[ReH_2(\eta^2\text{-}H_2)(CO)(PPhMe_2)_3]^+$ in agreement with the important influence that ancillary ligands have in determining the classical or non-classical nature of polyhydride complexes.

Treatment of a dichlorodideuteriomethane solution of $[ReH_5L_3]$ with $HBF_4{\cdot}Et_2O$ caused no gas evolution and gave a new species in quantitative yield the ^1H NMR spectrum of which shows in the hydride region a quartet at δ −4.12. This protonated species is stable until 20 °C and its ^1H NMR spectra show that the hydride resonance broadens as the temperature is lowered and appears at −90 °C as only one broad signal. Variable-temperature T_1 measurements carried out at 200 MHz in CD_2Cl_2 (Table 3) on this signal gave a $T_{1(\min)}$ value of 12 ms at 207 K (Fig. 1) for the PPh_2OEt derivative **7b***, which strongly supports the presence of an η^2-H_2 ligand in the molecule. Therefore, the compound could be formulated as the $[ReH_4(\eta^2\text{-}H_2)L_3]^+$ derivative containing both hydrides and molecular hydrogen ligands. Previous reports[2] on protonation reactions of rhenium pentahydrides do not include complexes with monodentate phosphine ligands, but only those with tridentate ones[2h] in $[ReH_5\{PPh[CH_2CH_2CH_2P(C_6H_{11})_2]_2\}]$ and therefore a strict comparison with our complexes **7** cannot be made. However, the protonation of the above ReH_5 species with $HSbF_6$ afforded a cationic complex[2h] formulated as a non-classical $[ReH_4(\eta^2\text{-}H_2)\{PPh[CH_2CH_2CH_2P(C_6H_{11})_2]_2\}]SbF_6$ derivative.

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