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# The Br and I analogues of $\text{ReCl}(\text{H}_2)(\text{PMePh}_2)_4$ ; crystal structures of $\text{ReBr}(\text{H}_2)(\text{PMePh}_2)_4$ and the $[\text{ReO}_2(\text{Py})_4]^+$ cation; possible solution state evidence of $\text{Re}-\text{H}\cdots\text{H}\cdots\text{N}(\text{Py})$ interactions as evident in $T_1$ measurements<sup> $\pm,\pm\pm$ </sup>

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#### Abstract

The syntheses of the Br and I analogues of  $\text{ReCl}(H_2)(\text{PMePh}_2)_4$  are reported together with their characterizations by NMR, and in the case of the Br analogue, FABMS and a single crystal X-ray diffraction study. The minimum  $T_1$  for the metal bonded hydrogen atoms in the Br and I analogues was determined to be 62 and 101 ms at 400 MHz, respectively. A decrease of 9 ms in the room temperature  $T_1$  measurement of  $\text{ReCl}(H_2)(\text{PMePh}_2)_4$  was observed upon addition of pyridine to the NMR tube. This is suggestive of an interaction between the dihydrogen ligand and the lone pair of electrons on the N-atom in py. The crystal structure of  $\text{ReBr}(H_2)(\text{PMePh}_2)_4$  revealed that the structure consisted of a *trans* dihydrogen to halide arrangement and was disordered with respect to the locations of the dihydrogen ligand and the halide in the crystal. The crystal structure of the *trans*-[ReO<sub>2</sub>(Py)<sub>4</sub>]<sup>+</sup> cation is also reported. © 2001 Elsevier Science Ltd. All rights reserved.

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# 1. Introduction

Complexes of the form  $\text{ReX}(\text{H}_2)(\text{PMePh}_2)_4$  are of interest because the results of X-ray crystallography data on the Cl analog [1] suggest that the dihydrogen ligand [2] may be bound in an unsymmetrical manner.  $\text{ReCl}(\text{H}_2)(\text{PMePh}_2)_4$  (1) has also been characterized in the past as having a nonclassical stretched (H<sub>2</sub>) ligand. This assignment was based on  $T_1$  NMR studies [3] which placed the spin-lattice relaxation time minimum well within the accepted range (25 ms at 200 MHz,  $-50^{\circ}$ C) of stretched molecular dihydrogen behavior and suggested an H···H interaction on the order of 1.08 Å (fast rotation) to 1.37 Å (slow rotation) [4]. The bidentate phosphine analogues  $\text{ReCl}(\text{H}_2)(\text{dppe})_2$  and  $\text{ReCl}(\text{H}_2)(\text{dppe})_2$  have also been previously synthesized and characterized [4]. These complexes have similar  $T_1$  (min) times (43 ms at  $-40^{\circ}$ C and 29 ms at 26°C, by 200 MHz NMR) and  $J_{\text{HP}}$  values (20 Hz for both) to  $\text{ReCl}(\text{H}_2)(\text{PMePh}_2)_4$ , but have greatly lessened reactivity to  $\text{H}_2$  displacement reactions.

The purpose of this work is to determine the effect that changing the identity of the halogen *trans* to the dihydrogen ligand in ReCl( $\eta^2$ -H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub> (1) would have on the (H–H) interaction, as it is anticipated that the nature of the dihydrogen ligand will change as the *trans* halogen is varied, [5]. This should allow us to understand more about the steric and electronic conditions which lead to classical and nonclassical behavior. An additional goal of this work is to place the dihydrogen ligand in circumstances which may be suitable to such an 'end-on' arrangement and observe the molecule via NMR and X-ray crystallography. This could be a useful endeavor because an  $\eta^1$ -H<sub>2</sub> ligand could display novel hydrogen activation properties. Recently, there

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have been reports of long-range interactions involving metal hydrides with H–NR and H–CR fragments, [6–8] and, alcohols [9,10].

# 2. Experimental

# 2.1. General considerations

All manipulations were carried out under either an argon or nitrogen atmosphere. Methanol was dried with magnesium methoxide, and THF, benzene, and hexane were dried with finely divided sodium metal. Standard Schlenck and drybox techniques were used in all cases. ReCl<sub>5</sub> and PMePh<sub>2</sub> were used as purchased from Strem Chemicals, Inc. and all other reagents were obtained from the Aldrich Chemical Company. Mass spectral data were obtained at the Michigan State University Mass Spectrometry Facility which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institutes of Health. <sup>1</sup>H data were recorded using a Varian XL-400 spectrometer. The microanalysis was done by Galbraith<sup>®</sup> Laboratories, Inc., Knoxville, TN.

# 2.2. Syntheses

 $ReCl(H_2)(PMePh_2)_4$  (1) was synthesized by the method reported by Cotton and Luck with no modification [3].  $ReBr(H_2)(PMePh_2)_4$  (2) and  $ReI(H_2)$ - $(PMePh_2)_4$  (3) were synthesized by dissolving 1 in a 4:1 mixture of THF + MeOH with 50 equiv. of KBr or KI, respectively, at room temperature. The mixture was stirred under argon for three days. The solvents were then removed under vacuum and benzene was added. The solid salts were separated by filtration. The remaining solution was frozen under vacuum and the benzene sublimed off overnight. 2 was recrystallized from benzene+MeOH (obtained in 50% yield overall from starting 1), but 3 could not be separated efficiently. The nature of the dihydrogen ligands in 1, 2 and 3 were ascertained by variable temperature  $T_1$  NMR measurements using the inversion-recovery method. The fluoride analogue of the above molecules could not be synthesized by the methods used for 2 or 3. Spectroscopic data for **2**: <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  6.6–7.8 (m, 40 H,  $(C_6H_5)_2$ MePRe), 2.1 (br., 12H, CH<sub>3</sub>Ph<sub>2</sub>PRe), -9.1 (q., 2H,  $J_{\rm HP} = 20.0$  Hz,  $H_2 Re$ ). Anal. Calc. for



Fig. 1. (H<sub>2</sub>)-lone pair interaction.

C<sub>52</sub>H<sub>54</sub>BrP<sub>4</sub>Re·SiO<sub>2</sub>: C, 55.12; H, 4.80. Found: C, 55.18, H, 5.28. Spectroscopic data for **3**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ 6.6–7.8 (m, 40 H, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>MePRe), 2.2 (br., 12H, CH<sub>3</sub>Ph<sub>2</sub>PRe), -9.4 (q., 2H, J<sub>HP</sub> = 20.5 Hz, H<sub>2</sub>Re). The <sup>1</sup>H NMR data also indicated the presence of silicone grease in the final sample sent off for elemental analysis (singlet at  $\delta$  0.29).

# 2.3. Dihydrogen ligand interaction studies

In an attempt to synthesize complexes containing dihydrogen ligands that exhibit bonding patterns of the geometry shown in Fig. 1, 1 was exposed to organic bases, namely pyridine and 2,4,6-collidine. Essentially, the lone pair of electrons on the nitrogen atom in the base could interact with the  $(H_2)$  ligand and potentially lend stability to an asymmetrical dihydrogen relative to the metal.

NMR samples were prepared consisting of 1, benzene- $d_6$  as the solvent, and one of the following added: one equivalent of pyridine, an excess of pyridine, 1 equiv. of 2,4,6-collidine, or an excess of 2,4,6-collidine. Each sample was subjected to <sup>1</sup>H NMR  $T_1$  inversion-recovery experiments at room temperature. In attempts to obtain crystals featuring this interaction, 1 was dissolved in benzene in a 1/4" I.D. tube and layered with a mixture of pyridine and MeOH.

# 2.4. HD exchange reaction

HD exchange for the dihydrogen ligand was performed on 1 by dissolving the compound in benzene and stirring overnight under HD gas generated by reacting sodium hydride with deuterated water.

# 2.5. X-ray structural analysis

Crystals of 2 acetone were obtained from a solution of 2 in acetone layered with hexane. Crystals of *trans*dioxo-[ReO<sub>2</sub>(Py)<sub>4</sub>][OH]·1.75H<sub>2</sub>O (4·1.75H<sub>2</sub>O) were obtained by placing 1 in a solution of 30% benzene, 20% pyridine, 20% water, and 30% hexane. This was done in an attempt to obtain crystals displaying pyridine interacting with a dihydrogen ligand. Unfortunately, we were unaware of the presence of water in the py used and only after the structure was completed made this discovery and subsequent experiments were conducted with dry pyridine.

In both cases, crystals were removed from the mother liquor to a microscope slide where they were stabilized by immersion in a mixture of the mother liquor and mineral oil. The crystal was then rolled in epoxy and mounted on the head of a thin glass fiber on a goniometer mounting pin. The pin mounted crystal is then inserted into the goniometer head of the X-ray diffractometer and centered in the beam path. Standard

	2	4
Chemical formula	C <sub>52</sub> H <sub>54</sub> BrP <sub>4</sub> Re·C <sub>3</sub> H <sub>6</sub> O	[(C <sub>5</sub> H <sub>5</sub> N) <sub>4</sub> O <sub>2</sub> Re][OH]·1.75H <sub>2</sub> O
Color	yellow	red
Habit	prism	oblong block
Size (mm <sup>3</sup> )	$0.30 \times 0.30 \times 0.15$	$0.40 \times 0.05 \times 0.05$
Behavior	oxygen sensitive	loses moisture to atmosphere
<i>a</i> (Å)	11.706(2)	30.758(4)
b (Å)	14.227(2)	9.149(3)
c (Å)	17.304(4)	18.035(5)
α (°)	76.499(17)	90
$\beta$ (°)	71.486(17)	107.967(19)
γ (°)	83.346(13)	90
$\lambda$ (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\overline{1}$	C2/c
Ζ	2	8
Type of diffractometer	Nonius Turbo CAD4 diffractometer	Nonius Turbo CAD4 diffractometer
Method of data collection	$\omega$ –2 $\theta$	ω
Total number of data collected	7331	4310
R <sub>int</sub> value	0.012	0.022
Number observed (cut-off parameter)	6453 with $> 2\sigma(I)$	2630 with $> 2\sigma(I)$
$2\theta$ value	45	50
Absorption correction <sup>a</sup>	psi scans	psi scans
R <sup>b</sup>	0.032	0.053
R <sub>w</sub> <sup>c</sup>	0.096 <sup>d</sup>	0.175 °
Number of parameters	554	286
Form of refinement	$F^2$	$F^2$
Treatment of hydrogens	fixed if refined	fixed if refined

<sup>a</sup> Ref. [11].

<sup>b</sup>  $R = \Sigma (F_{o} - F_{c}) / \Sigma (F_{o}).$ 

<sup>c</sup>  $R_{\rm w} = [\Sigma[w(F_{\rm o}^2 - F_{\rm c}^2)^2] / \Sigma[w(F_{\rm o}^2)^2]]^{1/2}.$ 

<sup>d</sup>  $w = 1/[\sigma^2(F_o^2) + (0.1106P)^2 + 25.78P]$ , where  $P = (\max(F_o^2, 0) + 2F_o^2)/3$ .

 $^{e}w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0493P)^{2} + 8.98P], \text{ where } P = (\max(F_{o}^{2}, 0) + 2F_{c}^{2})/3.$ 

CAD4 centering, indexing, and data collection programs were utilized. Twenty-five reflections between 10 and 15° in  $\theta$  were located by a random search pattern, centered, and used in indexing. The cell constants and orientation matrix were thus obtained and refined by a least-squares fit. The scan width for each reflection and the scan rate were dependent on the intensity of the observed diffraction signal. During data collection, three intensity standards and three orientation standards were measured at regular intervals to measure the rate of decay of the crystal and to accommodate for crystal movement.

In both cases, data were first reduced and corrected for absorption using psi-scans [11] and then solved using the program DIRDIF-96 [12]. The models were then refined using SHELXL-97 [13]. The refinement of **2** was straightforward and it was clear from the outset that there was a disorder between the Br and the H<sub>2</sub> ligands. Evidence for an acetone molecule of solvation was also present in the original solution. The Br disorder was accounted for by constraining the sum of the occupancies at both sites to be unity and allowing a free refinement of the occupancies to derive the final quantities. In the final model there was no evidence of electron density that would represent a disordered Cl atom bonded to the Re, thus, the crystal used was pure **2**.

With 4, it was clear that apart from the two Recontaining cations, there were several regions of electron density that could be defined as either water molecules or hydroxide anions. These atoms were refined first with isotropic and then some with anisotropic thermal parameters to convergence. It was clear due to elongated thermal ellipsoids that some of these water molecules were split. Indeed two of these atoms were refined this way. In the final cycles of refinement, H-atoms (apart from those on the O atoms belonging to the hydroxide anions and the water molecules) were fixed at ideal positions with common isotropic displacement parameters ( $U_{iso} = 0.05$ Å<sup>2</sup>) and this was the final model. The crystallographic data for 2 and 4 are listed in Table 1.

# 3. Results

## 3.1. Synthesis

The synthesis of  $\text{ReBr}(H_2)(\text{PMePh}_2)_4$  (2) was accomplished by a metathesis type reaction of 1 with a massive excess of KBr in a 4:1 vol/vol mixture of THF + MeOH over a period of 3 days under argon at room temperature. The pale green product was a mixture of 1 and 2 with the bromide analogue dominating by more than 80%. Attempts to increase the yield of the reaction by varying the solvent and temperature were unsuccessful. The synthesis of  $ReI(H_2)(PMePh_2)_4$  (3) was performed similarly to that of 2 by exposing 1 to a large excess of KI in a 4:1 mixture of THF + MeOH for 3 days under argon at room temperature. 3 dominated the products of this reaction by roughly 70% judging by the relative intensity of the NMR signals in the hydride region. Variance in the above reaction conditions did not change the product distribution in favor of the bromo or iodo analogues.

#### 3.2. NMR studies

The signal in the <sup>1</sup>H NMR hydride region shifts steadily to the right as the size of the halogen trans to the dihydrogen ligand is increased and the electronegativity of said halogen decreases.  $J_{\rm HP}$  displays a slight increasing trend as shown in Table 2. An increase in

 $J_{\rm HP}$  has been suggested to be associated with a more hydridic nature in the H<sub>2</sub> ligand [14] and this would imply that going from Cl to I results in a more hydridic nature in the H···H ligand on complexes 1, 2 and 3.

#### 3.3. HD exchange reactions

Hydrogen-deuterium coupling constants can be a source of information about how the hydrogens in a dihydrogen ligand interact with each other. Larger coupling constants have been suggested to indicate greater interaction and thus more non-classical behavior. This has been shown to be the case for those complexes whose neutron diffraction structures are known [2]. HD exchange of the  $H_2$  ligand in 1 produced mixed samples of ReCl(H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub> and ReCl(HD)(PMePh<sub>2</sub>)<sub>4</sub>. This exchange was accomplished by producing HD gas from the reaction of NaH and D<sub>2</sub>O and allowing the gas to pass through a liquid nitrogen trap and then react with 1 dissolved in benzene.

Fig. 2 displays the <sup>1</sup>H NMR spectrum of a sample of 1 upon which partial HD exchange has been performed. The  $H_2$  signal from 1 is visible as a quintet at  $\delta$  -8.55 and the HD resonance, also a quintet, is shifted to the right and centered at  $\delta - 8.60$ .

The HD quintet appears broad in the above spectra and it was thought that the H<sub>2</sub> quintet could be masking the HD coupling pattern. In an effort to resolve the complexity of the HD peaks, the  ${}^{1}H{}^{31}P{}$  NMR spec-

Table 2

J<sub>HP</sub> for ReCl(H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub>, ReBr(H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub>, ReI(H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub>

Compound	Chemical shift in acetone (ppm)	Coupling constant (Hz)	Pauling <sup>a</sup> electronegativity
ReCl(H <sub>2</sub> )(PmePh <sub>2</sub> ) <sub>4</sub>	-8.55	19.2	3.0
$ReBr(H_2)(PmePh_2)_4$	-9.1	20.0	2.8
ReI(H <sub>2</sub> )(PMePh <sub>2</sub> ) <sub>4</sub>	-9.35	20.5	2.5

<sup>a</sup> For the *trans* halogen [15].



Fig. 2. 400 MHz <sup>1</sup>H NMR of ReCl(H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub> and ReCl(HD)(PMePh<sub>2</sub>)<sub>4</sub> in benzene-d<sub>6</sub>.



Fig. 3. 400 MHz <sup>1</sup>H{<sup>31</sup>P} NMR of ReCl(H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub> and ReCl(HD)(PMePh<sub>2</sub>)<sub>4</sub> in benzene-d<sub>6</sub>

trum was collected and is shown below in Fig. 3. The  $H_2$  and HD peaks appear at  $\delta - 8.55$  and - 8.60 again, respectively. The HD peak is still broad here and partially obscured by the dihydrogen signal. The broadness of this peak may be suggestive of some HD coupling, but this is not resolved in our spectra. The analogous arsine compound, ReCl(HD)(AsMePh<sub>2</sub>)<sub>4</sub>, (where the HD signal is also to the right of the HH complex) displays a  $J_{HD}$  of 4 Hz [16].

Attempts to separate the two peaks by lowering the temperature caused the signals to coalesce. Further experiments were performed in which the delay time between the 90° pulse and the FID collection was varied so that only the species that relaxed more slowly [2] (i.e. the HD compound as D is not as effective as H in the  $T_1$  relaxation mechanism) would be observed. This experiment was not successful, as the peak assigned to the HD complex appeared to be decreasing in intensity relative to the other peak which would mean that it was relaxing faster than that assigned as the H-H complex. At this point it is not known if this was a complication due to inadequacies in our NMR probe design or if it is a meaningful experiment. Further, measurements at lower temperatures were complicated by the fact that the two resonances merged which hindered obtaining cleanly resolved spectra.

# 3.4. NMR study of metal-bonded dihydrogen to lone pair interactions

Transition metal hydrides have been shown to form unconventional intermolecular bonds with amine and alcohol hydrogens [6–10,17]. A pictorial representation of this for cases involving N atoms is displayed in Fig. 4. The difference between the left system and metalbound dihydrogens forming H-bonds with amines may only be one of degree, however, to our knowledge, the interaction on the right has never been observed previously (and certainly not by the  $T_1$  technique). To test this hypothesis, pyridine and 2,4,6-collidine were reacted with 1 to observe their interactions. Figs. 5 and 6 display <sup>1</sup>H NMR spectra of **5** with one equivalent and an excess of pyridine added, respectively.

The normal dihydrogen quintet can be observed at  $\delta$ -8.55 ppm along with what appears to be a doublet of triplets centered at  $\delta - 7.6$  ppm. As more pyridine is added, the new signals centered at  $\delta - 7.6$  ppm, grow in intensity and gradually replace the dihydrogen quintet completely when a sufficient excess is added. With excess pyridine, the resonance at  $\delta - 7.6$  resolves into a pair of triplets located at  $\delta$  - 7.88 and - 7.97. Each hydrogen is split by two phosphorous atoms with a different coupling constant for each splitting (14.2 and 15.2 Hz). This may be attributed to the displacement of two phosphine ligands with pyridine. One way of accounting for these resonances is by having the hydrogens on the metal in differing electronic environments with each forming a triplet from splitting by the two remaining phosphorus atoms and no (or very small) coupling between the different H-atoms. A drawing for this hypothetical complex, which we could not isolate or crystallize, is shown in Fig. 7.



Fig. 4. Intermolecular hydrogen bonding involving metal-hydrides.





Fig. 6. 400 MHz <sup>1</sup>H NMR of ReCl(H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub> with excess pyridine in acetone-d<sub>6</sub>.

When 2,4,6-collidine is added to 1, no changes in either the <sup>1</sup>H (hydride region) or <sup>31</sup>P spectra are observed. This suggests that no displacement of the phosphine ligands occurred.

Room temperature  $T_1$  data for the metal bound hydrogens of 1, 1 interacting with pyridine, 1 interacting with 2,4,6-collidine, ReCl(H)<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>(Py)<sub>2</sub> (5), ReH<sub>3</sub>(PMePh<sub>2</sub>)<sub>4</sub> (6) [18], and 6 interacting with pyridine are shown in Table 3.

Collidine had no effect on the dihydrogen ligand of 1, while pyridine decreased the  $T_1$  time for the ligand. Curiously, the dihydrogen quintet did not change location in the <sup>1</sup>H NMR spectrum, removing the possibility of phosphine ligand displacement as an explanation of the decrease in  $T_1$  time. This would imply that the nitrogen lone pair of the pyridine may be interacting very weakly with the metal-bound hydrogens of 1 albeit sufficient enough to slow down the rate of rotation. It is also possible that the addition of pyridine resulted in the formation of an unidentified paramagnetic species which reduced the  $T_1$  time for the H<sub>2</sub> ligand in 1. However, 5, in the same NMR tube, displayed markedly greater relaxation times for both triplets indi-



Fig. 7. ReCl(H)<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>(Py)<sub>2</sub>.

Table 3  $T_1$  NMR data for 1, 1 w/pyridine, 1 w/collidine, 5, 6 and 6 w/py in acetone- $d_6$  at 25°C

Compound	$T_1$ value (ms)	Error (ms)
ReCl(H <sub>2</sub> )(PMePh <sub>2</sub> ) <sub>4</sub>	147.0	1.8
ReCl(H <sub>2</sub> )(PMePh <sub>2</sub> ) <sub>4</sub> w/pyridine	138.4	1.2
ReCl(H <sub>2</sub> )(PMePh <sub>2</sub> ) <sub>4</sub> w/collidine	147.1	1.8
$\operatorname{ReCl}(H)_2(\operatorname{PMePh}_2)_2(\operatorname{Py})_2$	186.8 ( $\delta$ -7.88), 183.4 ( $\delta$ -7.97)	2.1, 2.3
ReH <sub>3</sub> (PMePh <sub>2</sub> ) <sub>4</sub>	218.7	5.1
ReH <sub>3</sub> (PMePh <sub>2</sub> ) <sub>4</sub> w/pyridine	216.8	6.6

cating a transition towards a classical dihydrogen ligand. Therefore, the ligand substitution of two methyldiphenylphosphine ligands by pyridine appears to be unrelated to the decrease in  $T_1$  NMR time for the quintet at  $\delta - 8.55$  ppm. ReH<sub>3</sub>(PMePh<sub>2</sub>)<sub>4</sub>, a known classical polyhydride [18], was also evaluated for possible interaction with pyridine, but no change in relaxation time was observed. This removes from consideration classical hydrogen to pyridine interactions as well as interactions with the tertiary phosphine ligands.

# 3.5. Variable temperature $T_1$ (min) of 1, 2 and 3

 $T_1$  (min) data for 1, 2 and 3 can be found in Table 4. As a means of testing the current method and instrumentation, the  $T_1$  (min) value for ReCl(H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub> was re-determined to be ~ 88 ms, which was slightly lower than the  $T_1$  (min) of 92 ms reported previously [3].

From a graph of the above data, one can by interpolation conclude that the  $T_1$  (min) for 2 is 62 ms and 3 is 101 ms at 400 MHz. Given the difficulties with scaling for rhenium complexes, these values may indicate that 2 has a less classical H<sub>2</sub> ligand and 3 possesses a more classical H<sub>2</sub> ligand than 1. In changing the

Table 4								
Variable	temperature	$T_1$	values	for	1,	2	and	3

Theoretical Ion Distribution: [ReBr(H₂)(PMePh₂)₄]<sup>+</sup>



Fig. 8. Theoretical ion distribution of the molecular ion  $[ReBr(H_2)(PMePh_2)_4]^+$ .

halogen trans to the dihydrogen ligand in ReX(H<sub>2</sub>)- $(PMePh_2)_4$ , the ability of the halogen to donate  $\sigma$ -electron density to the metal increases with the steric bulk of the halogen [19]. The data suggest that the electronic effects may be in competition with steric crowding effects in these molecules. 2, by virtue of the lowest  $T_1$ (min) at 62 ms, shows itself to possess greater molecular dihydrogen character than the parent complex. The greater size of the bromide ligand compared to the chloride may be forcing the hydrides closer together in spite of greater electron donation on the part of the bromide. This trend is reversed where 3 is concerned. Based on the  $T_1$  data, ReI(H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub> displays more classical H<sub>2</sub> ligand behavior than does ReCl(H<sub>2</sub>)- $(PMePh_2)_4$ . The iodide ligand's ability to donate electron density appears to outweigh steric considerations in this case and thus more extensive  $\sigma$ -donation by iodide results in an increased  $d-\pi^*$  metal-dihydrogen interaction.

## 3.6. Mass spectral analysis

FABMS was performed on a sample of compound **2** and Fig. 8 displays the theoretical ion distributions (TID) for a molecular ion of this complex.

TIDs are determined by the relative abundance of isotopes of the component elements of the expected sample. The peak profiles are then compared to the

Temperature (°C)	$T_1$ (ms) for ReCl(H <sub>2</sub> )(PMePh <sub>2</sub> ) <sub>4</sub> in CD <sub>2</sub> Cl <sub>2</sub>	$T_1$ (ms) for ReBr(H <sub>2</sub> )(PMePh <sub>2</sub> ) <sub>4</sub> in CD <sub>2</sub> Cl <sub>2</sub>	$T_1$ (ms) for ReI(H <sub>2</sub> )(PMePh <sub>2</sub> ) <sub>4</sub> in acetone- $d_6$
25	123.7	105.9	173.1
5	107.0	74.08	133.7
-5		63.46	
-15	89.91	62.28	113.2
-25		66.29	
-35	80.36	78.51	100.9
-45		88.53	101.3
-55	96.89		106.1
-75			121.5



Fig. 9. FABMS of ReBr(H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub> in acetone and 3-nitrobenzyl alcohol.

FABMS output to see if they are a good match at the mass points of interest. A section of a FABMS analysis of **2** is displayed in Fig. 9. The peaks located around 1017 are due to contamination of the sample with complex **1**.

The molecular ion pattern for **2** is centered at 1068 m/z as expected and thus we can conclude that the molecular ion for **2** under these conditions is simply the ionized version of the molecule, i.e. [ReBr(H<sub>2</sub>)-(PMePh<sub>2</sub>)<sub>4</sub>]<sup>+</sup>.

# 3.7. Structural results

Crystals of **2** were obtained in crystalline form with one molecule of acetone per Re-containing molecule in the unit cell. The geometry of the molecule is distorted octahedral with two trans phosphine ligands lying above and two below the equatorial plane as depicted in Fig. 10. The average Re–P distance was 2.443 Å, which was somewhat longer than reported for **1** [1] (2.423 Å) in the same solvent, see Table 5. There was a disorder in the packing of the bromide ligand with halogens appearing trans to each other and perpendicular to the plane of the phosphine ligands with one bromide refined at 44% occupancy and the other at 56% occupancy. The P–Re–P (*trans* phosphines) angles were 168.36 and 169.29° for **2** compared to 169.18 and 163.36° for **1** in earlier studies [1].

It is also noteworthy that the two Re-Br distances in **2** of 2.6592(15) and 2.688(3) Å are significantly longer than those for the Re-Cl ligand in **1** at 2.568 (3) and 2.587(3) Å [1]. These are data from a conformer of **1** where the phosphine ligands adopted a conformation that resulted in a disordered packing arrangement. These distances can be compared to the Re-I distance

in 3 of 2.707(8) and 2.807(10) Å. These data were obtained in structural studies on a solid state solution of 1 and 3 [21]. Unfortunately, final figures of merit worthy of publication were not obtained with this determination, despite collecting data on crystals grown from different sources. The point here is that it is not clear how the different halide ligands would be better able to  $\sigma$ -donate electron density if the distance between them and the metal increases as is apparently the case with 1, 2 and 3 [19].

The compound *trans*-dioxotetrakis(pyridine)rhenium(V) hydroxide (4), Fig. 11, was obtained in crystalline form with approximately 2.0 water molecules per Re-containing cation. Two *trans*-dioxotetrakis-(pyridine)rhenium cations (with the Re atoms on inversion points and one O atom and two pyridine molecules per Re atom forming a complete cation), two O atoms on special positions and three other O atoms



Fig. 10. ORTEP3 [20] representation of  $ReBr(H_2)(PMePh_2)_4$  (2) without the acetone solvate.

Table 5 Selected bond distances (Å) and bond angles (°) for  $ReBr(H_2)\text{-}(PMePh_2)_4\text{-}(C_3H_6O)$ 

Bond longths			
Donu lengins Rel D2	2 4377 (16)	P2 C21	1 837 (2)
Re1 = 12 Re1 = 12	2.4377(10) 2.4421(16)	P2 C221	1.037(2) 1.841(6)
$\mathbf{R} = \mathbf{I} - \mathbf{I} \mathbf{J}$	2.4421(10) 2.4450(15)	P2 C211	1.840 (6)
$R_{0}$ $P_{1}$ $P_{1}$	2.4450(15)	$P_{2} = C_{21}$	1.049(0) 1.827(2)
Rel Br?	2.4400(10) 2.6502(15)	P3 C321	1.837(2) 1.842(6)
Rel-Di2 Rel Brl	2.0392(13)	P3 C311	1.842 (0)
$\mathbf{P}$	2.000(5)	P4 C411	1.800 (0)
P1-C121	1.858 (0)	P4-C411	1.850(0) 1.852(2)
P1 C11	1.855(0)	$P_{4} = C_{4}^{21}$	1.055(2)
ri-Cii	1.654 (2)	F4-C421	1.854 (0)
Bond angles			
P2-Re1-P3	90.33 (5)	C11-P1-Re1	113.43 (8)
P2-Re1-P4	169.29 (5)	C21-P2-C221	101.4 (2)
P3–Re1–P4	90.87 (5)	C21-P2-C211	96.3 (2)
P2-Re1-P1	90.80 (5)	C221-P2-C211	100.2 (3)
P3-Re1-P1	168.36 (5)	C21-P2-Re1	113.52 (8)
P4–Re1–P1	90.16 (5)	C221-P2-Re1	122.0 (2)
P2-Re1-Br2	94.91 (5)	C211-P2-Re1	119.1 (2)
P3-Re1-Br2	83.88 (5)	C31-P3-C321	103.1 (2)
P4-Re1-Br2	95.80 (5)	C31-P3-C311	96.1 (2)
P1-Re1-Br2	84.47 (5)	C321-P3-C311	99.7 (3)
P2-Re1-Br1	85.02 (6)	C31–P3–Re1	113.52 (8)
P3-Re1-Br1	96.29 (6)	C321-P3-Re1	120.79 (19)
P4–Re1–Br1	84.27 (6)	C311-P3-Re1	119.73 (19)
P1-Re1-Br1	95.35 (6)	C411-P4-C41	102.7 (2)
Br2-Re1-Br1	179.81 (6)	C411-P4-C421	100.0 (3)
C121–P1–C111	99.4 (3)	C41-P4-C421	96.08 (19)
C121-P1-C11	102.2 (2)	C411-P4-Re1	122.3 (2)
C111–P1–C11	96.72 (19)	C41-P4-Re1	113.23 (4)
C121-P1-Re1	121.15 (19)	C421-P4-Re1	118.4 (2)
C111-P1-Re1	119.90 (19)		



Fig. 11. ORTEP3 [20] representation of the two  $[\text{ReO}_2(\text{py})_4]^+$  cations in **4**.

assigned as water molecules constitute the asymmetric unit. We were unable to determine which O atoms represented the hydroxide anions. The geometry around both Re atoms is octahedral with the four N atoms of the pyridine molecules and the Re atom defining the equatorial plane. There is no significant difference in the two Re–O bond lengths for the two cations.

4 was obtained in an experiment which was designed to produce material that would exhibit H-bonding between the dihydrogen ligand in 1 and the lone pair on the pyridine molecule. Unfortunately, despite NMR evidence that such an interaction may take place under stoichiometric quantities of 1 and pyridine, under the conditions of this particular experiment, ligand substitution of PMePh<sub>2</sub> by pyridine, oxidation of the Re atom, reaction with water and chloride and dihydrogen molecule displacement must have taken place to produce **4**.

There was a previous study of this cation obtained with a chloride counter anion and as a dihydrate [22]. Here the atoms in the Re-containing cation were located on general positions and it is noteworthy that the unit cell dimensions (monoclinic, Cc, a = 13.577 (4), b = 11.951 (3), c = 15.498 (4) Å,  $\beta = 116.3$  (1)°) are very different from those obtained in this study. However the density at 1.79 (1) g cm<sup>-3</sup> is similar to that obtained in this study at 1.718 g cm<sup>-3</sup> and this indicates a similar tight packing arrangement. The average of the Re-O distances at 1.764 (13) Å, see Table 6, obtained in that study are similar to those of Re1-O1 and Re2-O2 at 1.767 (8) and 1.765 (9) Å, respectively, in this study. Further, the range of Re-N distances at 2.139 (9)–2.166 (14) Å in the dihydrate study is also similar to those obtained in this report at 2.131 (11)-2.150 (11) A.

#### 4. Conclusions

The synthesis and characterization of ReBr(H<sub>2</sub>)-(PMePh<sub>2</sub>)<sub>4</sub> and ReI(H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub> was accomplished with this work. The  $T_1$  (min) times for these compounds were assessed and found to be 62 and 101 ms, respectively. These data would suggest a more

Table 6

Selected Bond distances (Å) and bond angles (°) for  $[(C_5H_5N)_4O_2Re]-[OH]\cdot 1.75H_2O$ 

Bond lengths			
Re1–O1	1.767 (8)	N1-C15	1.339 (18)
Re1-N1	2.140 (10)	N2-C25	1.319 (18)
Re1–N2	2.142 (11)	N2-C21	1.337 (17)
Re2–O2	1.765 (9)	N3-C35	1.39 (2)
Re2–N3	2.131 (11)	N3-C31	1.41 (2)
Re2–N4	2.150 (11)	N4-C41	1.320 (18)
N1-C11	1.313 (17)	N4-C45	1.341 (16)
Bond angles			
O1-Re1-N1	89.9 (4)	C25-N2-C21	116.1 (13)
O1-Re1-N2	90.1 (4)	C25-N2-Rel	122.7 (10)
N1-Re1-N2	90.8 (4)	C21-N2-Re1	121.0 (10)
O2–Re2–N3	89.5 (5)	C35-N3-C31	119.1 (15)
O2-Re2-N4	89.9 (4)	C35–N3–Re2	120.0 (11)
N3-Re2-N4	91.3 (4)	C31-N3-Re2	120.8 (12)
C11-N1-C15	117.3(12)	C41-N4-C45	118.6 (12)
C11-N1-Re1	122.4 (9)	C41-N4-Re2	120.3 (9)
C15–N1–Re1	120.2 (10)	C45–N4–Re2	121.0 (9)

classical dihydrogen ligand for the iodo complex and a less classical dihydrogen ligand for the bromo complex relative to the parent complex,  $\text{ReCl}(\text{H}_2)(\text{PMePh}_2)_4$ . The  $J_{\text{HP}}$  values for the compounds increase as the halogen is changed from Cl at 19.2 Hz, Br at 20.0 and I at 20.5 Hz. and the  $J_{\text{HD}}$  values for the HD exchanged version of the chloro analog could not be observed. The  $J_{\text{HP}}$  results suggest that the H<sub>2</sub> ligand may be adopting a more hydridic nature and this is at variance with the  $T_1$  min results. Our studies here considering the values for the  $T_1$  minimum and  $J_{\text{HP}}$  suggest that the Br complex **2** is not following the expected trends.

Some evidence suggestive of an  $\eta^1$ -H<sub>2</sub> ligand was obtained by novel  $T_1$  studies aimed at investigating the interaction of the dihydrogen ligand on 1 with the lone pair on the N-atom of pyridine and 2,4,6-collidine. The more hindered base displayed no interaction with the rhenium compound while pyridine showed two effects. First, the pyridine slightly lowered the  $T_1$  value of the dihydrogen ligand (original quintet) and second, it displaced phosphine ligands on the parent compound perhaps to form 'ReClH<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>(Py)<sub>2</sub>'. These effects are separate and not related. The  $T_1$  time reduction may be indicative of a hydrogen-lone pair interaction between the metal-dihydrogen complex and the nitrogen of the organic base. Clearly more studies with other dihydrogen compounds are needed in order to substantiate that conclusion. Perhaps the effect only pertains to stretched dihydrogen compounds.

The relationship between the halogen trans to a dihydrogen ligand and the nature of the dihydrogen ligand would appear to be more complex than had been previously reported [23]. The electronegativity, orbital overlap, and steric bulk of the atoms involved all combine to produce a pattern of behavior that defies simplistic models. These competing effects merit further halogen substitution studies with more rigid bidentate-diphosphine ligands [4]. Our results here are also at odds with earlier work on complexes of the series  $IrX(H_2)H_2(PR_3)_2$  [23–25]. It must be noted that the iridium complexes have a much less crowded coordination sphere than does the system studied herein.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 142490 for **2** and 142491 for **4**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam. ac.uk).

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