

Preparation and characterization of chloro- and polyhydride complexes of rhenium: Variable-temperature NMR spectroscopy and protonation studies

Jorge Bravo *, Jesús Castro, Soledad García-Fontán *,
Manuel Iglesias, Pilar Rodríguez-Seoane

Departamento de Química Inorgánica, Universidade de Vigo, Lagoas-Marcosende, E-36310 Vigo, Pontevedra, Spain

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Abstract

The rhenium complex *fac*-[ReOCl₃L] (**1**; L = 1,3-bis(diphenylphosphanyloxy)propane) was prepared by reacting L with [ReOCl₃(AsPh₃)₂]. Refluxing complex **1** in ethanol gave [ReOCl₂(OEt)L] (**2**), which X-ray crystallography showed to have an octahedral rhenium environment and an Re–O–Et fragment of unusual linearity. The paramagnetic chlorocomplexes *mer*-[ReCl₃LL'] (**3**; L' = P(OEt)₃ in **3a**, PPh(OEt)₂ in **3b**, PPh₂(OEt) in **3c**) were obtained by treating compound **1** with L'. Reaction of complexes **1** and **3a–c** with excess NaBH₄ gave the polyhydrides [ReH₇L] (**4**) and [ReH₅LL'] (**5a–c**), respectively, all of which were characterized by variable-temperature (VT) NMR spectroscopy as highly fluxional classical hydrides. Complete protonation of these polyhydrides with HBF₄ · OMe₂ required 3 equiv. of acid, and the cationic polyhydride complexes so obtained were characterized as non-classical species by VT NMR spectroscopy and T₁ measurements.

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1. Introduction

Rhenium polyhydride complexes are of interest for activation of C–H bonds [1], for studies of the mechanisms of hydrogenases and nitrogenases [2], and because of the possibility of their use for hydrogen storage [3]. Their properties are very much influenced by co-ligands of the hydride ligands. Ligands containing phosphine moieties have been extensively investigated in this respect, but less attention has been paid to phosphorus ligands containing fragments of the form P(R_n)(OR'_{3–n}) (n = 0–2) [4]. The stronger π-acceptor and weaker σ-donor capabilities of these ligands, as compared with the

corresponding phosphine-containing species, must influence the properties of their polyhydride complexes [5].

We have previously described the synthesis and properties of several families of rhenium polyhydride complexes containing the bidentate chelating ligands 1,2-bis(diphenylphosphanyloxy)ethane [6] and 1,2-bis(dicyclohexylphosphanyloxy)ethane [7]. We found that the nature of the hydrocarbyl groups of the chelating ligand had significant effects on, inter alia, the stability of non-classical dihydrogen complexes obtained by protonation of the complexes initially synthesized.

Here, we describe the synthesis, characterization and protonation reactions of a new family of rhenium polyhydride complexes featuring the bidentate phosphorus ligand 1,3-bis(diphenylphosphanyloxy)propane (L), which were prepared in order to investigate whether their larger chelate ring would significantly alter their

* Corresponding author. Tel.: +34 986812275; fax: +34 986813798.
E-mail addresses: jbravo@uvigo.es (J. Bravo), sgarcia@uvigo.es (S. García-Fontán).

Table 1
Bond lengths (Å) and angles (°) in **2**

Bond lengths (Å)	
Re–O(1)	1.695(6)
Re–Cl(1)	2.434(2)
Re–P(1)	2.451(2)
P(2)–O(11)	1.607(8)
Re–O(2)	1.844(6)
Re–Cl(2)	2.449(2)
Re–P(2)	2.455(2)
P(1)–O(12)	1.598(7)
Bond angles (°)	
O(1)–Re–O(2)	173.8(3)
O(2)–Re–Cl(1)	90.5(2)
O(2)–Re–Cl(2)	90.1(2)
O(1)–Re–P(1)	90.2(2)
Cl(1)–Re–P(1)	82.2(1)
O(1)–Re–P(2)	86.0(2)
Cl(1)–Re–P(2)	172.4(1)
P(1)–Re–P(2)	105.3(1)
C(2)–O(2)–Re	178.3(7)
O(1)–Re–Cl(1)	94.8(2)
O(1)–Re–Cl(2)	93.4(2)
Cl(1)–Re–Cl(2)	86.4(1)
O(2)–Re–P(1)	87.4(2)
Cl(2)–Re–P(1)	168.4(1)
O(2)–Re–P(2)	89.1(2)
Cl(2)–Re–P(2)	85.9(1)
O(11)–P(2)–C(31)	94.4(4)

plane they define, and C53 and C51 are respectively 0.99(1) Å below and 0.70(1) Å above this plane. The C(2)–O(2)–Re angle, 178.3(7)°, indicates that the ethoxy oxygen has a certain degree of sp character. Of the 36 previously known Re compounds with monodentate

OEt in the CCDC data base [12], only three have an Re–O–C angle wider than 160°.

2.1.4. *mer*-[ReCl₃LL'] [**3a**, L' = P(OEt)₃; **3b**, L' = PPh(OEt)₂; **3c**, L' = PPh₂(OEt)]

Refluxing a THF solution of **1** with a threefold excess of L' for 1 h under argon afforded yellow solutions from which the complexes *mer*-[ReCl₃LL'] (**3**) were obtained as yellow paramagnetic solids by concentration under reduced pressure. The absence of any band in the 900–1000 cm⁻¹ region of their IR spectra confirms the removal of the oxo ligand of **1**. Their ¹H NMR spectra in CDCl₃ (Fig. 2 shows that of **3a**) show the paramagnetically shifted resonances expected for mononuclear d⁴ systems in a low-spin octahedral environment [13]; their signals have been assigned on the basis of signal intensity and previous work [8a,14].

2.2. Polyhydride complexes

2.2.1. [ReH₇L] (**4**)

The rhenium heptahydride [ReH₇L] (**4**) was obtained as a diamagnetic solid that is stable in air by reaction of the oxochloro compound **1** with a 20-fold excess of NaBH₄ in absolute ethanol. Its IR spectrum shows two medium-strong bands at 1915 and 1971 cm⁻¹ that are attributable to Re–H stretching vibrations [15]. Like the homologous complexes of 1,2-bis(diphenylphosphanyloxy)ethane [6] and 1,2-bis(dicyclohexylphosphanyloxy)ethane [7] (hereinafter L^[6] and L^[7], respectively), compound **4** is converted into a dinuclear compound, [Re₂H₈L₂], when dissolved in CHCl₃, CH₂Cl₂, benzene

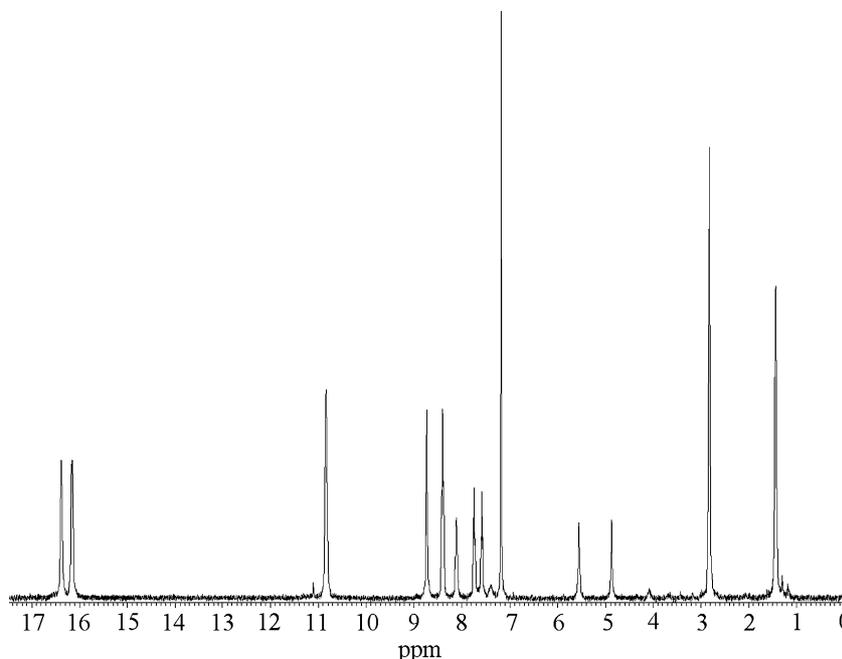


Fig. 2. ¹H NMR spectrum of compound **3a** in CDCl₃.

or toluene. The conversion rate is faster in the halogenated solvents than in the others, and in these halogenated solvents increases at room temperature in the order $[\text{ReH}_7\text{L}^{[7]}]$ (5 days [7]) < compound **4** (2 days) < $[\text{ReH}_7\text{L}^{[6]}]$ (12–18 h [6]).

In the ^1H NMR spectrum of **4** in CD_2Cl_2 , the hydride nuclei appear as a seven-proton triplet at $\delta = -6.06$ ppm due to coupling to the two phosphorus atoms ($^2J_{\text{HP}} = 16$ Hz). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in the same solvent displays a singlet at $\delta = 127.0$ ppm that becomes an octuplet [$J_{\text{PH}(\text{residual})} = 15$ Hz] when an off-resonance experiment is performed, confirming the number of hydride ligands directly bound to the rhenium atom.

Lowering the temperature from 293 to 174 K did not significantly alter the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4**, but in its ^1H NMR spectrum the high-field triplet began to undergo decoalescence at 193 K, and by 174 K had split into two broad peaks with an approximate intensity ratio of 2:5 (Fig. 3). Thus **4** appears to be significantly more rigid than analogous heptahydride diphosphinite complexes in which seven-membered chelate rings are formed by $\text{L}^{[6]}$ [6a] or $\text{L}^{[7]}$ [7], since the ^1H NMR spectra of both these latter complexes show just a slight broadening of the high-field triplet, even at 174 K. Like these latter complexes, however, **4** is a classical hydride [16], the value of $T_{1(\text{min})}$ measured for the high-field signal by the standard inversion-recovery method at 400 MHz being 98 ms at 218 K.

Protonation of compound **4** with $\text{HBF}_4 \cdot \text{Me}_2\text{O}$ at 183 K as described previously for other compounds [6a,7] shifted the $^{31}\text{P}\{^1\text{H}\}$ and high-field ^1H NMR sig-

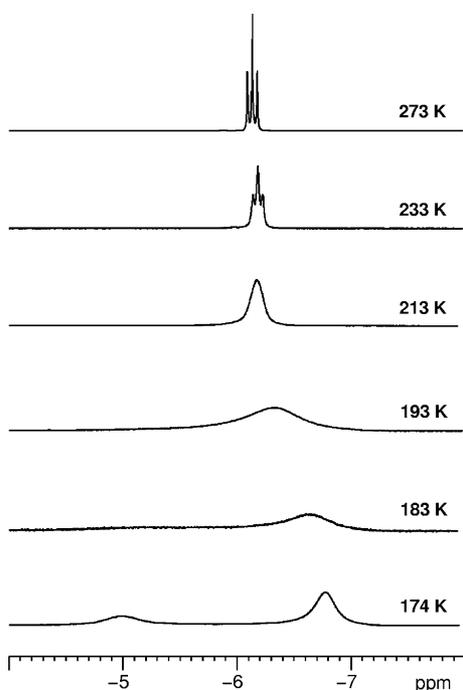


Fig. 3. High-field ^1H NMR spectra of $[\text{ReH}_7\text{L}]$ (**4**) in CD_2Cl_2 at various temperatures.

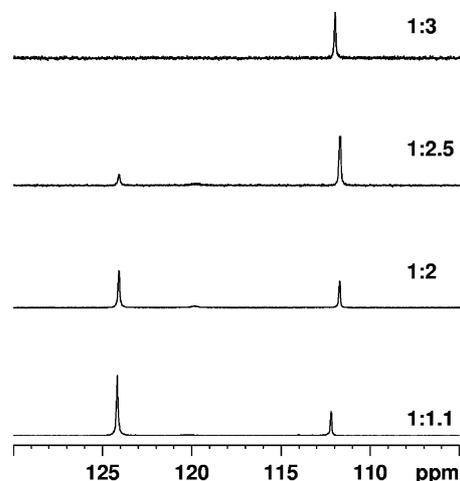


Fig. 4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{ReH}_7\text{L}]$ (**4**) in CD_2Cl_2 at 183 K when protonated with $\text{HBF}_4 \cdot \text{OMe}_2$ in various mole ratios.

nals recorded at this temperature to 112.2 and -4.3 ppm, respectively (Figs. 4 and 5). As Fig. 4 shows, total protonation required the use of 3 equiv. of acid instead of the 2 equiv. required by analogues with seven-membered chelate rings [6a,7]. Similar acidity has been shown by the monohydride $[\text{ReH}(\text{CO})_3\text{L}]$ [18] and, in this study, by the pentahydrides $[\text{ReH}_5\text{LL}']$ [$\text{L}' = \text{PPh}_n(\text{OR})_{3-n}$; see next paragraph], and may be due to increased steric hindrance associated with the increase in the size of the chelate ring [17].

The value of $T_{1(\text{min})}$ measured at 400 MHz and 203 K for the ^1H NMR signal of the protonated compound at -4.3 ppm is 18 ms, showing that this is a non-classical hydride that can tentatively be formulated as $[\text{Re}(\eta^2\text{-H}_2)\text{H}_6\text{L}]\text{BF}_4$. Upon raising the temperature to 243 K, new signals appear at 120.6 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR

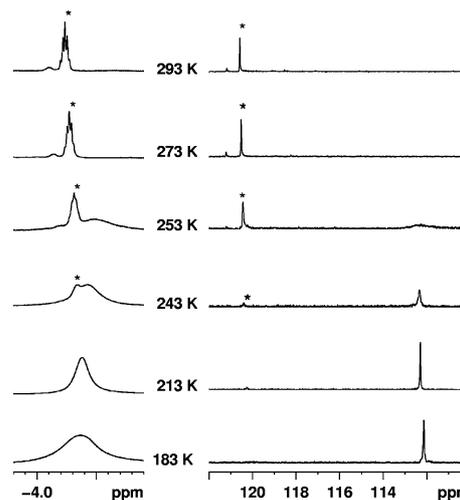
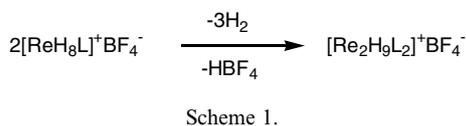


Fig. 5. High-field ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra obtained at various temperatures following protonation of $[\text{ReH}_7\text{L}]$ (**4**) with 3 equiv. of $\text{HBF}_4 \cdot \text{OMe}_2$ in CD_2Cl_2 . Signals with an asterisk correspond to the putative derivative $[\text{Re}_2\text{H}_9\text{L}_2]\text{BF}_4$.



spectrum and at -4.18 ppm in the ^1H NMR spectrum, coinciding with the release of $\text{H}_2(\text{g})$ (shown by the appearance of a singlet at 4.6 ppm in the ^1H NMR spectrum). At 293 K the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows only the 120.6 ppm signal (a singlet), and the ^1H NMR spectrum shows only the signal at -4.18 ppm (a quintuplet; $^2J_{\text{PH}} = 7.5$ Hz). Similar behaviour by related heptahydrides has been ascribed to formation of a cationic dinuclear compound as in Scheme 1, and the temperatures at which the putative non-classical mononuclear precursors $[\text{Re}(\eta^2\text{-H}_2)\text{H}_6\Lambda]\text{BF}_4$ begin to decompose ($\Lambda = \text{L}, \text{L}^{[6]}, \text{L}^{[7]}$) increase in the order L (243 K) $<$ $\text{L}^{[7]}$ (273 K $[7]$) $<$ $\text{L}^{[6]}$ (288 K $[6a]$). The value of T_1 for the ^1H NMR quintuplet at -4.18 ppm at 273 K, 153 ms, shows that the final product, presumably $[\text{Re}_2\text{H}_9\text{L}_2]\text{BF}_4$, is classical in nature.

2.2.2. Synthesis, properties and protonation reactions of $[\text{ReH}_5\text{LL}']$ [**5a**, $\text{L}' = \text{P}(\text{OEt})_3$; **5b**, $\text{L}' = \text{PPh}(\text{OEt})_2$; **5c**, $\text{L}' = \text{PPh}_2(\text{OEt})$]

Reaction of compounds **3a–c** with a 50-fold mol excess of NaBH_4 in ethanol yielded the pentahydrides $[\text{ReH}_5\text{LL}']$ (**5a–c**), which were isolated as whitish diamagnetic solids that were stable in air. Their IR spectra show two or three bands between 1900 and 1950 cm^{-1} that can be assigned to the $\nu(\text{Re–H})$ vibrations, and their room-temperature ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in CD_2Cl_2 are similar to those of $[\text{ReH}_5\text{L}^{[6]}\text{L}']$ [**6b**] and $[\text{ReH}_5\text{L}^{[7]}\text{L}']$ [**7**], the ^1H NMR spectra displaying a five-proton double triplet at high field and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra a doublet and a triplet in 2:1 intensity ratio corresponding to the L and L' ligands, respectively. As the electron-withdrawing character of L' increases with the number of OEt groups it contains, the hydride signal shifts upfield.

Lowering the temperature slowed the fast fluxional processes responsible for the magnetic equivalence of the hydrido ligands at room temperature. For example, at 183 K the ^1H NMR spectrum of complex **5a** shows four different signals that, from low to high field, integrate in the ratios 1:2:1:1 (Fig. 6). The various decoalescence events observed as the temperature falls are similar to those reported for $[\text{ReH}_5\text{L}^{[6]}\text{L}']$ [**6b**], but take place at temperatures 10 – 20° higher as a result of the increased size of the chelate ring diminishing fluxional behaviour. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, lowering the temperature results in the triplet corresponding to the phosphorus nucleus of L' becoming a broad double doublet due to coupling with the phosphorus nuclei of L , which at low temperature are not equivalent; and to

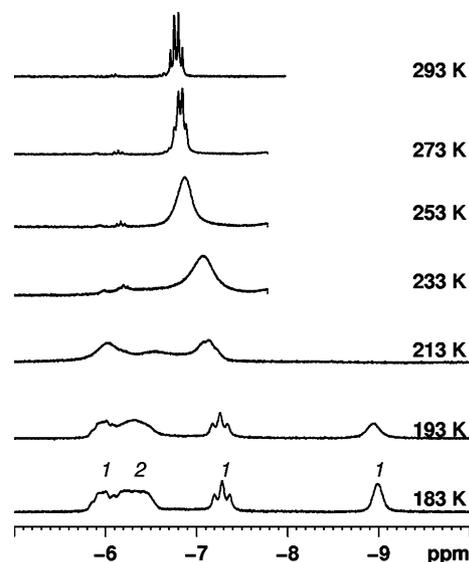


Fig. 6. Hydride region of the ^1H NMR spectrum of compound **5a** at various temperatures. Italic numbers indicate the relative values of the integrated signals.

the doublet that at 293 K corresponds to these latter nuclei becoming first two broad signals and then, in the case of complex **5a** (the most rigid of the series; rigidity increases with the number of OEt groups), a broad double doublet and a broad singlet (Fig. 7). The mechanisms responsible for this behaviour may be the same as those we have proposed for similar rhenium pentahydrides [**6b,7**]. The $T_{1(\text{min})}$ values of compounds **5** show that all three are classical in nature (Table 2).

Protonation of compounds **5** at 174 K with 3 equiv. of $\text{HBF}_4 \cdot \text{OME}_2$ in CD_2Cl_2 yielded the complexes $[\text{ReH}_6\text{LL}'](\text{BF}_4)$ (**5***), all of which had $T_{1(\text{min})}$ values indicative of a non-classical nature (Table 2). At 174 K

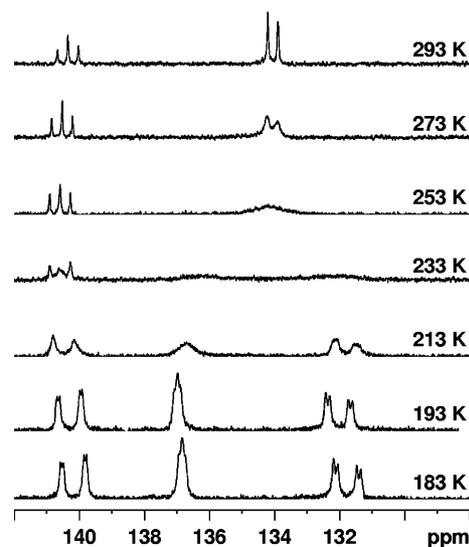


Fig. 7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound **5a** at various temperatures in CD_2Cl_2 .

Table 2
 $T_{1(\text{min})}$ values at 400 MHz for compounds **5** and **5***

Compound		T/K	$T_{1(\text{min})}/\text{ms}$
5a	$[\text{ReH}_5\text{L}\{\text{P}(\text{OEt})_3\}]$	234	124
5b	$[\text{ReH}_5\text{L}\{\text{PPh}(\text{OEt})_2\}]$	231	131
5c	$[\text{ReH}_5\text{L}\{\text{PPh}_2(\text{OEt})\}]$	231	117
5*a	$[\text{ReH}_4(\eta^2\text{-H}_2)\text{L}\{\text{P}(\text{OEt})_3\}]^+$	230	23
5*b	$[\text{ReH}_4(\eta^2\text{-H}_2)\text{L}\{\text{PPh}(\text{OEt})_2\}]^+$	233	22
5*c	$[\text{ReH}_4(\eta^2\text{-H}_2)\text{L}\{\text{PPh}_2(\text{OEt})\}]^+$	234	23

their ^1H NMR spectra show a broad hump at about -4 ppm indicating the initial freezing of the exchange of the hydride ligands (Table 3), which shows them to be significantly less fluxional than the corresponding complexes of $\text{L}^{[6]}$ [6b]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of compounds **5*** behave similarly. In particular, at 174 K that of **5a*** displays a broad doublet at 113.7 ppm corresponding to the monodentate ligand $\text{P}(\text{OEt})_3$, and a broad singlet at 127.1 ppm and a broad doublet at 112.1 ppm that correspond to the bidentate ligand L (Fig. 8). By contrast, in the case of the $\text{L}^{[6]}$ analogue [6b], these signals still show fluxional behaviour at 174 K, resembling those obtained from **5a*** at 193 K (Fig. 8). The similarity between the substructures of the two broad doublets observed at 174 K suggests that the $\text{P}(\text{OEt})_3$ phosphorus, P_1 , is located in a pseudo-*trans* position with respect to one of those of the bidentate ligand (P_2), making the coupling constant $J_{\text{P}_1\text{-P}_2}$ significantly larger than $J_{\text{P}_1\text{-P}_3}$ or $J_{\text{P}_2\text{-P}_3}$ (Scheme 2).

At about -4 ppm in the room temperature ^1H NMR spectra of compounds **5*** (Table 3), a broad quadruplet reflects coupling between the hydride and phosphorus nuclei ($J_{\text{PH}} \approx 14$ Hz). At this temperature compounds **5*** decay within a few hours, with loss of $\text{H}_2(\text{g})$ reflected by the appearance of a ^1H NMR singlet at 4.6 ppm. Their stabilities in CD_2Cl_2 at room temperature are thus similar to those of the homologous compounds of $\text{L}^{[6]}$ [6b] and significantly less than those of the $\text{L}^{[7]}$ homologues [7], which remain unaltered for more than 24 h.

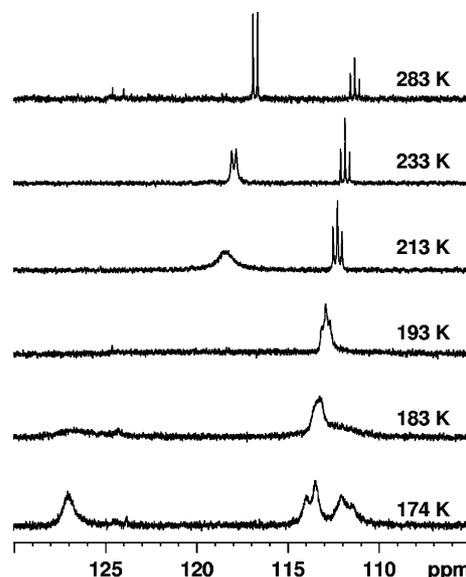
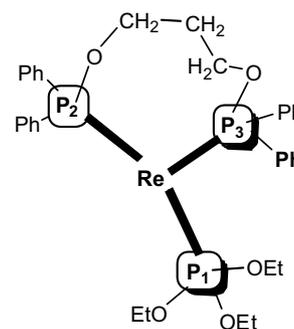


Fig. 8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{ReH}_4(\eta^2\text{-H}_2)\text{L}\{\text{P}(\text{OEt})_3\}]$ (**5*a***) in CD_2Cl_2 at various temperatures.



Scheme 2.

The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra display the doublet and triplet expected for an AX_2 system (Table 3).

Table 3
 Selected NMR data^a of complexes **5*a-c** at 174 and 293 K

Compound	^1H NMR ^b (δ , Hz)		$^{31}\text{P}\{^1\text{H}\}$ NMR (δ , Hz)	
	174 K	293 K	174 K	293 K
5*a $[\text{ReH}_4(\eta^2\text{-H}_2)\text{L}\{\text{P}(\text{OEt})_3\}]^+$	-4.37 (br)	-4.54 (q) $J_{\text{PH}} = 14$	112.1 (br,d) 113.7 (br,d) 127.1 (br,s)	111.2 (t) 116.5 (d) $J = 40$
5*b $[\text{ReH}_4(\eta^2\text{-H}_2)\text{L}\{\text{PPh}(\text{OEt})_2\}]^+$	-4.20 (br)	-4.29 (q) $J_{\text{PH}} = 14$	114.8 (br) 125.1 (br) 127.4 (br)	117.1 (d) 128.7 (t) $J = 29$
5*c $[\text{ReH}_4(\eta^2\text{-H}_2)\text{L}\{\text{PPh}_2(\text{OEt})\}]^+$	-4.00 (br)	-3.96 (q) $J_{\text{PH}} = 14$	102.6 (br) 114.0 (br) 130.3 (br)	105.4 (t) 117.7 (d) $J = 20$

^a In CD_2Cl_2 at 400 MHz.

^b Hydride region.

3. Conclusions

New chloro- and polyhydride rhenium complexes containing 1,3-bis(diphenylphosphanyloxy)propane (L) as supporting ligand have been prepared and characterized. X-ray crystallography of $[\text{ReOCl}_2(\text{OEt})\text{L}]$ showed an octahedral coordination polyhedron and unusual linearity of the Re–O–Et group. The classical nature of the heptahydride $[\text{ReH}_7\text{L}]$ (**4**) and the pentahydrides $[\text{ReH}_5\text{LL}']$ [**5**; $\text{L}' = \text{PPh}_n(\text{OEt})_{3-n}$; $n = 0-2$] is shown by $T_{1(\text{min})}$ values of 98–131 ms at 400 MHz. All are fluxional compounds, but significantly less so than analogous compounds in which the size of the chelate ring is reduced from 8 to 7 members by replacement of 1,3-bis(diphenylphosphanyloxy)propane by 1,2-bis(diphenylphosphanyloxy)ethane [**6**].

For their complete protonation, polyhydrides **4** and **5** need more $\text{HBF}_4 \cdot \text{Me}_2\text{O}$ than do their 1,2-bis(diphenylphosphanyloxy)ethane analogues, 3 equiv. instead of 2. This increase in acidity may be due to a greater degree of steric hindrance by their larger chelate ring. The protonated complexes have $T_{1(\text{min})}$ values of about 20 ms at 400 MHz, showing the presence of at least one dihydrogen ligand. These protonated compounds are unstable at room temperature in CD_2Cl_2 , decomposing in a few hours by loss of $\text{H}_2(\text{g})$. $[\text{Re}(\eta^2\text{-H}_2)\text{H}_6\text{L}]\text{BF}_4$ is less stable than its 1,2-bis(diphenylphosphanyloxy)ethane and 1,2-bis(dicyclohexylphosphanyloxy)ethane homologues, while the compounds $[\text{Re}(\eta^2\text{-H}_2)\text{H}_4\text{LL}']\text{BF}_4$ [$\text{L}' = \text{PPh}_n(\text{OEt})_{3-n}$; $n = 0-2$] are similar in stability to their 1,2-bis(diphenylphosphanyloxy)ethane homologues but significantly less stable than their 1,2-bis(dicyclohexylphosphanyloxy)ethane homologues.

4. Experimental

4.1. General

All experimental manipulations were carried out under argon using Schlenk techniques. All solvents were purified by conventional procedures [19] and distilled prior to use. The ligand 1,3-bis(diphenylphosphanyloxy)propane (L) was prepared using a published method [9]. ^1H and ^{31}P NMR spectra (δ , ppm) were recorded in CDCl_3 or CD_2Cl_2 (as indicated) on a Bruker ARX-400 spectrometer, respectively, using the solvent as internal lock; ^1H signals were recorded at 400 MHz and referred to internal TMS, and $^{31}\text{P}\{^1\text{H}\}$ were run at 161 MHz and referred to 85% H_3PO_4 . 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. IR spectra of samples in KBr pellets were obtained on a Bruker Vector IFS28 FT spectrometer. 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.

4.2. Synthesis of *fac*- $[\text{ReOCl}_3\text{L}]$ [$\text{L} = 1,3$ -bis(diphenylphosphanyloxy)propane] (**1**)

To a solution of $[\text{ReOCl}_3(\text{AsPh}_3)_2]$ (1.0 g, 1.09 mmol) in tetrahydrofuran (50 mL) was added 3.8 mL of a 0.27 M solution of L in toluene. The resulting mixture was stirred and refluxed for 1 h, and stirring was maintained at room temperature for a further 3 h. Concentration under reduced pressure then afforded an oil that was taken into ethanol, forming a violet precipitate that was filtered out, washed with ethanol and dried under reduced pressure. Yield 0.56 g, 73%. Anal. calc. for $\text{C}_{27}\text{H}_{26}\text{Cl}_3\text{O}_3\text{-P}_2\text{Re}$, C 43.07, H 3.48%; Found: C, 43.26; H, 3.50%. IR (cm^{-1}): 982 (s) $\nu(\text{Re}=\text{O})$. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 2.23 (m, 2H, CH_2), 4.18 (m, 2H, OCH_2), 4.50 (m, 2H, OCH_2), 7.22–7.90 (m, 20H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161 MHz): δ (ppm) = 78 (s). FAB MS: m/z (referred to the most abundant isotopes) 752.5, [M]; 717.0, [M – Cl]; 681.5 [M – 2Cl]; 308.5 [M – L].

4.3. Synthesis of $[\text{ReOCl}_2(\text{OEt})\text{L}]$ (**2**)

A suspension of **1** (0.10 g, 0.13 mmol) in 20 mL of ethanol was refluxed for 3 h. The resulting pink solid was filtered out and dried in vacuo. Single crystals suitable for X-ray diffractometry were obtained by recrystallization from 10:2 (v/v) $\text{CH}_2\text{Cl}_2/\text{EtOH}$. Yield 0.65 g, 80%. Anal. calc. for $\text{C}_{29}\text{H}_{31}\text{Cl}_2\text{O}_4\text{P}_2\text{Re}$, C, 45.67; H, 4.10%; Found: C, 45.85; H, 4.17%. IR (cm^{-1}): 980 (s) $\nu(\text{Re}=\text{O})$. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 0.05 (t, $^3J_{\text{HH}} = 7$ Hz, 3H, CH_3), 2.10 (m, 1H, CH_2), 2.26 (q, $^3J_{\text{HH}} = 7$ Hz, 2H, CH_2), 2.51 (m, 1H, CH_2), 4.11 (m, 4H, OCH_2), 7.59–8.33 (m, 20H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161 MHz): δ (ppm) = 102.0 (s).

4.4. Synthesis of *mer*- $[\text{ReCl}_3\text{LL}']$ [**3a**, $\text{L}' = \text{P}(\text{OEt})_3$; **3b**, $\text{L}' = \text{PPh}(\text{OEt})_2$; **3c**, $\text{L}' = \text{PPh}_2(\text{OEt})$]

L' was added in 3:1 mole ratio to a solution of **1** (0.30 g, 0.40 mmol) in tetrahydrofuran (30 mL), the mixture was refluxed for 1 h and stirred at room temperature for 3 h more, and the resulting yellow solution was concentrated under reduced pressure, giving an oil that when taken into ethanol afforded a yellow paramagnetic solid that was filtered out, washed with ethanol and dried under reduced pressure.

3a. Yield 0.12 g, 33%. Anal. calc. for $\text{C}_{33}\text{H}_{41}\text{Cl}_3\text{O}_5\text{-P}_3\text{Re}$, C 43.89, H 4.58%; Found: C, 43.11; H, 4.43%. ^1H NMR (CDCl_3 , 400 MHz; all signals are paramagnetically shifted): δ (ppm) = 2.81 (9H, CH_3), 4.87 (2H, Ph), 5.50 (2H, Ph), 7.58 (2H, OCH_2), 7.74 (2H, OCH_2), 8.11 (2H, CH_2), 8.40 (4H, Ph), 8.73 (4H, Ph), 10.83 (6H,

OCH₂CH₃), 16.15 (4H, Ph), 16.37 (4H, Ph). FAB MS: *m/z* (referred to the most abundant isotopes) 902.7, [M]; 867.2, [M – Cl]; 736.7, [M – L']; 629.5, [M – L' – 3Cl]; 458.7 [M – L].

3b. Yield 0.23 g, 61%. Anal. calc. for C₃₇H₄₁Cl₃O₄P₃Re, C, 47.52; H, 4.42%; Found: C, 46.90; H, 4.38%. ¹H NMR (CDCl₃, 400 MHz; all signals are paramagnetically shifted): δ (ppm) = 3.45 (6H, CH₃), 5.58 (1H, Ph), 6.77 (2H, Ph), 7.72 (2H, Ph), 8.22 (4H, Ph), 8.59 (2H, CH₂), 8.79 (2H, OCH₂), 9.48 (2H, OCH₂), 11.60 (2H, OCH₂CH₃), 12.25 (2H, OCH₂CH₃), 16.09 (2H, Ph), 16.60 (4H, Ph), 17.68 (4H, Ph). FAB MS: *m/z* (referred to the most abundant isotopes) 934.7, [M]; 899.2, [M – Cl]; 736.7, [M – 2L']; 701.2, [M – L' – Cl]; 665.7, [M – 2L' – 2Cl]; 490.7 [M – L].

3c. Yield 0.27 g, 68%. Anal. calc. for C₄₁H₄₁Cl₃O₃P₃Re, C, 50.91; H, 4.27%; Found: C, 51.31; H, 4.26%. ¹H NMR (CDCl₃, 400 MHz; all signals are paramagnetically shifted): δ (ppm) = 3.75 (3H, CH₃), 4.40–8.50 (18H, Ph), 9.00 (2H, CH₂), 10.37 (2H, OCH₂), 10.75 (2H, OCH₂), 11.50 (2H, OCH₂CH₃), 14.11 (4H, Ph), 16.05 (4H, Ph), 17.21 (4H, Ph). FAB MS: *m/z* (referred to the most abundant isotopes) 966.7, [M]; 931.2, [M – Cl]; 736.7, [M – 2L']; 701.2, [M – L' – Cl]; 522.7 [M – L].

4.5. Synthesis of [ReH₇L] (4)

A solution of NaBH₄ (0.25 g, 6.64 mmol) in ethanol (10 mL) was added to a suspension of **1** (0.10 g, 0.13 mmol) in the same solvent (10 mL). After 4 h of vigorous stirring, the solvent was removed under vacuum and the residue was extracted with dichloromethane (5 mL). This solution was concentrated in vacuo, giving an oil that when taken into ethanol afforded a tan-coloured solid that was filtered out, washed with ethanol and dried under vacuum. Yield 0.35 g, 41%. Anal. calc. for C₂₇H₃₃O₂P₂Re, C, 50.85; H, 5.22%; Found: C, 50.20; H, 4.97%. IR (cm⁻¹): 1915 (m), 1971 (m) ν(Re–H). ¹H NMR (CD₂Cl₂, 400 MHz): δ (ppm) = –6.06 (t, ²J_{PH} = 16 Hz, 7H, Re–H), 2.00 (m, 2H, CH₂), 3.98 (m, 4H, OCH₂), 7.38 (m, 12H, Ph), 7.76 (m, 8H, Ph). ³¹P{¹H} NMR (CD₂Cl₂, 161 MHz): δ (ppm) = 127 (s).

4.6. Synthesis of [ReH₅LL'] (5) [5a, L' = P(OEt)₃; 5b, L' = PPh(OEt)₂; 5c, L' = PPh₂(OEt)]

A suspension of **3** (0.1 g) and NaBH₄ 1:50 (mol/mol) in 20 mL of ethanol was stirred for 4 h, during which time its colour changed from yellow to brown. The solvent was removed under reduced pressure and the residue was extracted with 10 mL of dichloromethane. The resulting solution was concentrated in vacuo, giving an oil that when treated with ethanol (2 mL) afforded a whitish solid that was filtered out, washed with ethanol and dried under vacuum.

5a. Yield, 0.26 g, 29%. Anal. calc. for C₃₃H₄₆O₅P₃Re, C, 49.43; H, 5.78%; Found: C, 49.02; H, 5.80%. IR (cm⁻¹): 1889 (m), 1932 (w), 1970 (w) ν(Re–H). ¹H NMR (CD₂Cl₂, 400 MHz): δ (ppm) = –6.77 (dt, ²J_{P(A)H} = 16 Hz, ²J_{P(B)H} = 20 Hz, 5H, Re–H), 1.03 (t, ³J_{HH} = 7 Hz, 9H, CH₃), 1.80 (m, 2H, CH₂), 3.63 (q, ³J_{HH} = 7 Hz, 6H, OCH₂CH₃), 3.81 (m, 4H, OCH₂), 7.28 (m, 12H, Ph), 7.72 (m, 8H, Ph). ³¹P{¹H} NMR (CD₂Cl₂, 161 MHz): δ (ppm) = 140.6 (t, P_A), 134.0 (d, P_B), J_{P(A)P(B)}} = 33 Hz.

5b. Yield, 0.24 g, 25%. Anal. calc. for C₃₇H₄₆O₄P₃Re, C, 53.29; H, 5.56%; Found: C, 52.87; H, 5.25%. IR (cm⁻¹): 1884 (m), 1926 (w), 1963 (w) ν(Re–H). ¹H NMR (CD₂Cl₂, 400 MHz): δ (ppm) = –6.43 (dt, ²J_{P(A)H} = 16 Hz, ²J_{P(B)H} = 21 Hz, 5H, Re–H), 1.06 (t, ³J_{HH} = 7 Hz, 6H, CH₃), 1.80 (m, 2H, CH₂), 3.80 (m, 8H, OCH₂CH₃ and OCH₂), 7.27 (m, 16H, Ph), 7.65 (m, 9H, Ph). ³¹P{¹H} NMR (CD₂Cl₂, 161 MHz): δ (ppm) = 148.5 (t, P_A), 135.3 (d, P_B), J_{P(A)P(B)}} = 38 Hz.

5c. Yield, 0.21 g, 24%. Anal. calc. for C₄₁H₄₆O₃P₃Re, C, 56.87; H, 5.35%; Found: C, 56.50; H, 5.50%. IR (cm⁻¹): 1888 (m), 1935 (m), 1958 (m) ν(Re–H). ¹H

Table 4
Crystal and structure refinement data for **2**

Identification code	2
Empirical formula	C ₂₉ H ₃₁ Cl ₂ O ₄ P ₂ Re
Formula weight	762.58
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 ₁
Unit cell dimensions	
<i>a</i> (Å)	9.9380(15)
<i>b</i> (Å)	14.914(2)
<i>c</i> (Å)	10.3853(15)
β (°)	110.217(3)
Volume (Å ³)	1444.5(4)
<i>Z</i>	2
Density (calculated) (Mg/m ³)	1.753
Absorption coefficient (mm ⁻¹)	4.536
<i>F</i> (000)	752
Crystal size (mm)	0.35 × 0.21 × 0.07
θ range for data collection (°)	2.18–28.01
Index ranges	–13 ≤ <i>h</i> ≤ 13; –19 ≤ <i>k</i> ≤ 19; –13 ≤ <i>l</i> ≤ 7
Reflections collected	9231
Independent reflections [<i>R</i> _{int}]	6204 [0.0446]
Reflections observed (>2σ)	4514
Data completeness	0.976
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.614987
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6204/1/344
Goodness-of-fit on <i>F</i> ²	0.805
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0434, <i>wR</i> ₂ = 0.0637
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0642, <i>wR</i> ₂ = 0.0677
Absolute structure parameter	0.008(8)
Largest difference peak and hole (e Å ⁻³)	1.868 and –1.116

NMR (CD₂Cl₂, 400 MHz): δ (ppm) = -6.10 (dt, $^2J_{P(A)H} = 17$ Hz, $^2J_{P(B)H} = 20$ Hz, 5H, Re-H), 1.04 (t, $^3J_{HH} = 7$ Hz, 3H, CH₃), 1.75 (m, 2H, CH₂), 3.45 (m, 2H, OCH₂CH₃), 3.76 (m, 4H, OCH₂), 7.27–7.65 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (CD₂Cl₂, 161 MHz): δ (ppm) = 124.5 (t, P_A), 135.3 (d, P_B), $J_{P(A)P(B)} = 34$ Hz.

4.7. Crystal structure determination

A single crystal of compound **2** was mounted on a glass fibre and studied in a SIEMENS Smart CCD area-detector diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The crystal parameters and experimental details of data collection are summarized in Table 4. Fig. 1 was obtained using ORTEP [20]. Absorption corrections were made using SADABS [21]. The structure was solved by direct methods (with determination of absolute stereochemistry; Flack parameter 0.006(8)), and was refined by full-matrix least-squares on F^2 [22]. All hydrogen atoms were refined with isotropic displacement parameters, and all non-hydrogen atoms with anisotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from *International Tables for X-ray Crystallography* [23].

5. Supplementary material

Crystallographic data for the structural analysis of compound **2** have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 272961). Copies of this information may be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336003; e-mail: deposit@ccdc.cam.ac.uk; www: <http://www.ccdc.cam.ac.uk>.

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