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# Synthesis and characterization of the bromide and hydride derivatives of rhenium(I) 1,2-bis(diphenylphosphinite)ethane complexes

Sandra Bolaño<sup>a</sup>, Jorge Bravo<sup>a</sup>, Rosa Carballo<sup>a</sup>, Soledad García-Fontán<sup>a,1</sup>, Ulrich Abram<sup>b</sup>, Ezequiel M. Vázquez-López<sup>a,\*</sup>

<sup>a</sup>Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Vigo, E-36200 Vigo, Galicia, Spain <sup>b</sup>Institut für Radiochemie des Forschungszentrums Rossendorf, D-01062 Dresden, Germany

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#### Abstract

The reaction of  $[ReX(CO)_5]$  (X=Br, H) with the bidentate phosphinite ligand 1,2-bis(diphenylphosphinite)ethane (L–L), synthesized by reaction of PPh<sub>2</sub>Cl and ethylene glycol in a 2:1 ratio in the presence of NEt<sub>3</sub>, at room temperature, affords the mononuclear rhenium(I) complexes *fac*-[ReBr(CO)<sub>3</sub>(L–L)] (1) and *fac*-[ReH(CO)<sub>3</sub>(L–L)] (2). The coordination geometry of the complexes was established by diffraction studies and confirmed by spectroscopic data of both complexes. Compound 1 crystallizes in the P2<sub>1</sub>/c (No. 14) monoclinic space group while the hydride complex does so in P2<sub>1</sub> (No. 4). The coordination polyhedron around the rhenium atom in both cases is a slightly distorted octahedron with three carbonyl groups in *facial* positions. The link of the bidentate ligand to the metal atom leads to a seven-membered ReP<sub>2</sub>O<sub>2</sub>C<sub>2</sub> ring, adopting a conformation better described as a twisted chair. © 1999 Elsevier Science Ltd. All rights reserved.

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# 1. Introduction

The coordination chemistry of rhenium(I) derivatives with monodentate and bidentate phosphine ligands is well developed. Recently, studies of the phosphite complexes have also received attention due to the different electronic and steric properties of these ligands [1-11]. However, the coordination chemistry of bidentate phosphites has been explored much less thoroughly than that of the phosphine analogs, probably due to the lack of stability and difficulty of isolating the former [12].

On the other hand, an increasing number of studies have been undertaken to evaluate the effects on structure, bonding and chemical properties of the hydride and the corresponding  $\eta^2$ -H<sub>2</sub> rhenium complexes [13,14] when an oxygen atom, near the phosphorous belonging to an ancillary ligand, is introduced.

As a way of continuing with these studies, we report here on the synthesis and spectroscopic and diffractometric

*E-mail address:* ezequiel@uvigo.es (M. Vásquez-López) <sup>1</sup>Corresponding co-author.

characterization of rhenium(I) carbonyl bromide and hydride derivatives of the bidentate ligand bis(diphenylphosphinite)ethane,  $Ph_2PO-CH_2CH_2-OPPh_2$ .

# 2. Experimental

#### 2.1. Materials and instrumentation

All operations were carried out under an atmosphere of dry dinitrogen or argon, using standard Schlenk techniques. All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled in an Ar atmosphere [15].

 $Ph_2PCl$ , ethylene glycol (Aldrich, Steinheim, Germany) and  $Re_2(CO)_{10}$  (ABCR, Karlsruhe, Germany) were used without any further purification. [ReBr(CO)<sub>5</sub>] and [ReH(CO)<sub>5</sub>] were synthesized by reported methods [16,17].

Elemental analyses were carried out on a Fisons EA-1108. Melting points (m.p.) were determined on a Gallen-Kamp MFB-595 and are uncorrected.

Infrared spectra were recorded on a Bruker Vector 22FT spectrophotometer. NMR spectra were obtained on a

<sup>\*</sup>Corresponding author. Tel.: +34-986-812-319; fax: +34-986-812-382.

Bruker AMX 400 spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} chemical shifts refer to internal tetramethylsilane (TMS), while  ${}^{31}P{}^{1}H$  chemical shifts are reported with respect to 85% H<sub>3</sub>PO<sub>4</sub>, with downfield shifts considered positive.

Longitudinal relaxation time values of the hydride resonance were measured in  $CD_2Cl_2$  solutions at 400 MHz by the inversion-recovery method using a standard 180°- $\tau$ -90° pulse sequence between 183 and 283 K in **2** and 183 and 238 K in **3**. The resulting  $T_1$  (min) values are included in Table 3, while plots of  $T_1$  (ms) vs. T (K) parameters corresponding to compound **3** are shown in Fig. 4.

# 2.2. Synthesis of the ligand $Ph_2PO(CH_2)_2OPPh_2$ (L-L)

The synthesis of the ligand is based on the method described by Rabinowitz and Pellon [18]. Ph<sub>2</sub>PCl (13 mL, 72.4 mmol) was slowly added dropwise (ca. 30 min) to a cooled (-80°C) solution of freshly distilled Et<sub>3</sub>N (10 mL, 72.1 mmol) and ethylene glycol (2.23 g, 35.9 mmol) in 30 mL of toluene. The solution was stirred for 1 h and the formation of the ligand was established by the presence of a unique signal at 132.6 ppm in the  ${}^{31}P{}^{1}H$  spectrum. The formed solid, [Et<sub>3</sub>NH]Cl, was filtered off and the resulting solution was vacuum concentrated to yield a yellow oil. Attempts to purify this oil (by distillation or column chromatography) were unsuccessful because the product is unstable, as shown by the disappearance of the characteristic signal in the  ${}^{31}P{}^{1}H$  spectrum. So, for the synthesis of the complexes, a toluene solution of the oil was used. This solution is stable at room temperature for several months when it is stored under an inert atmosphere.

# 2.3. Synthesis of fac-[ $ReBr(CO)_3(L-L)$ ], 1

To a suspension of  $[\text{ReBr}(\text{CO})_5]$  (200 mg, 0.5 mmol) in toluene (20 mL), 4 mL of the ligand solution (0.45 M) were added and the mixture was stirred for 12 h. The solvent was removed under vacuum and the resulting oil was tritured with ethanol (2 mL). The white precipitate that formed was filtered off, washed with ethanol and vacuum dried. Yield, 142 mg (37%); m.p., 160°C. Anal. Found: C, 45.4; H, 3.2%. C<sub>29</sub>H<sub>24</sub>BrO<sub>5</sub>P<sub>2</sub>Re requires C, 44.6; H, 3.1%. Single crystals were obtained by slow evaporation of an EtOH/CH<sub>2</sub>Cl<sub>2</sub> (10:2, v/v) solution.

# 2.4. Synthesis of fac-[ $ReH(CO)_3(L-L)$ ], 2

To 3 mL of the solution of the ligand L–L (0.50 M), [ReH(CO)<sub>5</sub>] (230 mg, 0.7 mmol) dissolved in 10 mL of tetrahydrofuran (THF) was added. After 4 h of stirring, the resulting solution was vacuum concentrated to ca. 4 mL. The white precipitate obtained by the addition of 2 mL of MeOH was filtered off, washed with methanol and vacuum dried. Yield, 80 mg (16%); m.p.: 132°C. Found: C, 49.8; H, 3.6%. C<sub>29</sub>H<sub>25</sub>O<sub>5</sub>P<sub>2</sub>Re requires: C, 49.6; H, 3.6%. Single crystals were obtained by slow evaporation of an EtOH/  $CH_2Cl_2$  (10:2, v/v) solution.

# 2.5. Synthesis of $[Re(\eta^2 - H_2)(CO)_3(L-L)]^+$ , 3

The complex was prepared by the addition of HBF<sub>4</sub>· Et<sub>2</sub>O (3.78  $\mu$ L, 0.02 mmol) with a microsyringe to a solution of hydride compound **2** (0.02 mmol) in 0.5 mL of CD<sub>2</sub>Cl<sub>2</sub>, placed inside a 5-mm NMR tube and cooled to 193 K. The tube was shaken to complete the reaction and then the NMR spectra (<sup>1</sup>H and <sup>31</sup>P) were registered. The compound was not isolated as solid due to the easy loss of hydrogen above 230 K.

#### 2.6. X-ray data collection, structure and refinement

Crystallographic measurements of both compounds were performed on a CAD4 Enraf-Nonius diffractometer. Crystal data and experimental conditions are listed in Table 1. Data were corrected for polarization and Lorentz effects.  $\Psi$ -scan absorption corrections were also applied [19].

Structure analyses for both compounds were carried out by the heavy atom method [20] followed by difference Fourier techniques until all non-hydrogen atoms were located. All non-H atoms were anisotropically refined. The positions of H-atoms were calculated geometrically and included in structure factor calculations, except the hydride ligand in compound 2 that was located and isotropically refined.

For compound 2, the obtained Flack parameter [21], of 0.11(2), refined simultaneously with the other atomic and crystal parameters, is rather high. However, all attempts to refine it as a racemic twin did not improve the model.

Scattering factors and anomalous dispersion terms were taken from Ref. [22]. Most calculations were performed with programs SHELXS97 [20] and SHELXL97 [23].

Important intramolecular bond distances and angles for compounds 1 and 2 are given in Table 2.

# 3. Results and discussion

The chelating 1,2-bis(diphenylphosphinite)ethane ligand  $Ph_2PO(CH_2)_2OPPh_2$  (**L**-**L**) is produced by the reaction of 35.9 mmol of ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH) and 72.4 mmol of diphenylphosphine chloride (Ph<sub>2</sub>PCl) in the presence of triethylamine. Attempts to isolate the ligand from the solution, after separating [Et<sub>3</sub>NH]Cl, were unsuccessful; therefore, the synthesis of the rhenium derivatives must always be performed from a toluene solution of **L**-**L** (see Section 2) (Scheme 1).

After treatment of a toluene solution of L-L with  $[ReX(CO)_5]$  (X=Br, H), suspended or dissolved in toluene at room temperature, the corresponding 1:1 complexes were obtained (Scheme 2), as indicated by the appearance of IR-bands due to the stretching vibrations of

Table 1		
Crystallographic data	for compounds 1	and 2

	1	2
Formula	$C_{29}H_{24}BrO_5P_2Re$	$C_{29}H_{25}O_5P_2Re$
Molecular weight	780.53	701.63
Crystal class	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	P2 <sub>1</sub> (No. 4)
a (Å)	10.5090(8)	12.136(2)
b (Å)	11.2070(10)	9.244(1)
c (Å)	24.719(5)	12.958(1)
$\beta$ (°)	99.456(8)	110.76(2)
$V(\dot{A}^3)$	2871.7(7)	1359.3(3)
Ζ	4	2
Temperature (K)	293(2)	213(2)
Dc $(g \text{ cm}^{-3})^2$	1.805	1.714
Crystal size (mm)	$0.25 \times 0.25 \times 0.10$	$0.30 \times 0.05 \times 0.05$
$\lambda$ (Å)	Mo-Ka=0.71073	$Cu-K\alpha = 1.54184$
$\mu$ (mm)	5.771	10.167
$\theta$ (°) range	2-31	6-65
h, k, l range	0,14; 0,15; -35,34	-1,14; -10,10; -15,14
Reflections measured	9087	4569
Independent reflections/ $R_{int}$	8661/0.0707	4569/0.0242
No. reflections with $I > 2\sigma(I)$	3812	4392
$R_1/wR_2[I>2\sigma(I)]^a$	0.0461/0.0760	0.0528/0.1473
$Peak/hole (eÅ^{-3})$	1.143/-2.202	0.807/-1.763

<sup>a</sup> Dc=calculated density;  $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ ;  $wR_2 = [\Sigma w (F_0 - F_c)^2 / \Sigma w (F_0)^2]^{1/2}$ .

Table 2 Selected bond distances and angles

$[\text{ReBr(CO)}_3(\textbf{L}-\textbf{L})], (1)$		$[\text{ReH(CO)}_{3}(\mathbf{L}-\mathbf{L})], (2)$		
Re-C(1)	1.911(9)	Re-C(1)	1.961(14)	
Re-C(2)	1.938(8)	Re-C(2)	1.944(14)	
Re-C(3)	1.962(9)	Re-C(3)	1.941(15)	
Re-P(1)	2.4423(19)	Re-P(1)	2.425(3)	
Re-P(2)	2.4654(18)	Re-P(2)	2.410(3)	
Re-Br	2.6259(9)	Re-H(1)	1.75(14)	
C(1)-O(1)	1.120(8)	C(1) - O(1)	1.149(17)	
C(2)–O(2)	1.137(8)	C(2)–O(2)	1.147(17)	
C(3)–O(3)	1.130(9)	C(3)–O(3)	1.147(18)	
P(1)–O(4)	1.638(5)	P(1)–O(4)	1.623(9)	
P(1)-C(11)	1.812(7)	P(1)-C(11)	1.824(13)	
P(1)-C(21)	1.821(7)	P(1)-C(21)	1.825(14)	
P(2)–O(5)	1.608(5)	P(2)–O(5)	1.631(9)	
P(2)–C(31)	1.825(8)	P(2)-C(31)	1.824(13)	
P(2)-C(41)	1.834(7)	P(2)-C(41)	1.831(17)	
C(4)–O(4)	1.458(8)	C(4)–O(4)	1.428(16)	
C(4) - C(5)	1.478(9)	C(4) - C(5)	1.480(19)	
C(5)-O(5)	1.436(7)	C(5)–O(5)	1.448(16)	
C(1)-Re- $C(2)$	89.1(3)	C(1)-Re- $C(2)$	92.1(6)	
C(1)-Re- $C(3)$	92.4(3)	C(1)-Re- $C(3)$	93.2(6)	
C(2)–Re–C(3)	86.2(3)	C(2)-Re- $C(3)$	89.1(6)	
C(1) - Re - P(1)	92.7(2)	C(1)-Re-P(1)	96.8(4)	
C(2) - Re - P(1)	95.2(2)	C(2)-Re-P(1)	91.5(4)	
C(3)-Re-P(1)	174.8(2)	C(3)-Re-P(1)	170.0(5)	
C(1)-Re-P(2)	94.6(2)	C(1)-Re-P(2)	90.7(4)	
C(2)–Re–P(2)	174.3(3)	C(2)-Re-P(2)	176.1(4)	
C(3)-Re-P(2)	89.4(2)	C(3)-Re-P(2)	88.1(4)	
P(1) - Re - P(2)	88.92(6)	P(1)-Re-P(2)	90.78(10)	
C(1)-Re-Br	178.4(2)	C(1)-Re-H(1)	177(5)	
C(2)–Re–Br	89.8(3)	C(2)-Re-H(1)	90(5)	
C(3)–Re–Br	86.4(2)	C(3)-Re-H(1)	89(5)	
P(1)–Re–Br	88.55(5)	P(1)-Re-H(1)	81(5)	
P(2)–Re–Br	86.41(5)	P(2)-Re-H(1)	87(5)	

$$\begin{array}{rrrr} 2 \ \text{PPh}_2\text{Cl} \ + \ \text{HOCH}_2\text{CH}_2\text{OH} & \underbrace{\text{Et}_3\text{N}}_{\text{toluene}} & 2 \ \text{Ph}_2\text{POCH}_2\text{CH}_2\text{OPPh}_2 \ + \ [\text{Et}_3\text{N} \ \text{H}]\text{Cl} \\ & (\textbf{L-L}) \\ & \text{Scheme 1.} \end{array}$$

CO groups in 1 and the change in the  ${}^{31}P{}^{1}H$  spectrum of 1 and 2. The resulting complexes can be isolated as air-stable white solids. They can be partially dissolved in alcohols or completely in solvents such as chloroform, dichloromethane and dimethylsulfoxide (DMSO).



The nature of the complexes as fac-[ReX(CO)<sub>3</sub>(**L**-**L**)] was established by spectroscopic and diffractometric studies of both complexes (vide infra).

# 3.1. X-ray structure of the $[ReX(CO)_3(L-L)]$ complexes

Figs. 1 and 2 show ZORTEP plots [24] of asymmetric units of the structures, together with the numbering scheme



Fig. 1. ZORTEP plot of the molecular structure of compound 1. The thermal ellipsoids correspond to 30% probability.

used for  $[\text{ReBr}(\text{CO})_3(\mathbf{L}-\mathbf{L})]$  and  $[\text{ReH}(\text{CO})_3(\mathbf{L}-\mathbf{L})]$  compounds, respectively.

The complexes exist as discrete molecules in the unit cells, with no unusually short intermolecular contacts.

The coordination polyhedron around the rhenium atom can be described as distorted octahedron (main distortions involving Br–Re–P angles, 88.55(5) and 86.41(5)° and, C(2)–Re–C(3), 86.2(3)° in compound **1**; H(1)–Re–P(1)= 81(5)°, H(1)–Re–P(2)=87(5)° and C(3)–Re–P(1)= 170.0(5)° angles in compound **2**; Table 2). The distances Re–C in both compounds and Re–Br in **1** are similar to those found in other rhenium(I) bromide–carbonyl complexes [25–30]. It is worth mentioning that the distance Re–C(1) in compound **2** [1.961(14) Å] is significantly longer than in compound **1** [1.911(9) Å]. This fact can be explained in terms of a stronger *trans* influence of H ligand compared to Br. The position of the hydride ligand in **2** was determined from an analysis of the Fourier map and the distance H(1)–Re=1.75(14) Å is similar to that found in other rhenium terminal hydride complexes [14,31] and, like the bromine atom in **1**, is located in the *trans* position to a carbonyl group.

The Re–P distances [2.443(2) and 2.466(2) Å in **1** and 2.425(3) and 2.410(3) Å in **2**] fall into the range observed in rhenium(I) complexes with bidentate phosphorus donor ligands [32], although an increase in the bite ligand angle in our complexes does not impose geometric restrictions. This bite angle is slightly deviated from the ideal value  $[P-\text{Re}-\text{P}=88.92(7)^{\circ} \text{ in } \mathbf{1} \text{ and } 90.78(10)^{\circ} \text{ in } \mathbf{2}].$ 

The coordination of the bidentate ligand to rhenium leads to a seven-membered  $\text{ReP}_2\text{O}_2\text{C}_2$  ring. The torsion angles and the distances of the atoms to the ideal plane involving the chelate ring are represented in Fig. 3. Study of these data suggests that, in both complexes, the ring conformation is better described as a twisted chair [32].

#### 3.2. Spectroscopic results

The IR spectrum of the bromide derivative in toluene solution shows three strong bands at 2034, 1951 and 1907 cm<sup>-1</sup> with similar intensity, corresponding to  $\nu$ (CO), and at similar positions to those observed in the complexes *fac*-[ReX(CO)<sub>3</sub>(L)<sub>2</sub>] (L=phosphine or phosphite ligand) [33]. When the bromide ligand is replaced by the hydride ligand, the first two bands shift to lower wavelength numbers and a contrary effect is observed with respect to



Fig. 2. ZORTEP plot of the molecular structure of compound **2**. The thermal ellipsoids correspond to 30% probability.



Fig. 3. Distances to ideal plane and torsion angles (in italics) of the seven-membered chelate ring of compounds 1 (bold) and 2.

the third band (2019, 1939 and 1923 cm<sup>-1</sup>). However, the net result is the shift towards smaller wavenumbers, in agreement with the structural data obtained by X-ray diffraction (C–O distances shorter in 1 than 2). In complex 2, the Re–H band, which usually appears as a weak band around 1990 cm<sup>-1</sup>, is obscured by the presence of carbonyl bands.

The <sup>1</sup>H-NMR spectrum of compound **2** shows the signal due to the hydride ligand at -4.87 ppm; it appears as a triplet due to its coupling with the two phosphorus atoms of the phosphinite ligand  $({}^{2}J({}^{1}H-{}^{31}P)=26$  Hz). For both complexes, the signals corresponding to  $-CH_{2}-$  groups of the bidentate ligand appear as two groups of multiplets at around 3.9 and 4.68 (**1**) and 4.29 ppm (**2**).

The *fac*-geometry of the complexes can also be proposed by the study of the <sup>13</sup>C{<sup>1</sup>H} spectra. The spectra show two signals, a triplet (**1**, 187.0 ppm; **2**, 194.3 ppm) due to a carbonyl group *trans* to X ligand (*cis* to phosphinites groups,  ${}^{2}J({}^{13}C-{}^{31}P) \approx 7$  Hz) and a multiplet (collapsed double doublet) at a lower field (**1**, 188.9; **2**, 195.1 ppm), corresponding to carbonyl groups at *trans* positions with respect to phosphorous atoms. At the same time, the methylene carbons are magnetically equivalent, showing a unique signal around 66 ppm.

Finally, the  ${}^{31}P{}^{1}H$  spectra of both compounds present a single signal at positions close to those corresponding to the free ligand (132.6 ppm), suggesting the magnetic equivalence of the two phosphorus nuclei at room temperature.

#### 3.3. Protonation of hydride complex 2

The reaction of **2** with HBF<sub>4</sub>·Et<sub>2</sub>O at  $-80^{\circ}$ C gives the non-classical dihydrogen complex  $[\text{Re}(\eta^2-\text{H}_2)(\text{CO})_3(\text{L}-\text{L})]^+$ , **3** (Scheme 3). This cationic compound is fairly stable in solution at low temperatures but was not isolated as a solid because of easy dihydrogen release (around 233 K). The <sup>1</sup>H NMR spectrum exhibits a broad resonance in the hydride region at -3.5 ppm, due to a more deshielded nuclide than in **2** (-4.87 ppm) and close to those chemical shifts observed in  $[\text{Re}(\eta^2-\text{H}_2)(\text{CO})_3(\text{L})_2]^+$  ( $\text{L}=P(\text{OEt})_3$ , PPh(OMe)<sub>2</sub>, PPh(OEt)<sub>2</sub>, PPh<sub>2</sub>(OMe) and PPh<sub>2</sub>(OEt)) [14].



Experiments of longitudinal relaxation times measured at different temperatures of hydride resonance were performed to establish the nature of the H<sub>2</sub>-Re bond [34-36] in compound **3** but also in compound **2** for comparative purposes. The plotting of  $T_1$  (ms) versus T (K) in both compounds shows a well defined V-shaped curve, shown in Fig. 4, from which the  $T_1$  (min) can easily be determined. The  $T_1$  (min) values and the corresponding

Relevant spectral data				
	$[\text{ReBr(CO)}_3(\mathbf{L}-\mathbf{L})], (1)$	$[\text{ReH(CO)}_{3}(\mathbf{L}-\mathbf{L})], (2)$	$[\text{Re}(\eta^2 - H_2)(\text{CO})_3(\textbf{L}-\textbf{L})]^+, (3)$	
IR spectra <sup>a</sup>				
ν(CO) 2034 s 1951 s,b 1907 s,b	2034 s	2019 s		
	1951 s,b	1939 s,b		
	1907 s,b	1923 s,b		
NMR spectra <sup>b</sup>				
Solvent	CDCl <sub>3</sub>	$CD_2Cl_2$	$CD_2Cl_2$	
<sup>1</sup> H				
$\delta$ (H–Re)		-4.87 t	-3.5 br	
		$^{2}J(^{1}H-^{3}P)=26$		
$T(\mathbf{K})^{c}$		218	225	
$T_1$ (min) ms		267.7	15.3	
T stability $(K)^d$			233	
$\delta(\text{CH}_2)$ 3.97 m, 4.68 m ${}^{3}J({}^{1}\text{H}-{}^{31}\text{P})=7$	3.97 m, 4.68 m;	3.99 m, 4.29 m;	3.9 m, 4.2 m	
	${}^{3}J({}^{1}H-{}^{31}P)=7$ (4H)	$^{3}J(^{1}H-^{3}P)=6-7$	(4H)	
		(4H)		
$\delta(\mathrm{Ph})$	7.1-8 m (20H)	7.3-7.8 m (20H)	7.3-7.8 m (20H)	
<sup>13</sup> C				
$\delta(CO) = \begin{cases} 187.0 \text{ t} \\ {}^{2}J({}^{13}C-{}^{31}P) = 7.2 \\ 188.9 \text{ m} \end{cases}$	187.0 t	194.3 t		
	$^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P})=7.2$	$^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P})=7.4$		
	188.9 m	195.1 m		
<sup>31</sup> P	122.3 s	135.5 s	129.3 s	

<sup>a</sup> 1 in toluene, 2 in dichloromethane.  $\nu$  in cm<sup>-1</sup>. b=broad and s=strong.

<sup>b</sup>  $\delta$  in ppm and J in Hz. m=multiplet; s=singlet; t=triplet.

<sup>c</sup> Temperature (K) for  $T_1$  (min).

<sup>d</sup> Limit for thermal stability.

Table 3



Fig. 4. Plot of T (K) vs.  $T_1$  (ms) for compound 3.

temperatures determined from these curves are included in Table 3.

Compound **2** shows a  $T_1$  (min) value of 267.7 ms at 218 K, which is similar to those found in  $[\text{ReH}(\text{CO})_3(\text{L})_2]$  complexes [14]. The value for derivative **3** is 15.3 ms at 225 K, in agreement with the existence of  $\eta^2 - H_2$  ligand [34–36], although it is slightly greater than those observed in cationic complexes  $[\text{Re}(\eta^2 - H_2)(\text{CO})_3(\text{L})_2]^+$  (3–7 ms).

On the other hand, the dihydrogen complex 3 shows a lesser stability, to the loss of  $H_2$ , than similar complexes with phosphinite ligands [14]. It seems that, as several authors had previously reported [14,37], the stability of rhenium dihydrogen complexes depends on a set of different factors, amongst which, the number of carbonyl groups and the nature of the ancillary ligands are outstanding.

#### Supplementary data available

Supplementary data are available from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CD2 1EZ, UK, on request, quoting the deposition numbers 103154 (1) and 103155 (2).

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