

Synthesis, characterization, protonation studies and X-ray crystal structure of $\text{ReH}_5(\text{PPh}_3)_2(\text{PTA})$ (PTA = 1,3,5-triaza-7-phosphaadamantane)

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Abstract

The novel rhenium pentahydride complex $[\text{ReH}_5(\text{PPh}_3)_2(\text{PTA})]$ (**2**) was synthesized by dihydrogen replacement from the reaction of $[\text{ReH}_7(\text{PPh}_3)_2]$ with PTA in refluxing THF. Variable temperature NMR studies indicate that **2** is a classic polyhydride ($T_{1(\text{min})} = 133$ ms). This result agrees with the structure of **2**, determined by X-ray crystallography at low temperature. The compound shows high conformational rigidity which allows for the investigation of the various hydride-exchanging processes by NMR methods. Reactions of **2** with equimolecular amounts of either HFIP or $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ at 183 K afford $[\text{ReH}_5(\text{PPh}_3)_2\{\text{PTA}(\text{H})\}]^+$ (**3**) via protonation of one of the nitrogen atoms on the PTA ligand. When 5 equivalents of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ are used, additional protonation of one hydride ligand takes place to generate the thermally unstable dication $[\text{ReH}_4(\eta^2\text{-H}_2)(\text{PPh}_3)_2\{\text{PTA}(\text{H})\}]^{2+}$ (**4**), as confirmed by ^1H NMR and T_1 analysis. IR monitoring of the reaction between **2** and CF_3COOD at low temperature shows the formation of the hydrogen bonded complex $[\text{ReH}_5(\text{PPh}_3)_2\{\text{PTA} \cdots \text{DOC}(\text{O})\text{CF}_3\}]$ (**5**) and of the ionic pair $[\text{ReH}_5(\text{PPh}_3)_2\{\text{PTA}(\text{D}) \cdots \text{OC}(\text{O})\text{CF}_3\}]$ (**6**) preceding the proton transfer step leading to **3**.

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1. Introduction

The unique properties of transition metal hydrides and their widespread presence in different areas of chemistry and biochemistry are increasingly enticing chemists to explore their use in topical fields of industrial interest such as catalysis, material science, etc. [1]. As far as inorganic and organometallic chemistry is concerned, transition metal hydrides are important not only for their applications in these fields, but also for their intriguing properties which

have contributed to the discovery and the understanding of key structural and bonding issues such as σ -bond complexes [2], hydrogen-bonding and agostic interactions [3], quantum-mechanical exchange phenomena [4], etc. Among transition metal hydrides, polyhydride complexes with high coordination numbers are the subject of considerable attention because of their structural properties, their fluxional behaviour in solution, and the possibility of accommodating in the same molecular assembly both H- and $\eta^2\text{-H}_2$ ligands [5,6]. Rhenium polyhydrides [7] are particularly remarkable for their scrambling behaviour [8]. In such compounds, a complete exchange of all the coordinated classical and non-classical hydrides is frequently occurring via low-energy pathways [7,8]. The nature of these

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exchange processes and their thermodynamics can be explored by several methods, mainly by means of variable temperature NMR spectroscopy.

In view of the uncertainty in locating hydride ligands by X-ray diffraction and solid-state NMR methods, the unambiguous assignment of the classical vs. non-classical nature of the different H_x arrays has been unequivocally accomplished only for a limited number of transition-metal polyhydride complexes by neutron diffraction crystallography [9]. In contrast, structural assignments by NMR methods in solution have been generally hampered by low energy fluxional processes still active at the lowest attainable temperature. Indirect evidences have therefore been proposed to discriminate between classical and non-classical hydrides including the evaluation of $J_{H,D}$ coupling constants in the partially deuterated isotopomers [10] and the measurement of the spin-lattice relaxation time, T_1 [11]. The validity of the latter method [12] is however debatable as in some cases $T_{1(\min)}$ values apparently associated with non-classical hydrides had to be considered still compatible with classical structures upon comparison with the corresponding solid state structures [5a,13]. Thus, to safely conclude from the direct measurement of a small longitudinal relaxation time that a polyhydride has a non-classical structure, two conditions must be satisfied: (i) only dipole–dipole interactions can contribute to relaxation, and (ii) the $T_{1(\min)}$ values must be inconsistent with classical structures [12].

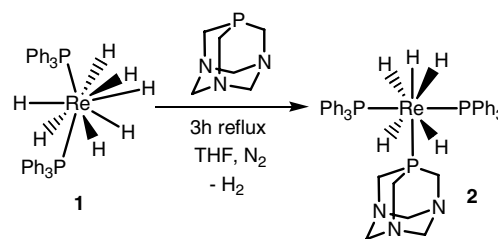
As a part of our enduring interest in the synthesis of transition metal hydrides stabilised by the water soluble monodentate phosphine PTA (PTA = 1,3,5-triaza-7-phosphaadamantane) [14,15], we attempted to synthesize a new class of water soluble rhenium polyhydrides. In this paper, we describe the synthesis of the new rhenium pentahydride complex $[ReH_5(PPh_3)_2(PTA)]$ and its characterization by X-ray diffraction analysis, variable temperature IR and NMR experiments, including T_1 analysis and protonation studies.

2. Results and discussion

2.1. Synthesis and characterization of $[ReH_5(PPh_3)_2(PTA)]$ (**2**)

Due to the known ability of the rhenium heptahydride complex $[ReH_7(PPh_3)_2]$ (**1**) [16] to eliminate H_2 upon reaction with different donor molecules [17], this was reacted in 1:1 ratio with PTA, to obtain the monosubstituted complex $[ReH_5(PPh_3)_2(PTA)]$ (**2**) in about 65% yield after gentle reflux in THF for 3 h under nitrogen, as shown in Scheme 1. Increasing the PTA/**1** ratio and/or the reaction time or using higher boiling solvents did not provide other products than **2**, but lowered the yield to less than 50%.

Compound **2** is a new member of the family of ReH_5 complexes of formula $[ReH_5(PPh_3)_2(PR_3)]$ firstly described by Chatt and Coffey [17a], obtained as a pale yellow microcrystalline material which is air stable in the solid state and soluble in THF and CH_2Cl_2 where it slowly decomposes



Scheme 1.

unless an inert N_2 atmosphere is provided. In spite of the presence of the highly hydrosoluble PTA ligand [14], **2** does not dissolve in water either at neutral or in slightly acidic pH. Addition of a large excess of CD_3OD (ca. 250 equivalents) to a solution of **2** in CD_2Cl_2 at room temperature resulted in the fast H/D exchange, as confirmed by the rapid nulling of the hydride resonance in the proton NMR spectrum.

The NMR analysis of **2** is straightforward and matches the data previously reported for similar compounds [17a]. In keeping with the proposed formula, the $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2 , 293 K) shows an AX_2 spin system consisting of a doublet at 37.3 ppm and a triplet at -70.32 ppm which are attributable to the two PPh_3 and the PTA ligands, respectively. The 1H NMR spectrum recorded under the same experimental conditions shows a doubled triplet resonance at -6.35 ppm (dt, $^2J_{HP} = 17.1$, $^2J_{HP} = 19.5$) for the five crystallographically non-equivalent hydride ligands (see below, X-ray crystal structure). In the $^1H\{^{31}P\}$ NMR spectrum the hydride resonance appears as a singlet without any H–H scalar coupling (Fig. 1, top trace). Complex **2** is highly fluxional in CD_2Cl_2 at room temperature suggesting the occurrence of a dynamic process with fast scrambling at room temperature of the five magnetically equivalent hydrides on the NMR time scale [18].

On cooling, the hydride signal at -6.35 ppm markedly broadens and then coalesces slightly below 253 K. At 193 K the spectrum shows three separated resonances integrating to 1:1:3, two partially superimposed at ca. $\delta -5.7$ and -5.9 ppm (a triplet and a complex multiplet), and a broad singlet at -6.9 ppm, respectively [see Figs. 1(bottom trace) and 2(top trace)]. The latter resonance accounting for three protons is due to the three hydrides freely exchanging at very low temperature.

Although the low exchange spectrum of **2** could not be attained within the temperature window of CD_2Cl_2 , we can reasonably assume that the dynamic process follows the mechanism previously reported by Crabtree et al. to account for the stereochemical fluxionality exhibited by the structurally related pentahydride $[ReH_5(PPh_3)_2(py)]$ [18b–20].

Longitudinal relaxation times (T_1) were measured for the hydride resonances of **2** using the standard inversion-recovery method [21]. The plot of $\ln T_1$ against $1/T$ for this compound shows a well-defined ‘V-shaped’ curve from

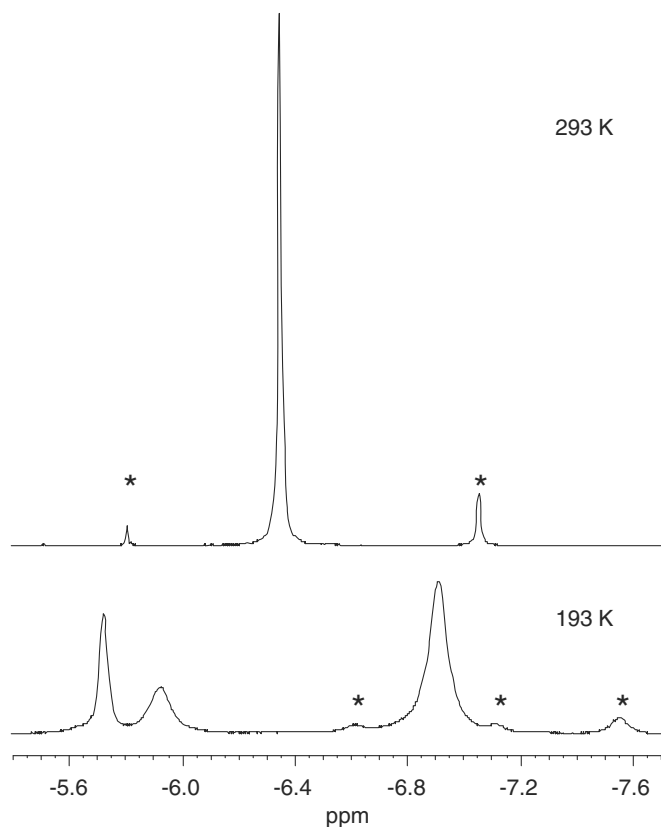


Fig. 1. $^1\text{H}\{^{31}\text{P}\}$ NMR spectra of **2** in the hydride region (CD_2Cl_2 , 400.13 MHz). Top, 293 K; bottom: 193 K. Asterisks (*) denote minor unassigned impurities.

which a minimum value ($T_{1(\text{min})}$) of 133 ms at ca. 237 K was calculated for the two hydride resonances at -6.9 and -5.7 ppm [22]. In line with the common behaviour

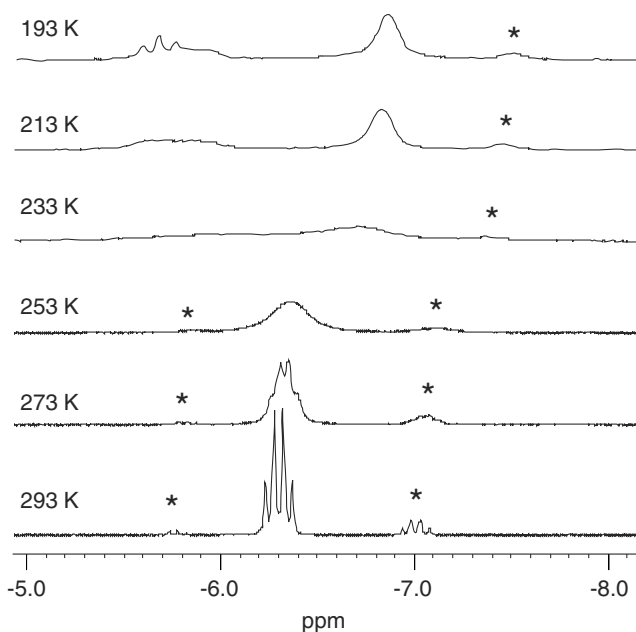


Fig. 2. Variable-temperature ^1H NMR spectra of **2** in the hydride region (CD_2Cl_2 , 400.13 MHz). Asterisks (*) denote minor unassigned impurities.

of rhenium pentahydrides, this value indicates the classical nature of the whole set of five hydrides in **2** [12,19,23].

Following the criteria indicated by Halpern et al., [12] we have calculated the relaxation rate of the hydride ligands (R_{cal}) for **2** using the available structural data as determined by X-ray crystallography (see below). The calculated $T_{1(\text{min})}$ at 132.8 ms (400 MHz) is in excellent agreement with the experimental value, indirectly confirming the validity of the data obtained from the X-ray analysis [24].

In CH_2Cl_2 the IR spectrum of **2** displays one ν_{ReH} broad absorption featuring a complex shape with maxima at 1903, 1933 and 1967 cm^{-1} , resulting from the combination of several M–H vibrational normal modes [25]. Both the shape and the intensity of this band change as the temperature is decreased (Fig. 3). The extinction coefficient of the ν_{ReH} band at 1903 cm^{-1} increases from 45.8 to 58.3 $\text{l mol}^{-1} \text{cm}^{-1}$ upon cooling from 290 to 190 K in dichloromethane. Other absorptions, including few weaker bands present in the 2000–1750 cm^{-1} region due to overtones of the phenyl group vibrations, are less significant and do not deserve additional comments.

2.2. X-ray crystal structure of $[\text{ReH}_5(\text{PPh}_3)_2(\text{PTA})]$ (**2**)

An ORTEP view of the structure is shown in Fig. 4. The molecules in the crystal are held together by van der Waals interactions with no short contacts between them. The immediate coordination sphere around the rhenium atom consists of the five hydride ligands and the three phosphorus atoms. The coordination geometry, shown in Fig. 5, may be described as a dodecahedron with two orthogonal trapezoidal planes: one containing the atoms P1, H1i, H2i and H5i, and the other defined by P3, P2, H3i and H4i. The bulkier P donors occupy the B sites of the dodecahedron, less sterically hindered [26].

The most relevant bond distances and angles are listed in Table 1. The three Re–P distances at 2.385(1), 2.383(1) and 2.391(1) Å are comparable to those found in similar MP_3H_5 complexes [27], such as $\text{OsH}_5(\text{PMe}_2\text{Ph})_3^+$ [27a], and $\text{ReH}_5(\text{PMePh}_2)_3$ [27b] with the longest separation Re–P(1), 2.391(1) Å corresponding to the PTA-phosphorus atom pseudo-*trans* to a hydride ligand. The Re–H bond lengths have values in the range 1.3–1.6 Å (average 1.45(5) Å) expected for the terminal hydrides, taking into account both the limited accuracy of the location of hydrides by X-ray diffraction and the systematic shortening of the observed distances. The intramolecular separations between the hydride ligands (in the range 1.6–1.8 Å) are outside the values found for dihydrogen ligands and consistent with the classical nature of this compound as determined in solution by T_1 analysis.

The bond angles $\text{P}(2)\text{--Re--P}(3)$ at $146.55(4)^\circ$, $\text{P}(2)\text{--Re--P}(1)$ and $\text{P}(3)\text{--Re--P}(1)$ [$101.29(4)^\circ$ and $101.89(4)^\circ$, respectively] define the two different angles, characteristic for this type of co-ordination [23,27b,28].

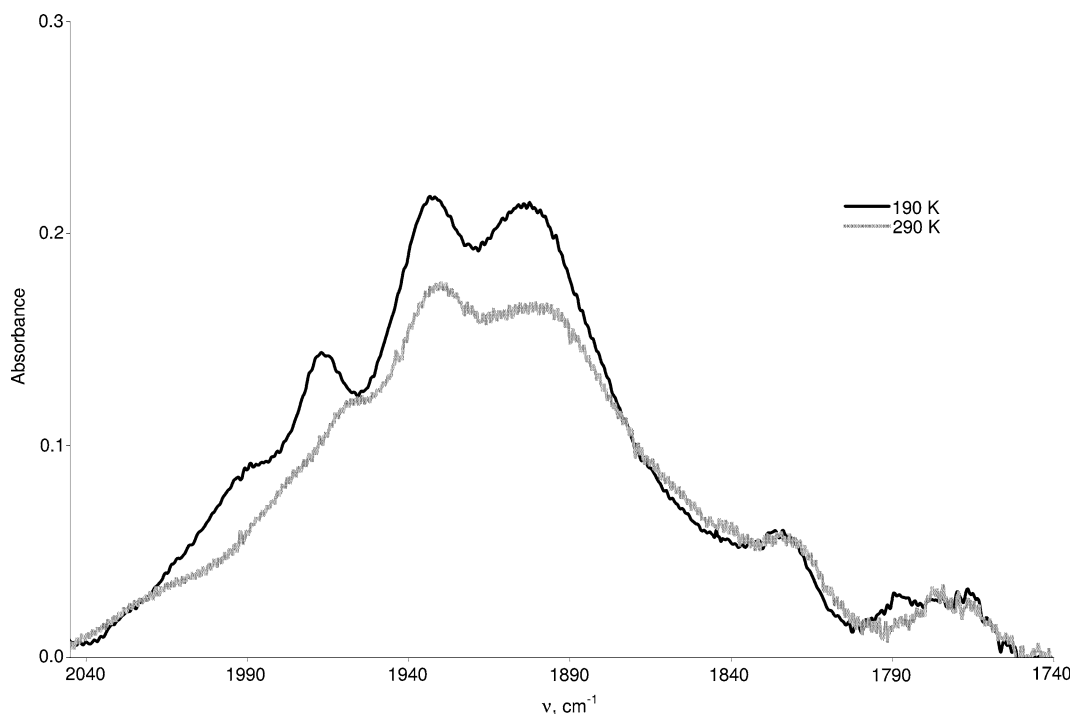


Fig. 3. IR spectra in the ν_{ReH} region of **2** (0.02 M) in CH_2Cl_2 at 190 and 290 K.

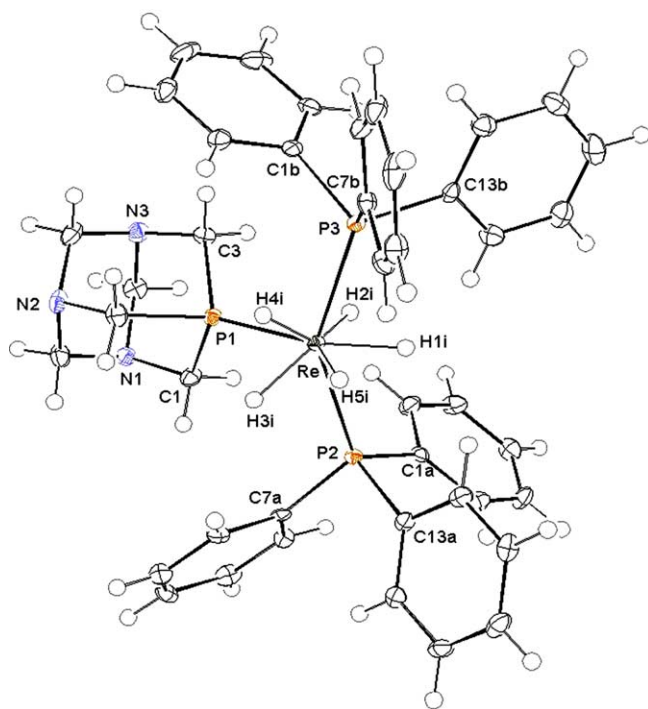


Fig. 4. An ORTEP view of **2**, ellipsoids drawn at 50% probability.

2.3. Protonation studies of $[\text{ReH}_5(\text{PPh}_3)_2(\text{PTA})]$ (**2**)

Complex **2** was reacted in CD_2Cl_2 with acids of increasing strength such as $(\text{CF}_3)_2\text{CHOH}$ (HFIP), CF_3COOD and $\text{HBF}_4 \cdot \text{OEt}_2$ at 193 K and the protonation was followed by both ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR at variable temperature (see

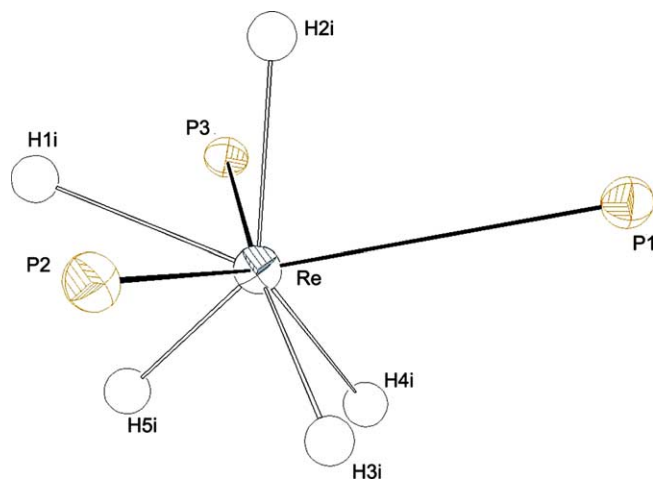
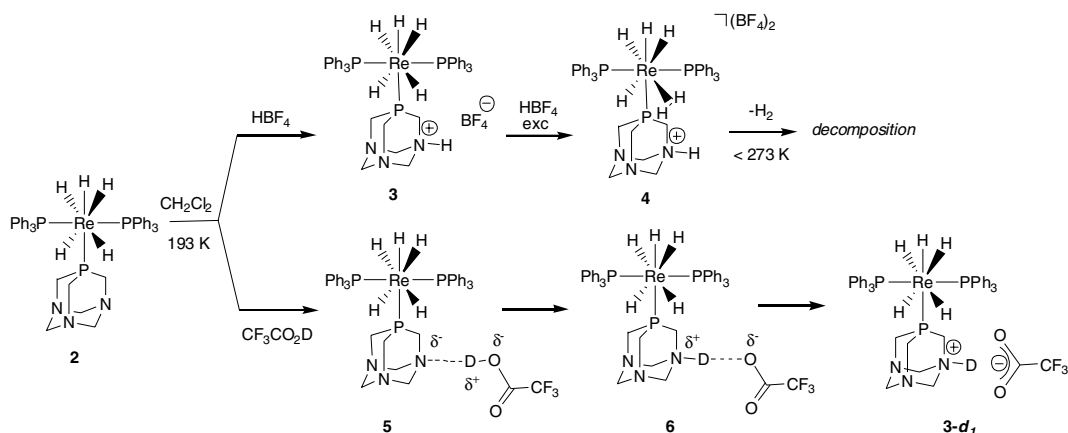


Fig. 5. Perspective views of the ReH_5P_3 core in **2** illustrating the dodecahedral coordination about the rhenium centre.

Table 1
Selected bond lengths [\AA] and angles [$^\circ$] for $[\text{ReH}_5(\text{PPh}_3)_2(\text{PTA})]$ (**2**)

Bond distances		Bond angles	
Re–P(2)	2.383(1)	P(2)–Re–P(3)	146.55(4)
Re–P(3)	2.385(1)	P(2)–Re–P(1)	101.29(4)
Re–P(1)	2.391(1)	P(3)–Re–P(1)	101.89(4)
Re–H(1i)	1.56(4)		
Re–H(3i)	1.53(4)		
Re–H(2i)	1.53(4)		
Re–H(4i)	1.30(5)		
Re–H(5i)	1.33(5)		
P–C _{av}	1.856(7)		



Scheme 2.

Scheme 2). The reaction with CF_3COOD and $\text{HBF}_4 \cdot \text{OEt}_2$ was also studied by low temperature IR spectroscopy in CH_2Cl_2 (see below). Addition of 5 equivalents of HFIP resulted in the interaction of the OH proton with one nitrogen atom of the PTA ligand, presumably yielding the PTA-protonated complex $[\text{ReH}_5(\text{PPh}_3)_2\{\text{PTA}(\text{H})\}]^+$ (**3**). In agreement with the occurrence of *N*-protonation, the pattern for the hydride resonances, apart from a slight downfield shift of one hydride resonance (-5.2 vs. -5.7 ppm), is comparable to that of the non-protonated complex **2**. This indicates that the classical nature of the five hydrides of **2** is maintained even after treatment with a fivefold excess of HFIP, as confirmed also by the $T_{1(\text{min})}$ values of ca. 125 ms (238 K) measured for the three hydride resonances after protonation with excess HFIP.

Treatment of **2** in CD_2Cl_2 with 1 equivalent of $\text{HBF}_4 \cdot \text{OEt}_2$ at 193 K similarly led to the protonation of one nitrogen on PTA with loss of the C_3 symmetry of the CH_2 protons (Fig. 6(a)). Three hydride resonances integrating 1:1:3 protons are observed at -5.3 , -6.0 and -6.7 ppm, respectively, at this temperature (Fig. 6(b)). Again, T_1 values from relaxation measurements for the hydride resonances are in accordance with a classical nature ($T_1 = 97$, 112, 136 ms at 223 K, $T_1 = 255$, 268, 264 ms at 193 K).

When 5 equivalents of $\text{HBF}_4 \cdot \text{OEt}_2$ were added to a CD_2Cl_2 solution of **2**, a double protonation took place with delivery of the second proton to one of the hydride ligands. Indeed, the ^1H NMR spectrum shows a single broad hydride resonance at ca. -4.1 ppm at 193 K. In keeping with the formation of the dication $[\text{ReH}_4(\eta^2\text{-H}_2)(\text{PPh}_3)_2\{\text{PTA}(\text{H})\}]^{2+}$ (**4**), the newly obtained hexahydride exhibited a T_1 value of 28 ms at this temperature. The broad NMR resonance and the short T_1 value agree with the presence of four classical hydrides freely and quickly exchanging with one dihydrogen ligand. However, it was impossible to determine the $T_{1(\text{min})}$ of **4** because of the slow decomposition occurring on increasing the temperature as indicated by the rising of a singlet at ca. 4.6 ppm due to free H_2 .

Monitoring the protonation of **2** by $\text{HBF}_4 \cdot \text{OEt}_2$ in CH_2Cl_2 by variable temperature IR spectroscopy showed,

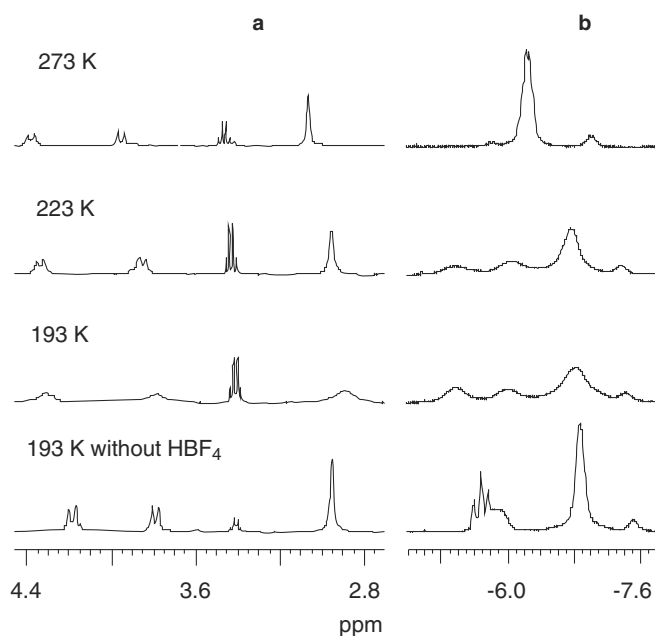


Fig. 6. Variable-temperature ^1H NMR spectra of **2** after treatment with 1 equivalent of $\text{HBF}_4 \cdot \text{OEt}_2$ (CD_2Cl_2 , 400.13 MHz): (a) PTA, CH_2 region; (b) hydride region.

apart from a new band at 2880 cm^{-1} assigned to the N–H stretching vibration of the protonated PTA ligand in agreement with NMR data, a minor shift of the ν_{ReH} bands to higher frequencies by 2–8 cm^{-1} , with new absorptions maxima at 1911, 1935 and 1969 cm^{-1} . Upon the addition of a second equivalent of HBF_4 , the ν_{ReH} bands disappear, while a new weak band appears at 1932 cm^{-1} ($\epsilon = 33\text{ l mol}^{-1}\text{ cm}^{-1}$ and $\Delta\nu_{1/2}$ ca. 20 cm^{-1}). This latter finally disappears upon further addition of the acid. The appearance of ν_{MH} bands at higher frequency upon protonation represents a highly diagnostic spectroscopic evidence for the protonation of a metal hydride complex. A perusal of the available literature shows only a slight intensity decrease of the new bands when a classical proton transfer product is formed [25]. In contrast, the intensity of the terminal ν_{MH} vibrations is substantially

(more than two times) decreased when non-classical cationic hydrides are formed [29]. On this basis, the IR changes observed in the present case suggest that the second equivalent of the acid protonates the hydride ligand yielding the non-classical complex **4** prior to decomposition.

In contrast to HBF_4 , CF_3COOD does not protonate the hydride ligand of **2**, but selectively yields **3-d**₁ (Fig. 7). After protonation of **2**, the ν_{CO} bands typical of CF_3COOD at 1801 and 1778 cm^{-1} [30] disappear and new $\nu_{\text{OCO}}^{\text{as}}$ bands ascribable to the trifluoroacetate anion appear in the

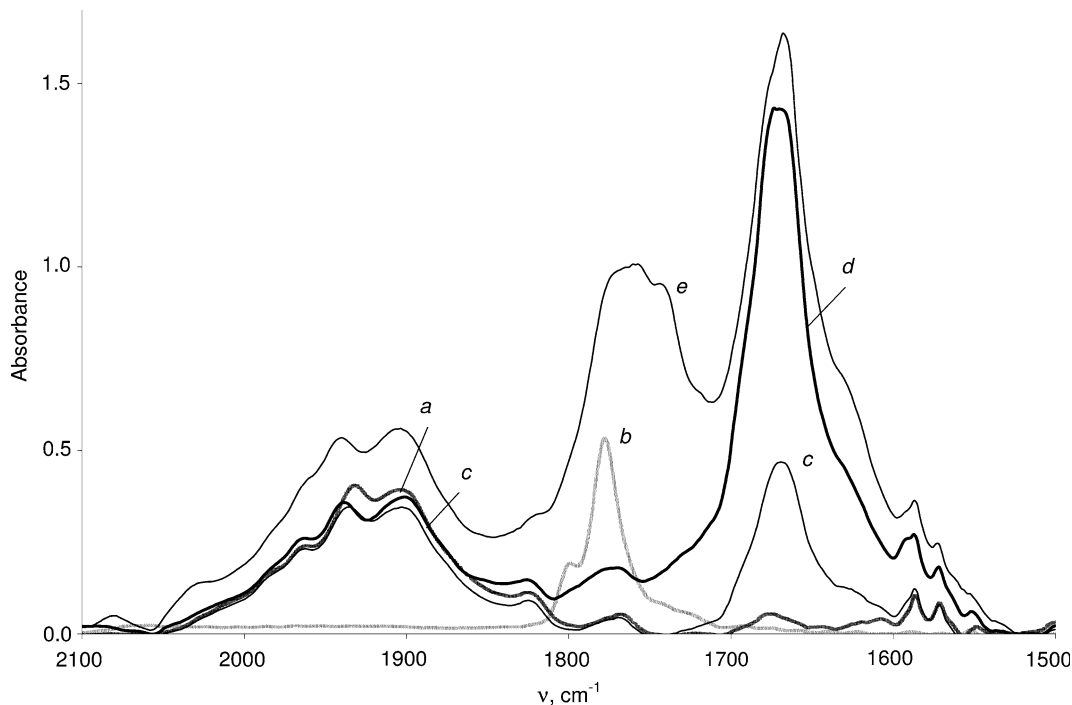


Fig. 7. IR spectra for protonation of **2** by CF_3COOD (CH_2Cl_2 , 190 K). (a) Complex **2** alone (0.04 M); (b) CF_3COOD alone (0.01 M); and **2** (0.04 M) in the presence of CF_3COOD : (c) 0.01 M; (d) 0.04 M; (e) 0.08 M.

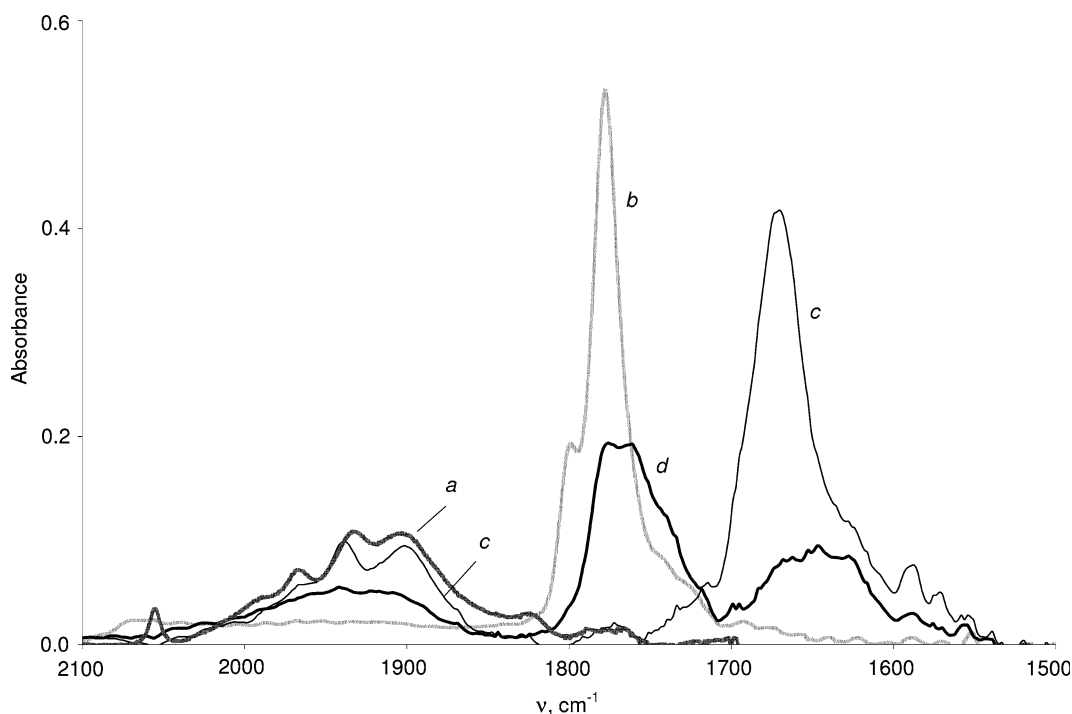


Fig. 8. IR spectra for the protonation of **2** by CF_3COOD (CH_2Cl_2 , 190 K). (a) Complex **2** alone (0.01 M); (b) CF_3COOD alone (0.01 M); (c) **2** (0.01 M) in the presence of CF_3COOD (0.01 M); (d) **2** (0.003 M) in the presence of CF_3COOD (0.012 M).

spectrum near 1674 cm^{-1} (Fig. 7) suggesting the occurrence of a proton transfer reaction. Addition of equimolar to excess amounts of CF_3COOD led to high-frequency shift of one of the maxima of ν_{ReH} band from 1933 to 1941 cm^{-1} . In the presence of more than two equivalents of the acid two new bands at 1765 and 1743 cm^{-1} appear in the spectra, overlapped to each other and to the band at 1778 cm^{-1} of the CF_3COOD dimer. These bands could be reasonably attributed to the formation of the hydrogen bonded complex $[\text{ReH}_5(\text{PPh}_3)_2\{\text{PTA}\cdots\text{DOC}(\text{O})\text{CF}_3\}]$ (**5**) and the ionic pair $[\text{ReH}_5(\text{PPh}_3)_2\{\text{PTA}(\text{D})\cdots\text{OC}(\text{O})\text{CF}_3\}]$ (**6**) which precedes the formation of $[\text{ReH}_5(\text{PPh}_3)_2\{\text{PTA}(\text{D})\}][\text{OC}(\text{O})\text{CF}_3]$ (**3-d₁**). By adding a fourth equivalent of CF_3COOD , the $\nu_{\text{OCO}}^{\text{as}}$ absorption assigned to the homoconjugate trifluoroacetate anion $[\text{CF}_3\text{COO}(\text{DOCOCF}_3)_n]^-$ appears in the spectrum at 1650 cm^{-1} (Fig. 8).

This behaviour is in agreement with previous studies on proton transfer from trifluoroacetic acid to organic [31] and organometallic [32] bases. Slow H/D exchange at the hydride sites was observed during these experiments in the temperature range between 190 and 290 K . This observation confirms the higher nucleophilicity of the PTA-nitrogen atom in **2** with respect to the hydride ligands.

Finally, a careful comparison of the IR spectra in the $3700\text{--}2100\text{ cm}^{-1}$ region after protonation of **2** with $\text{HBF}_4\cdot\text{OEt}_2$ and CF_3COOD allowed us to assign the bands of ν_{NH} and ν_{ND} vibration in **3** and **3-d₁** at 2880 and 2180 cm^{-1} , respectively, with an isotopic ratio $\nu_{\text{NH}}/\nu_{\text{ND}} = 1.32$.

3. Conclusions

The first rhenium polyhydride containing the water soluble phosphine, $[\text{ReH}_5(\text{PPh}_3)_2(\text{PTA})]$ (**2**) has been prepared, showing a classical nature both in the solid state and in solution as confirmed by X-ray diffraction analysis, VT NMR spectroscopy and proton relaxation measurements. Stoichiometric protonation of **2** results in proton uptake by the ancillary PTA ligand yielding the cationic rhenium pentahydride $[\text{ReH}_5(\text{PPh}_3)_2\{\text{PTA}(\text{H})\}]^+$ (**3**). Further addition of HBF_4 provides some evidence that an unstable dicationic non-classical species, $[\text{ReH}_4(\eta^2\text{-H}_2)(\text{PPh}_3)_2\{\text{PTA}(\text{H})\}]^{2+}$ (**4**), may be formed, decomposing by loss of H_2 . IR study of the proton transfer reaction with CF_3COOD gives evidence for the formation of both the hydrogen bonded adduct $[\text{ReH}_5(\text{PPh}_3)_2\{\text{PTA}\cdots\text{DOC}(\text{O})\text{CF}_3\}]$ (**5**) and the hydrogen bonded ion pair species $[\text{ReH}_5(\text{PPh}_3)_2\{\text{PTA}(\text{D})\cdots\text{OC}(\text{O})\text{CF}_3\}]$ (**6**) along the reaction pathway eventually transferring a proton to one of the nitrogen atoms of PTA.

4. Experimental

4.1. General methods

All operations were carried out under nitrogen using standard Schlenk techniques. Solvents were purified by dis-

tillation from the appropriate drying agents and degassed before use [33]. PTA [34] and $[\text{ReH}_7(\text{PPh}_3)_2]$ (**1**) [16b] were prepared as described in the literature. Deuterated solvents for NMR measurements (Merck and Aldrich) were dried with molecular sieves (4 \AA). ^1H NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer operating at 400.13 MHz . Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on the same instrument operating at 161.95 MHz . Chemical shifts were measured relative to external $85\%\text{ H}_3\text{PO}_4$, with downfield shifts reported as positive. Variable-temperature spin-lattice relaxation times (T_1) were measured in CD_2Cl_2 at 400 MHz by the inversion-recovery method using the standard $180^\circ\text{-}\tau\text{-}90^\circ$ pulse sequence and 16 different values of τ at each temperature. The calculations of the relaxation times were made using the fitting routines of the NMR spectrometer. The 90° pulse on the hydride samples was carefully measured at each temperature before running the T_1 measurements. Infrared spectra of samples in KBr pellets were recorded on a Perkin–Elmer Spectrum BX series FT-IR spectrometer. IR measurements in CH_2Cl_2 solution were carried out on “Infracum FT 801” spectrometer using 0.12 cm width CaF_2 cell. For the low-temperature measurements a Carl Zeiss Jena cryostat was employed in the temperature range $193\text{--}300\text{ K}$ using a stream of liquid nitrogen as a cooling agent. The accuracy of temperature adjustment was $\pm 0.5^\circ\text{C}$. Elemental analyses (C, H, N) were performed using a Carlo Erba model 1106 elemental analyser by the Microanalytical Service of the Department of Chemistry at the University of Florence.

4.2. Synthesis of $[\text{ReH}_5(\text{PPh}_3)_2(\text{PTA})]$ (**2**)

Solid PTA (26.4 mg , 0.17 mmol) was added to a solution of $[\text{ReH}_7(\text{PPh}_3)_2]$ (100.0 mg , 0.14 mmol) in THF (30 mL). The mixture was heated to reflux for 3 h and then concentrated under vacuum to dryness to leave an oil to which diethyl ether was added. The pale yellow solid formed was filtered under nitrogen, washed with diethyl ether ($2\times 5\text{ mL}$) and dried under vacuum (79 mg , 65% yield). Anal. Calc. for $\text{C}_{42}\text{H}_{47}\text{N}_3\text{P}_3\text{Re}$ (872.98) calcd. C, 57.79 ; H, 5.43 ; N, 4.81 . Found: C, 57.59 ; H, 5.39 ; N 4.76% . IR (KBr pellets): $\nu_{\text{Re-H}}$ (cm^{-1}) = 1889 (m), 1924 (m), 1952 (w), 1973 (vw), 1991 (vw). ^1H NMR (CD_2Cl_2 , 400 MHz , 293 K): -6.35 (dt, $J_{\text{PH}} = 17.1\text{ Hz}$, $J_{\text{PH}} = 19.5\text{ Hz}$, 5H , ReH), 3.13 (s, 6H , NCH_2N), 3.86 (d, $^2J_{\text{HH}} = 12.7\text{ Hz}$, 3H , PCH_2N), 4.22 (d, $^2J_{\text{HH}} = 12.7\text{ Hz}$, 3H , PCH_2N), $7.24\text{--}7.69$ (m, 30H , Ph). $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2 , 161 MHz , 293 K): 37.13 (d, $\text{P}_{(\text{PTA})}$, $J_{\text{PP}} = 5.4\text{ Hz}$); -70.32 (t, $\text{P}_{(\text{PPh}_3)}$, $J_{\text{PP}} = 5.4\text{ Hz}$).

4.3. In situ protonation of **2** with HY [$\text{Y} = \text{BF}_4$, CF_3COO , $(\text{CF}_3)_2\text{C}(\text{H})\text{O}$]

Hydride **2** was protonated following the procedure described in the literature [35], under inert atmosphere at

Table 2
Experimental data for the X-ray diffraction study of compound [ReH₅(PPh₃)₂(PTA)] (2)

Compound	2
Formula	C ₄₂ H ₄₇ N ₃ P ₃ Re
Molecular weight	872.98
Diffractometer	Bruker SMART
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>T</i> (K)	120(2)
<i>a</i> (Å)	9.742(5)
<i>b</i> (Å)	10.767(5)
<i>c</i> (Å)	19.946(5)
α (°)	76.641(5)
β (°)	82.226(5)
γ (°)	65.966(5)
<i>Z</i>	2
ρ (calcd) (g cm ⁻³)	1.536
μ (cm ⁻¹)	34.34
Radiation	Mo K α (graphite monochromated, $\lambda = 0.71069$ Å)
θ range,	1.5° < θ < 27.6°
Number of data collected	19,666
Number of independent data	8509
Number of observed reflections (<i>n</i> _o)	7171 [<i>F</i> _o ² > 4.0 σ (<i>F</i> ²)]
Number of refined parameters	462
Transmission coefficient	0.705–1.000
<i>R</i> _{av}	0.0471
<i>R</i> (observations – reflections)	0.0332
<i>R</i> _w ²	0.0649
Goodness-of-fit	1.028

$$R_{av} = \frac{\sum |F_o^2 - F_{o,av}^2|}{\sum |F_o^2|}, R = \frac{\sum (|F_o - (1/k)F_c|)}{\sum |F_o|}, R_w^2 = \frac{\sum w(F_o^2 - (1/k)F_c^2)^2}{\sum w |F_o^2|^2}.$$

$$\text{GOF} = \left[\frac{\sum w(F_o^2 - (1/k)F_c^2)^2}{(n_o - n_v)} \right]^{1/2}.$$

193 K. In a typical experiment, 10 mg (0.014 mmol) of **2** were dissolved in 0.5 mL of CD₂Cl₂ in a 5 mm screw cap NMR tube and the appropriate acid added with a microsyringe through the serum cap to the cooled solution of **2**. After immediate shaking the tube was quickly inserted into the probehead of the NMR spectrometer pre-cooled at the same temperature.

4.4. Crystal structure determination

Air stable pale yellow crystals of **2**, suitable for X-ray diffraction, were obtained by diffusion from a diluted THF/Et₂O (10 mL, 1:1 v/v) mixture. The crystals were mounted on a Bruker SMART CCD diffractometer for unit cell and space group determinations. Crystals of **2** were cooled, using a cold nitrogen stream, to 120(2) K for the data collection. The centrosymmetric *P* $\bar{1}$ space group was chosen and later confirmed by the successful solution and refinement of the structure. Selected crystallographic and other relevant data are listed in Table 2 and in the supporting information. Data were corrected for Lorentz and polarization factors with the data reduction software SAINT [36] and empirically for absorption using the SADABS program [37].

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares [38] (the function minimized being $\sum [w(F_o - 1/k F_c)^2]$). Anisotropic

displacement parameters were used for all atoms except for the hydrogens; their contribution (in calculated positions, C–H = 0.95(Å), B(H) = 1.3/1.5 × B(C_{bonded})(Å²)) was included in the refinement using a riding model. No extinction correction was deemed necessary. Upon convergence no significant features were found in the Fourier difference map. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature [39]. All calculations were carried out by using the PC version of the programs: WINGX, [40] SHELX-97 [38] and ORTEP [41].

5. Supplementary information

Crystallographic data (excluding structure factors) for the structure of **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 280325. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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References

- [1] (a) M. Peruzzini, R. Poli (Eds.), Recent Advances in Hydride Chemistry, Elsevier, Amsterdam, 2001;
(b) A. Dedieu (Ed.), Transition Metal Hydrides, VCH Publishers, New York, 1991;
(c) G.G. Hlatky, R.H. Crabtree, Coord. Chem. Rev. 65 (1985) 1.
- [2] G.J. Kubas, Metal Dihydrogen and σ -Bond Complexes, Kluwer Academic/Plenum Publishers, New York, 2001.
- [3] For a review on agostic interactions, see: M. Brookhart, M.L.H. Green, L.-L. Wong, Prog. Inorg. Chem. 36 (1988) 1;
For recent reviews on hydrogen bonding interactions, see: L.M. Epstein, E. Shubina, Coord. Chem. Rev. 231 (2002) 165;
V.I. Bahkmutov, Eur. J. Inorg. Chem. (2005) 245;
N.V. Belkova, E.S. Shubina, L.M. Epstein, Acc. Chem. Res. 38 (2005) 624.
- [4] B. Manzano, F. Jalon, J. Matthes, S. Sabo-Etienne, B. Chaudret, S. Ulrich, H.-H. Limbach, J. Chem. Soc., Dalton Trans. (1997) 3153.
- [5] (a) D.G. Hamilton, R.H. Crabtree, J. Am. Chem. Soc. 110 (1988) 4126;
(b) R.H. Crabtree, X. Luo, D. Michos, Inorg. Chem. 3 (1991) 245.
- [6] (a) G.G. Hlatky, R.H. Crabtree, Coord. Chem. Rev. 65 (1985) 1;
(b) P.G. Jessop, R.H. Morris, Coord. Chem. Rev. 121 (1992) 155;
(c) D.M. Heinekey, W.J. Oldham Jr., Chem. Rev. 93 (1993) 913;
(d) F. Maseras, A. Lledós, E. Clot, O. Eisenstein, Chem. Rev. 100 (2000) 601.

- [7] (a) K.A. Conner, R.A. Walton, in: *Comprehensive Coordination Chemistry*, Pergamon, Oxford, England, 1987, pp. 125–213 (Chapter 43);
(b) R.H. Crabtree, *Acc. Chem. Res.* 23 (1990) 95.
- [8] D.G. Gusev, H. Berke, *Chem. Ber.* 129 (1996) 1143.
- [9] (a) For example: J.A.K. Howard, S.A. Mason, O. Johnson, I.C. Diamond, S. Crennell, P.A. Keller, J.L. Spencer, *J. Chem. Soc., Chem. Commun.* (1988) 1502;
(b) D.G. Hamilton, R.H. Crabtree, *J. Am. Chem. Soc.* 110 (1988) 4126;
(c) F.A. Cotton, R.L. Luck, *J. Chem. Soc., Chem. Commun.* (1988) 1277;
(d) L.S. Van Der Sluys, J. Eckert, O. Eisenstein, J.H. Hall, J.C. Huffman, S.A. Jackson, T.F. Koetzle, G.J. Kubas, J.P. Vergamini, K.G. Caulton, *J. Am. Chem. Soc.* 112 (1990) 4831.
- [10] (a) P.E. Bloyce, A.J. Rest, I. Whitwell, W.A.G. Graham, R. Holmes-Smith, *J. Chem. Soc., Chem. Commun.* (1988) 846;
(b) K.W. Zilm, M.J. Millar, *Adv. Magn. Opt. Reson.* 15 (1990) 163;
(c) Z.-W. Li, H. Taube, *J. Am. Chem. Soc.* 113 (1991) 8946;
(d) R. Paciello, J.M. Manriquez, J.E. Bercaw, *Organometallics* 9 (1990) 260.
- [11] (a) G.J. Kubas, *Acc. Chem. Res.* 21 (1988) 120;
(b) X.-L. Luo, R.H. Crabtree, *Inorg. Chem.* 28 (1989) 3775;
(c) P. Amendola, S. Antoniutti, G. Albertin, E. Bordignon, *Inorg. Chem.* 29 (1990) 318;
(d) F.A. Cotton, R.L. Luck, *J. Am. Chem. Soc.* 111 (1989) 5757.
- [12] P.J. Desrosiers, L. Cai, Z. Lin, R. Richards, J. Halpern, *J. Am. Chem. Soc.* 113 (1991) 4173.
- [13] G.J. Kubas, R.R. Ryan, B.I. Swanson, P.J. Vergamini, H.J. Wasserman, *J. Am. Chem. Soc.* 106 (1984) 451.
- [14] A.D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini, *Coord. Chem. Rev.* 248 (2004) 955.
- [15] (a) D.N. Akbayeva, L. Gonsalvi, W. Oberhauser, M. Peruzzini, F. Vizza, P. Brüggeller, A. Romerosa, G. Sava, A. Bergamo, *Chem. Commun.* (2003) 264;
(b) S. Bolaño, L. Gonsalvi, F. Zanobini, F. Vizza, V. Bertolasi, A. Romerosa, M. Peruzzini, *J. Mol. Catal. A: Chem.* 224 (2004) 61;
(c) M.C. Lidrissi, A. Romerosa, M. Saoud, M. Serrano-Ruiz, L. Gonsalvi, M. Peruzzini, *Angew. Chem. Int. Ed.* 44 (2005) 2568.
- [16] (a) D. Baudry, M. Ephritikhine, H. Felkin, *J. Organomet. Chem.* 224 (1982) 363;
(b) W.D. Jones, J.A. Maguire, *Organometallics* 6 (1987) 1301.
- [17] (a) J. Chatt, R.S. Coffey, *J. Chem. Soc. (A)*. (1969) 1963;
(b) M. Freni, D. Giusto, V. Valenti, *J. Inorg. Nucl. Chem.* 27 (1965) 755;
(c) M. Freni, R. De Michelis, D. Giusto, *J. Inorg. Nucl. Chem.* 29 (1967) 1433;
(d) C. Bianchini, M. Peruzzini, F. Zanobini, L. Magon, L. Marvelli, R. Rossi, *J. Organomet. Chem.* 451 (1993) 97.
- [18] (a) Hydride fluxionality is commonly observed in rhenium polyhydride complexes. See, for example: X. Luo, R.H. Crabtree, *J. Chem. Soc., Dalton Trans.* (1991) 587;
(b) D. Michos, X. Luo, R.H. Crabtree, *J. Chem. Soc., Dalton Trans.* (1992) 1735;
(c) R. Bosque, F. Maseras, O. Eisenstein, Ben P. Patel, W. Yao, R.H. Crabtree, *Inorg. Chem.* 36 (1997) 5505.
- [19] R.H. Crabtree, J.C. Lee Jr., W. Yao, H. Rüegger, *Inorg. Chem.* 35 (1996) 695.
- [20] (a) Notably, the fluxional behaviour shown by **2** and **3** has many precedents in rhenium polyhydride chemistry. See, for example: F.A. Cotton, R.L. Luck, *Inorg. Chem.* 28 (1989) 6;
(b) F.A. Cotton, R.L. Luck, *J. Am. Chem. Soc.* 111 (1989) 5757;
(c) S. Bolaño, J. Bravo, S. García-Fontán, *Eur. J. Inorg. Chem.* (2004) 4812.
- [21] V.I. Bakhmutov, *Practical Nuclear Magnetic Resonance Relaxation for Chemists*, Wiley, New York, 2005.
- [22] The calculated $T_{1(\min)}$ values are: $\delta - 5.7$: $T_{1(\min)}$ 133 ms at 236 K; $\delta - 6.9$: $T_{1(\min)}$ 134 ms at 237 K. The $T_{1(\min)}$ for the broad resonance at $\delta - 5.9$ could not be calculated due to broadness of this signal below 213 K and its partial superimposition with the triplet at $\delta - 5.7$.
- [23] M.T. Bautista, K.A. Earl, P.A. Maltby, R.H. Morris, C.T. Schawiter, A. Sella, *J. Am. Chem. Soc.* 110 (1988) 7031.
- [24] The calculate relaxation rates of the hydride ligands in **2** ($R_{\text{cal}} = 6.0304 \text{ s}^{-1}$ at 500 MHz) were obtained by the additive method of Desrosiers et al. [12] by summing up the several contributions taking into account the interaction of each hydride with both the other hydrides and the neighbouring nuclei (including rhenium, phosphorus, the *ortho* hydrogens of the phenyl rings and the hydrogens located on C1, C2, C3 carbons of the PTA ligand).
- [25] (a) R.B. Girling, P. Grebenik, R.N. Perutz, *Inorg. Chem.* 25 (1986) 31;
(b) A. Albinati, V.I. Bakhmutov, N.V. Belkova, C. Bianchini, L.M. Epstein, I. de los Rios, E.I. Gutsul, L. Marvelli, M. Peruzzini, R. Rossi, E.S. Shubina, E.V. Vorontsov, F. Zanobini, *Eur. J. Inorg. Chem.* (2002) 1530;
(c) M. Baya, N.V. Belkova, M. Besora, L.M. Epstein, A. Lledós, R. Poli, P.O. Revin, E.S. Shubina, E.V. Vorontsov, in preparation.
- [26] See for example: S. Bolaño, J. Bravo, S. García Fontan, J. Castro, *J. Organomet. Chem.* 667 (2003) 103.
- [27] (a) T.J. Johnson, A. Albinati, T.F. Koetzle, J. Ricci, O. Eisenstein, J.C. Huffman, K.G. Caulton, *Inorg. Chem.* 33 (1994) 4966;
(b) T.J. Emge, T.F. Koetzle, J.W. Bruno, K.G. Caulton, *Inorg. Chem.* 23 (1984) 4012.
- [28] Y. Kim, H. Deng, J.C. Gallucci, A. Woycicki, *Inorg. Chem.* 35 (1996) 7166.
- [29] E.I. Gutsul, N.V. Belkova, M.S. Sverdlov, L.M. Epstein, E.S. Shubina, V.I. Bakhmutov, T.N. Gribanova, R.M. Minyaev, C. Bianchini, M. Peruzzini, F. Zanobini, *Chem. Eur. J.* 9 (2003) 2219.
- [30] These two absorptions are assigned to the monomeric and dimeric forms of CF_3COOD , respectively. Absorptions due to dimeric aggregates of CF_3CCOH are visible in the solution IR spectrum at concentrations above 10^{-4} M.
- [31] Z. Dega-Szafran, M. Grundwald-Wyspinka, M. Szafran, *Spectrochim. Acta A* 47 (1991) 543.
- [32] (a) L.M. Epstein, A.N. Krylov, E.S. Shubina, *J. Mol. Struct.* 322 (1994) 345;
(b) E.S. Shubina, A.N. Krylov, A.Z. Kreindlin, M.I. Rybinskaya, L.M. Epstein, *J. Organomet. Chem.* 465 (1994) 259;
(c) N.V. Belkova, A.V. Ionidis, L.M. Epstein, E.S. Shubina, S. Gruendemann, N.S. Golubev, H.-H. Limbach, *Eur. J. Inorg. Chem.* (2001) 1753.
- [33] D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, third ed., Butterworth and Heinemann, Oxford, 1988.
- [34] (a) D.J. Daigle, A.B. Pepperman Jr., S.L. Vail, *J. Heterocycl. Chem.* 11 (1974) 407;
(b) D.J. Daigle, *Inorg. Synth.* 32 (1998) 40.
- [35] S. García Fontán, A. Marchi, L. Marvelli, R. Rosi, S. Antoniutti, G. Albertin, *J. Chem. Soc., Dalton Trans.* (1996) 2779.
- [36] BrukerAXS, SAINT, Integration Software; Bruker Analytical X-ray Systems, Madison, WI, 1995.
- [37] G.M. Sheldrick, SADABS, Program for Absorption Correction, University of Göttingen, Göttingen, Germany, 1996.
- [38] G.M. Sheldrick, SHELX-97 Structure Solution and Refinement Package, Universität Göttingen, Göttingen, 1997.
- [39] A.J.C. Wilson (Ed.), *International Tables for X-ray Crystallography*, vol. C, Kluwer Academic Publisher, Dordrecht, The Netherlands, 1992.
- [40] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [41] L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.