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Research paper

Fluxionality, substitution, and hydrogen exchange at eight-coordinate rhenium(V) polyhydride centers

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ABSTRACT

Towards a better understanding of the dynamic processes within eight-coordinate rhenium pentahydride complexes, a set of eight-coordinate rhenium(V) pentahydride complexes supported by two triphenylphosphine ligands and either a bidentate amine with a pendant functional group (1,2-diaminoethane, 1,3-diaminopropane, 2-aminoethanol) or by an unsymmetrically-substituted aromatic amine ligand (3-aminopyridine or 3-picoline) was prepared from thermolysis reactions of $ReH_7(PPh_3)_2$. Variable temperature ^1H NMR spectroscopy and simulation of those results indicate a previously uncharacterized exchange of hydrogen between the unique hydride ligand residing in a dodecahedral B site and hydrogen atoms from adventitious water. The same data also indicate two processes for hydride ligand fluxionality and a process for isomer interconversions of the complexes supported by an unsymmetrically substituted aromatic amine ligand. The hydride exchange process that exchanges A site hydride ligands also exchanges B site ligands. The likely mechanism for the A and B site atom exchanges involves concerted, successive, inversions of the A site ligands into B sites and concomitant inversions of B site ligands into A sites of the D_{2d} dodecahedron. Values of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for all of the dynamic processes were determined.

1. Introduction

Rhenium polyhydride complexes catalytically transform small molecules through reductive coupling reactions that include C—H bond activation or through other mechanisms [1–8]. Foundational studies on the chemistry of rhenium polyhydride complexes demonstrate that these complexes interact readily with hydrogen in a variety of environments by: (1) catalytically transferring molecular hydrogen from one small molecule to another small molecule [9–11], (2) forming rhenium-carbon bonds at rhenium polyhydride centers, oftentimes through insertion into C—H bonds [12–19], and (3) participating in intermolecular exchange of hydride ligands with the hydride ligands of second metal centers, the exchangeable protons of water, alcohols or amines, or the aromatic protons of molecules such as benzene, toluene, or tertiary phosphines [20–24]. As a foundational part of understanding the transformative chemical properties of rhenium polyhydride complexes there is a need to thoroughly understand the physical and chemical properties of these complexes. The physical properties of rhenium polyhydride complexes can be complex because of dynamic processes such as intramolecular ligand fluxionality or isomer interconversions and because of intermolecular exchange of hydrogen atoms in the rhenium coordination sphere with hydrogen atoms in the solvent matrix [12]. Previous work has presented several mechanisms for the fluxionality of hydride ligands and isomer interconversions at eight coordinate rhenium polyhydride complexes [14,25–32]. This study primarily uses variable temperature NMR spectroscopy to determine the activation parameters for inner sphere ligand rearrangements and intermolecular hydrogen exchanges at eight-coordinate rhenium(V) pentahydride complexes. Four of the five new complexes examined include a ligand with a pendant functional group. Pendant functional groups often promote hydrogen exchange reactions in similar complexes [33–36].

2. Experimental

2.1. General

NMR spectra were acquired with deuterated toluene as the solvent using standard pulse sequences on a Bruker AVANCE 400 NMR spectrometer. NMR spectra were simulated with the program TEDDY –

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Dynamic NMR Module version 1.1.2. Syntheses were performed using Schlenk techniques under an atmosphere of nitrogen. Reagents were purchased from Sigmaaldrich. The complexes $ReH_5(PPh_3)_3$ and $ReH_7(PPh_3)_2$ were prepared using standard synthetic routes [20,23].

2.2. $ReH_5(PPh_3)_2(\eta^1\text{-}NH_2CH_2CH_2NH_2)$

The complex $ReH_7(PPh_3)_2$, 57 mg, was added to a 50 mL round-bottomed flask. The solid was dissolved in a mixture of 5 mL of deoxygenated THF and 0.5 mL of 1,2-diaminoethane, refluxed for 30 min, and then cooled to room temperature. The addition of 25 mL of methanol followed by 10 mL of water induced a yellow precipitate which was collected by filtration, 35 mg or 57% yield. Anal. Calcd for $C_{38}H_{43}N_2P_2Re$: C, 58.82; H, 5.59; N 3.61. Found: C, 59.10; H, 5.85; N, 3.58. $^1H\text{-}\{^{31}P\}$ NMR (C_7D_8, 220 K): −2.06 (s, 1H, H1), −2.94 (s, 2H, H2,H2), −7.91 (s, 1H, H3), −8.35 (s, 1H, H4), 8.13 (d 6.0 Hz, 12H, *o*-Ph), 7.10–6.98 (m, 18H, *m*- and *p*-Ph), 1.42 (s, 2 H, Re-NH_2), 1.31 (s, 4 H, C(1)H_2 and C(2)H_2), −0.56 (s, 2 H, pendant-NH_2). $^{31}P\text{-}\{^1H\}$ NMR (C_7D_8, 220 K): 48.13 (s).

2.3. $ReH_5(PPh_3)_2(\eta^1\text{-}NH_2CH_2CH_2CH_2NH_2)$

This compound was prepared in a method similar to 2.2 starting from 54 mg of $ReH_7(PPh_3)_2$ with the use of 50 mL of methanol and 25 mL of water to induce precipitation, 31 mg or 52% yield. Anal. Calcd for $C_{40}H_{46}NP_2Re$: C, 59.30; H, 5.74; N 3.55. Found: C, 59.10; H, 5.82; N, 3.58. $^1H\text{-}\{^{31}P\}$ NMR (C_7D_8, 220 K): −2.22 (s, 1H, H1), −2.96 (s, 2H, H2,H2), −7.94 (s, 1H, H3), −8.22 (s, 1H, H4), 8.14 (s, 12H, *o*-Ph), 7.12–7.00 (m, 18H, *m*- and *p*-Ph), 1.79 (s, 2 H, Re-NH_2), 0.97 (s, 2 H, C(1)H_2), 1.10 (s, 2 H, C(2)H_2), 1.46 (s, 2 H, C(3)H_2), 0.14 (s, 2 H, pendant-NH_2). $^{31}P\text{-}\{^1H\}$ NMR (C_7D_8, 220 K): 47.96 (s).

2.4. $ReH_5(PPh_3)_2(\eta^1\text{-}NH_2CH_2CH_2OH)$

This compound was prepared in a method similar to 2.2 from 54 mg of $ReH_7(PPh_3)_2$ using 50 mL of methanol and 25 mL of water, 29 mg or 50% yield. Anal. Calcd for $C_{38}H_{42}NOP_2Re$: C, 59.99; H, 5.28; N 1.75. Found: C, 60.24; H, 5.47; N, 1.64. $^1H\text{-}\{^{31}P\}$ NMR (C_7D_8, 230 K): −2.15 (s, 1H, H1), −2.95 (s, 2H, H2,H2), −7.98 (s, 1H, H3), −8.47 (s, 1H, H4), 8.10 (d 7.1 Hz, 12H, *o*-Ph), 7.09–6.98 (m, 18H, *m*- and *p*-Ph), 2.19 (s, 2 H, Re-NH_2), 1.49 (s, 2 H, C(1)H_2), 1.42 (s, 2 H, C(2)H_2), −0.43 (s, 1H, pendant-OH). $^{31}P\text{-}\{^1H\}$ NMR (C_7D_8, 230 K): 47.51 (s).

2.5. $ReH_5(PPh_3)_2$(3-picoline)

This compound was prepared in a method similar to 2.2 from 51 mg of $ReH_7(PPh_3)_2$ using 50 mL of methanol and 20 mL of water, 18 mg or 31% yield. Anal. Calcd for $C_{42}H_{42}NP_2Re$: C, 62.36; H, 5.23; N 1.73. Found: C, 62.36; H, 5.47; N, 1.64. $^1H\text{-}\{^{31}P\}$ NMR (C_7D_8, 210 K): (−0.50 and −0.62) (s and s, 1H combined, H1), (−1.67 and −1.72) (s and s, 2H combined, H2,H2), −7.55 (s, 1H, H3), −8.14 (s, 1H, H4), 8.07 (s, 12H, *o*-Ph), 7.03–6.92 (m, 18H, *m*- and *p*-Ph), 1.35 (s, 1.4 H, *E*-CH_3), 0.99 (s, 1.6 H *Z*-CH_3), 8.28 (s, 0.55H, *Z*-pic-C(2)H), 8.14 (s, 0.45H, *E*-pic-C(2)H), 6.04 (d 5.4 Hz, 0.45H, *E*-pic-C(4)H), 5.98 (d 6.0 Hz, 0.55H, *Z*-pic-C(4)H), 5.62 (t 6.1 Hz, 0.55H, *Z*-pic-C(5)H), 5.32 (t 6.6 Hz, 0.45H, *E*-pic-C(5)H), 7.73 (d 7.0 Hz, 0.55H, *Z*-pic-C(6)H), 7.66 (d 7.0 Hz, 0.45H, *E*-pic-C(6)H). $^{31}P\text{-}\{^1H\}$ NMR (C_7D_8, 210 K): 47.07 (s, 0.90P, *E*-isomer), 46.69 (s, 1.10P, *Z*-isomer).

2.6. $ReH_5(PPh_3)_2$(3-aminopyridine)·1/2H_2O

This compound was prepared in a method similar to 2.2 from 54 mg of $ReH_7(PPh_3)_2$ with a 15 min reflux followed by a filtration into 50 mL of methanol and the addition of 20 mL of water, 25 mg or 41% yield. The purpose of the filtration was to remove a black solid that formed during the reflux period. The presence of the hemihydrate was determined by ^1H NMR spectroscopy. Anal. Calcd for $C_{41}H_{42}N_2O_{0.5}P_2Re$: C, 60.13; H, 5.18; N 3.42. Found: C, 60.36; H, 5.09; N, 3.15. $^1H\text{-}\{^{31}P\}$ NMR (C_7D_8, 210 K): (−0.46 and −0.65) (s and s, 1H combined, H1), −1.71 (s, 2H, H2,H2), (−7.55 and −7.60) (s and s, 1H combined, H3), −8.21 (s, 1H, H4), 8.10 (d 9.0 Hz, 12H, *o*-Ph), 7.03–6.90 (m, 18H, *m*- and *p*-Ph), (2.08 and 1.51) (s and s, 2 H combined, NH_2), (5.55 and 5.45) (s and s, 1H combined, 3-ampy-C(2)H), (7.72 and 7.66) (d 7.2 Hz and d 7.2 Hz, 1H combined, *Z*-3-ampy-C(4)H), 7.38 (m , 1H, *E*-3-ampy-C(5)H), (5.40 and 5.30) (s and s, 1H, 3-ampy-C(6)H). $^{31}P\text{-}\{^1H\}$ NMR (C_7D_8, 210 K): 47.09 (s, 1.12P, isomer one), 46.40 (s, 0.88P, isomer two).

3. Results

3.1. Syntheses

Reactions between $ReH_7(PPh_3)_2$ and 1,2-diaminoethane (en), 1,3-diaminopropane (pn), and 2-aminoethanol (MET), result in the complexes $ReH_5(PPh_3)_2(NH_2R)$ where R = $CH_2CH_2NH_2$, $CH_2CH_2CH_2NH_2$, or CH_2CH_2OH respectively. The identities of the three complexes were established by low temperature $^1H\text{-}\{^{31}P\}$ NMR spectroscopy. The presumed dodecahedral structure of each complex and hydride ligand locations are shown in Fig. 1. (A description of the D_{2d} dodecahedral representations presented in Fig. 1 and elsewhere is found in the Supporting Material.) A low temperature $^1H\text{-}\{^{31}P\}$ NMR spectrum (220 K) for $ReH_5(PPh_3)_2$(en) is typical for these complexes (Fig. 2) [30]. The spectrum consists of four hydride resonances (−2.05, −2.94, −7.90, and −8.32 ppm) with relative integrated areas of 1:2:1:1 respectively. The spectrum also includes a resonance at −0.56 ppm (pendant NH_2, two protons), two overlapping resonances at 1.31 ppm (tentatively both CH_2 groups, four protons), and a resonance at 1.42 ppm (tentatively the rhenium-bound amine group, two protons). All of the hydride, amine, and methylene protons appear as relatively broad singlets in the 220 K $^1H\text{-}\{^{31}P\}$ spectrum.

The reactions of $ReH_7(PPh_3)_2$ with aromatic amines are widely reported [14,20,29,30,37–39]. The aromatic amine reactants used in this study, 3-picoline and 3-aminopyridine, were selected with unsymmetrical substitution located away from the rhenium center to minimize interactions between the substituent groups and the hydride ligands. Preparations of the new aromatic amine-supported complexes proceeded in a routine fashion and, as expected because of the unsymmetrical substitution on the aromatic amine ligand, *E* and *Z* isomers were observed for the products by low temperature NMR spectroscopy (Fig. 3) [14,40–43]. Several distinct *E* and *Z* isomer resonances were observed for the proton resonances of both compounds in low temperature $^1H\text{-}\{^{31}P\}$ NMR spectra (Fig. 4 and Experimental Section) as well as separate E and *Z* isomer resonances in the $^{31}P\text{-}\{^1H\}$ spectrum of each complex at low temperature. Justification for the D_{2d} dodecahedral structure of these complexes is provided in the Supporting Material.

3.2. Intramolecular and intermolecular hydrogen exchange

3.2.1. Intramolecular hydride ligand fluxionality

All five new rhenium(V) pentahydride complexes display the typical pattern of four hydride resonances at low temperature in their $^1H\text{-}\{^{31}P\}$

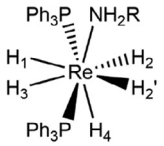

Fig. 1. The presumed D_{2d} dodecahedral structure of the aliphatic bifunctional complexes with hydride ligands labelled to correspond with the low temperature ^1H NMR resonances going from downfield to upfield.

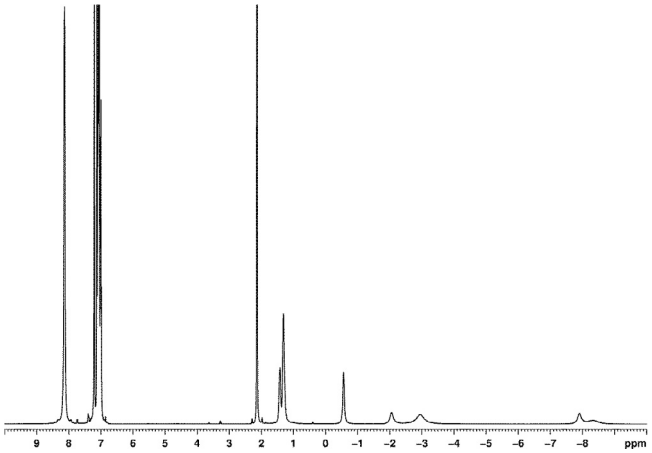

Fig. 2. The 220 K ^{1}H-{^{31}P} NMR spectrum of $ReH_5(PPh_3)_2$(en) measured in d_8-toluene.

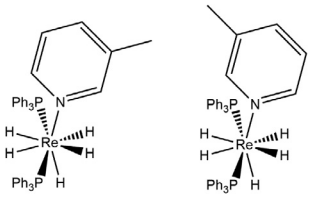

Fig. 3. The *E* (left) and *Z* (right) isomers of $ReH_5(PPh_3)_2$(3-picoline). The E and Z assignments refer to the steric relationship between the aromatic ring substituent and the PPh_3 groups with respect to the bond between Re and N.

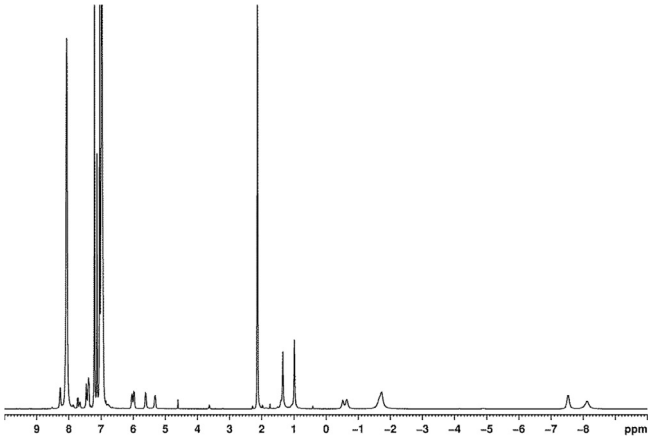

Fig. 4. The ^{1}H-{^{31}P} NMR spectrum of $ReH_5(PPh_3)_2$(3-pic) measured at 210 K.

NMR spectra corresponding to the patterns of other rhenium(V) pentahydride complexes supported by an amine ligand [14,30,32,38,39,44]. For temperatures at or near room temperature, the hydride region of the proton spectrum simplifies to a single broad resonance devoid of any indication of spin coupling with the rhenium-bound phosphorus atoms. At temperatures near 220 K, two-dimensional proton exchange spectroscopy (EXSY) with a 100 ms mixing time gives results that are consistent with hydride ligand exchange among all hydride ligand locations (Supporting Material). At temperatures less than 260 K, the ^{1}H NMR hydride resonances from complexes supported by primary amine ligands were simulated (Fig. 5) using the software dNMR. For the ^{1}H-{^{31}P} hydride region simulations, the best model for hydride ligand fluxionality includes three independent hydrogen atom exchanges (Fig. 6). The model has a turnstile exchange of the H2 and H2′ hydride ligand pair with the unique B site hydride ligand H4 (Exchange α in Fig. 6). Exchange α has been described previously [25,29]. The second exchange in the model is an exchange of hydride ligands among the A sites in a pairwise fashion (Exchange β in Fig. 6). This pairwise exchange of A site hydride ligands has previously been described as a pseudorotation [25,29]. These two hydrogen atom exchanges produce good simulations of the hydride region of the ^{1}H-{^{31}P} spectrum except for the contribution from hydride ligand H4. Simulations of the H4 resonances appear too sharp for the experimental data based only on the pairwise and turnstile exchanges (Fig. 7). Inclusion of a third hydrogen exchange between H4 and an adventitious water proton (Exchange γ in Fig. 6) provides a good fit for the entire hydride region of all three ^{1}H-{^{31}P} spectra, at temperatures up to 250 K.

3.2.2. Intermolecular hydrogen exchange

Evidence of Exchange γ, the hydride for water-proton exchange, manifests itself in several aspects of the room temperature NMR spectra for a sample of $ReH_5(PPh_3)_2$(3-pic) (6 mg) in d_8-toluene (1.0 mL) when the sample is spiked with 10 μL of D_2O. In the room temperature ^{1}H-{^{31}P} spectrum, the hydride resonance (−3.98 ppm) (Fig. 8D) decreases in intensity by 32% in 69 min due to incorporation of deuterons from D_2O. The coalesced resonance near 0.43 ppm (Fig. 8C) shifts slightly downfield (due to the kinetic isotope effect) and decreases in intensity by 69% in 69 min due to incorporation of deuterons from D_2O. The key observation from the spectrum of the sample spiked with D_2O is the appearance of the lost ^{1}H intensity (lost from the hydride resonance and the coalesced "water" resonance at 0.43 ppm) in a new resonance that arises between 5 and 6 ppm (Fig. 8B). A water resonance between 5 and 6 ppm in room temperature toluene must arise from water in an unusual environment because the usual chemical shift for water in toluene is 0.4 ppm, very near the coalesced resonance which occurs at 0.43 ppm. The resonance between 5 and 6 ppm may arise from water that is closely associated with the rhenium complex, perhaps in the form of a molecular couple, or from water in some type of cluster arrangement. Similar water resonances between 5 and 6 ppm are apparent in ^{1}H-{^{31}P} spectra of analogous samples of $ReH_5(PPh_3)_2$(3-pic) or the other new pentahydride complexes, without a D_2O spike, at lower temperatures (240 K to 280 K) but not at room temperature. At room temperature, faster exchange of hydrogen (due to the lack of the heavier deuterium isotope) in the nonspiked samples, leads to coalescence of the resonance near 6 ppm with resonances from other protons into the resonance near 0.45 ppm (see below). Additional evidence of the H-D exchange between D_2O and hydride in the spiked sample of $ReH_5(PPh_3)_2$(3-pic) is found in a series of ^{31}P-{^{1}H} NMR spectra (Fig. 9). In the series of spectra, the ^{31}P-{^{1}H} resonance for the PPh_3 phosphorus atoms of $ReH_5(PPh_3)_2$(3-pic) becomes a complex multiplet due to isotopic shifts and coupling between ^{31}P and inner-sphere deuterons. An isobestic point for the series of spectra indicates no decomposition of $ReH_5(PPh_3)_2$(3-pic) occurs over the course of 66 min. The ^{31}P-{^{1}H} NMR spectrum changes slowly during the first 66 min following the D_2O spike until finally a spectrum that corresponds to an equilibrium mix of isotopomers remains unchanged beyond that point in time. After equilibrium was established, a second spike of D_2O into the sample once again changes the intensities of the isotopomer resonances.

Exchange α and Exchange β, which combine to exchange all of the hydride ligands on a complex, have consistently been reported for physical studies of similar rhenium(V) pentahydride complexes [25–29,32]. Reports of hydride ligand exchange for adventitious water protons for rhenium(V) polyhydride complexes, though, are limited. Support for the hydride for water-proton exchange reported here includes: the relative width of the exchanging H4 hydride resonances compared with other hydride resonances in one-dimensional ^{1}H-{^{31}P} spectra, the superior simulations that include this H4 – water-proton hydrogen exchange, and the consistency from compound to compound of the activation parameters arising from the simulations (see below).

At lower temperatures slow hydrogen exchange in the one-dimensional proton NMR spectrum should appear as individual resonances for

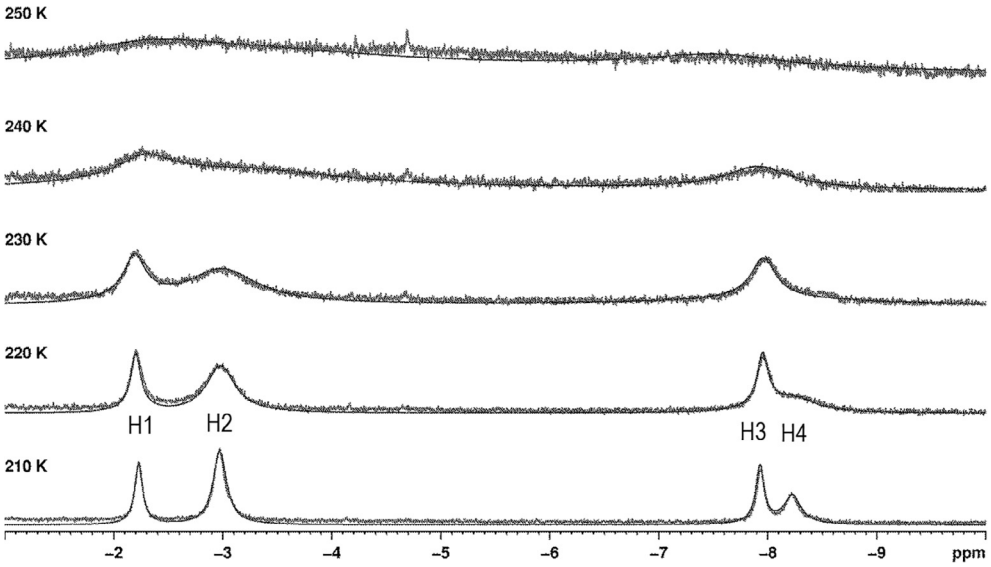

Fig. 5. The low temperature ^{1}H-{^{31}P} NMR hydride region spectra for the complex $ReH_5(PPh_3)_2$(pn) (noise is apparent on spectral traces) and the simulations (no apparent noise).

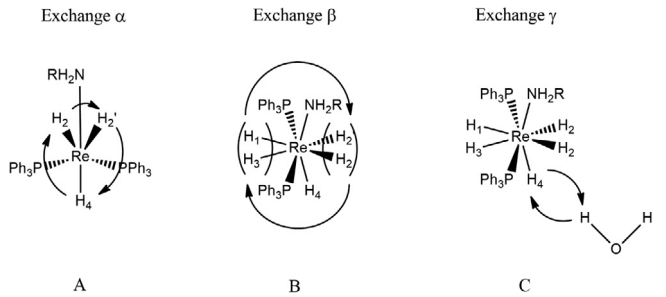

Fig. 6. The three hydrogen atom exchange models that produced the simulations found in Figs. 5 and 7. The drawings describe the models used in the simulation and not necessarily the mechanisms for the atom exchanges. Drawing A illustrates the turnstile exchange model (Exchange α). Hydride ligands H_1 and H_3 were omitted from Drawing A to simplify the illustration. Drawing B illustrates the pseudorotational or pairwise exchange model which exchanges hydride ligands H_1 and H_3 with the pair of H_2 hydride ligands (Exchange β). Drawing C illustrates the model that exchanges hydride ligand H_4 with a proton of an adventitious water molecule (Exchange γ).

the exchanging atoms and faster hydrogen exchange at higher temperatures should appear as a coalescence resonance at the intermediate frequency. For the room temperature ^{1}H-{^{31}P} spectrum of each new rhenium pentahydride complex a coalescence resonance is observed near 0.45 ppm in deuterated toluene (en 0.47, pn 0.45, MET 0.45, 3-ampy 0.47, 3-pic 0.46). This coalescence resonance includes the signal from adventitious water from the solvent and sample tube, and for the en and pn complexes, the pendant amine protons contribute to the resonance as well as hydride ligand H4. Separate T_1 measurements on the water resonance for d_8-toluene solutions of the 3-pic and 3-ampy complexes found values of 2.1 s and 1.9 s respectively. Adventitious water in d_8-toluene, without any complex present, gave a T_1 value of 2.7 s for the water resonance. The decrease in the T_1 value for "water" in the presence of the complexes results from exchange of water protons with the rhenium-bound hydride ligands.

In the VT ^{1}H NMR temperature series going from 200 K upwards in temperature, for the en complex (Fig. 10), the above-mentioned coalescence resonance (0.47 ppm at room temperature) first appears at 240 K with a chemical shift of 0.67 ppm. The pendant amine protons for the same complex resonate at −0.50 ppm at the same temperature. (At 280 K, the amine protons and the second resonance (0.67 ppm) have coalesced.) Also in the 240 K ^{1}H spectrum of the en complex another major resonance appears at 6.29 ppm. This resonance, which we attribute to water closely associated with but not coordinated to the inner sphere of the rhenium complex, is not apparent at lower temperatures. As the temperature of the sample is increased the resonance at 6.29 ppm increases and then decreases in intensity, undergoes a temperature-dependent upfield shift, and a shoulder on the resonance emerges and then disappears. Similar behavior is observed for all five complexes in the ^{1}H NMR spectral region near 6 ppm at intermediate temperatures. As the intensity of any of the resonances near 6 ppm begins to decrease at higher temperatures, that intensity is shifted to the

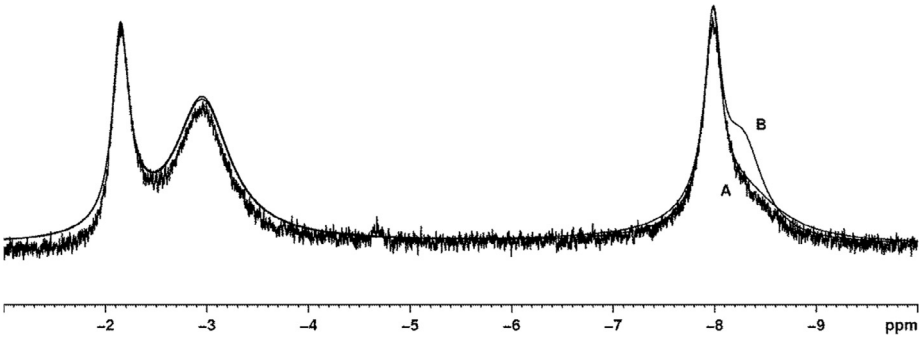

Fig. 7. The 230 K ^{1}H-{^{31}P} NMR hydride region spectrum (noise is apparent) of $ReH_5(PPh_3)_2$(MET) and its best simulation with hydride H_4 and water-hydrogen atom exchange (Trace A) and without H_4 and water-hydrogen atom exchange (Trace B). Traces A and B are both offset slightly above the spectrum for ease of comparison.

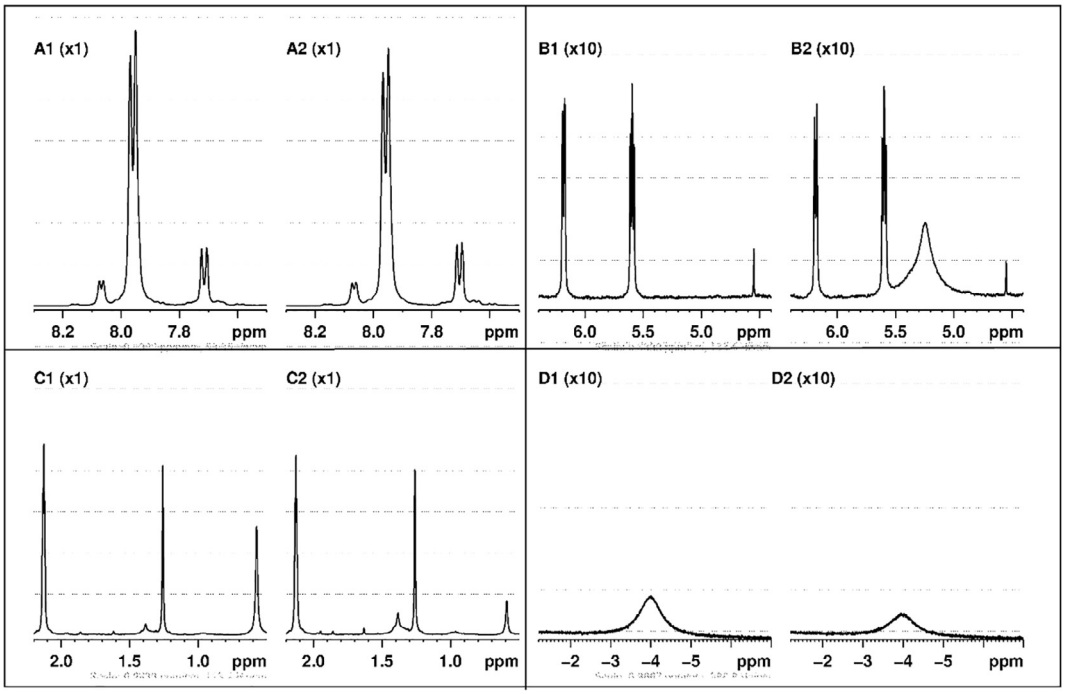

Fig. 8. A room temperature ^{1}H-{^{31}P} NMR spectrum for a sample of $ReH_5(PPh_3)_2$(3-pic) before (labels of 1) and after (labels of 2) the sample is spiked with 10 μL of D_2O and allowed to equilibrate for 69 min. The important spectral regions are shown separately for ease of comparison.

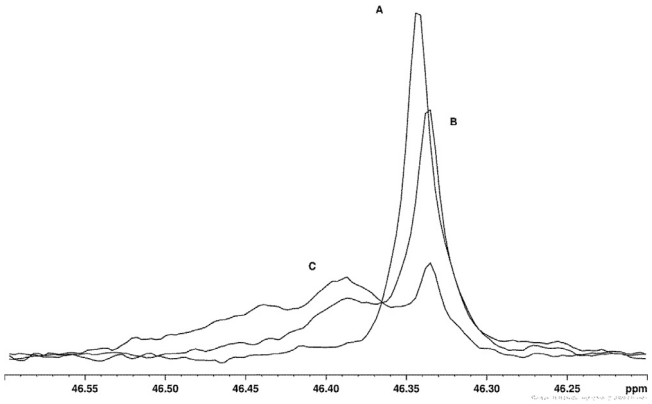

Fig. 9. The room temperature ^{31}P-{^{1}H} NMR spectra of a sample of $ReH_5(PPh_3)_2$(3-pic) at: (A) the time of the addition of 10 μL of D_2O, (B) 27 min after the sample was spiked, and (C) 66 min after the sample was spiked.

resonance near 0.45 ppm. At least one ^{1}H EXSY experiment, for each complex, at temperatures from 250 to 270 K indicates exchange between the protons that resonate near 6 ppm and the protons that resonate near 0.45 ppm as well as between the protons that resonate near 0.45 ppm and the pendant amine protons or the pendant hydroxyl proton for the en, pn, and MET complexes (Fig. 11). No exchange peaks are observed for the amine protons of the 3-aminopyridine ligand with the resonances that arise near 6 ppm or 0.45 ppm.

3.3. Activation parameters

Activation parameters ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$) (Table 1) can be determined from the rate constants found for simulations of NMR spectra of these rhenium(V), pentahydride complexes at various temperatures. For the compounds with pendant functional groups, activation parameters were determined from simulations of the hydride region of the ^{1}H NMR spectra. Of the three activation parameters determined for each of the three modelled exchanges (α, β, and γ); $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, or $\Delta S^{\ddagger}$; the activation entropies are the most informative parameters. Activation entropies for a turnstile exchange of three hydride ligands (Fig. 6, Exchange α) are negative or near zero (Table 1). Activation entropies for a pairwise A-site hydrogen exchange of all four A site hydride ligands (Fig. 6, Exchange β) are all negative. Activation entropies for the exchange of hydride ligand H4 for a water proton (Fig. 6, Exchange γ) are all significantly positive. Due to the complications of isomer hydride resonances and isomer interconversion associated with the unsymmetrically-substituted aromatic amine complexes, hydride region simulations of the hydride resonances for the aromatic amine-supported complexes were not undertaken.

For the new complexes supported by unsymmetrically-substituted aromatic amine ligands, activation parameters were determined for the *E* and *Z* isomer interconversions. The ^{31}P-{^{1}H} resonances of the aromatic amine-supported complexes were used for the calculation of the reported parameters in Table 1. Of note, all three activation parameters ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$) for the isomer interconversions are consistent with the same activation parameters for Exchange γ of the pendant functional group complexes described above and are not consistent with either Exchange α or Exchange β for those pendant functional group complexes. Given the large positive activation entropies for Exchange γ and for the *E* and *Z* isomer interconversions, the activation entropies suggest a single activation step may allow for both Exchange γ and the interconversion of *E* and *Z* isomers for eight coordinate rhenium(V) pentahydride complexes and that the activation step is favorable with respect to entropy.

3.4. Amine ligand exchange

An examination of amine dissociation found that amine ligands exchange with free amine added to NMR samples of these compounds. The ^{31}P-{^{1}H} resonances of the complexes are convenient for monitoring the conversion of one complex to another by substitution of the free amine for the bound ligand (Fig. 12). The rate law for the amine substitution reaction, as determined from a designed set of four experiments with two levels of $ReH_5(PPh_3)_2$(3-pic) concentration [0.0030 g/mL (3.7×10^{-3} mmol Re) or 0.0060 g/mL (7.4×10^{-3} mmol

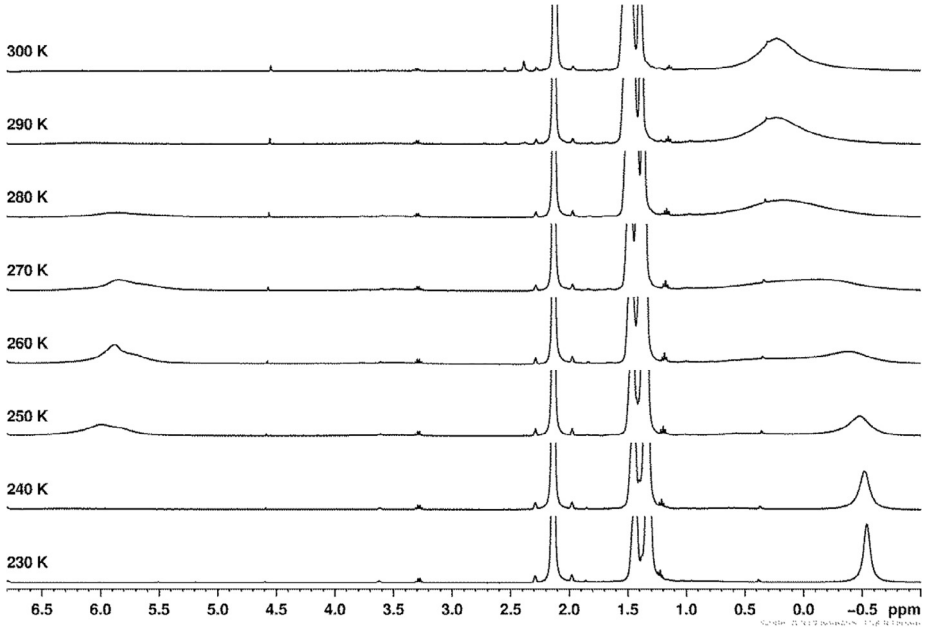

Fig. 10. The temperature dependence of the coalescence resonance and other resonances that appear at intermediate temperatures in the ^{1}H-{^{31}P} NMR spectra of $ReH_5(PPh_3)_2$(en).

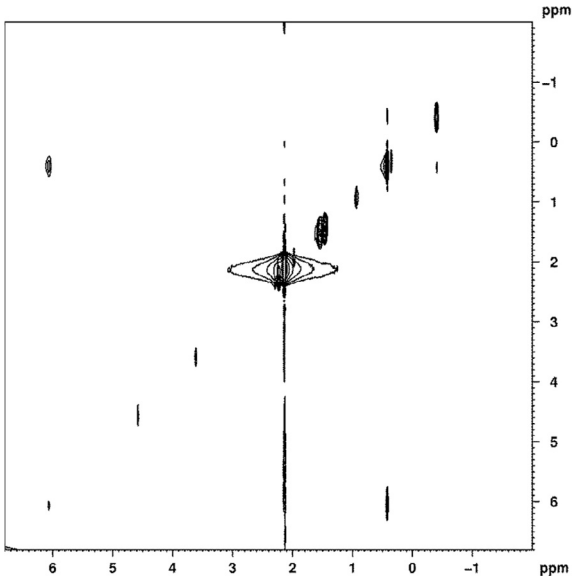

Fig. 11. A region of the ^{1}H EXSY spectrum for $ReH_5(PPh_3)_2$(MET) (mixing time of 100 ms) measured at 260 K that shows exchange between the protons that resonate near 6 ppm and the protons that resonate near 0.45 ppm as well as exchange between the protons that resonate near 0.45 ppm and the pendant hydroxyl proton that resonates near −0.4 ppm.

Re)] and two levels of en concentration [1.0×10^{-2} mL/mL (1.5×10^{-1}mmol en) or 4.0×10^{-2} mL/mL (6.0×10–1 mmol en)] in C_7D_8, is first order in rhenium complex concentration and zero order in en concentration. The results are consistent with amine ligand dissociation as the rate determining step for the amine substitution reactions.

A variable temperature study of a solution containing the 3-picoline complex and the 3-aminopyridine complex, by ^{31}P-{^{1}H} NMR spectroscopy found exchange of the amine ligands occurs between the two complexes. At room temperature some broadening of the ^{31}P-{^{1}H} resonances is observed due to exchange of the amine ligands. At 330 K, exchange of the amine ligands causes the phosphorus resonances to coalesce. Based on a 41.6 Hz peak separation for the phosphorus resonances of the pure compounds at room temperature and a

Table 1
Activation parameters for the three modelled hydrogen exchanges α, β, and γ and for the E and Z isomer interconversions. All values of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ are ± 0.3 kcal/mol. All values of $\Delta S^{\ddagger}$ are ± 1.5 cal/mol·K.

Amine	Exchange	$\Delta G^{\ddagger}$ (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol·K)
2-Aminoethanol	α	10.4	10.4	0.5
	β	9.9	9.7	−3.6
	γ	10.8	14.5	18.5
1,2-Diaminoethane	α	8.5	10.1	−0.8
	β	10.2	8.9	−7.3
	γ	10.5	13.4	14.4
1,3-Diaminopropane	α	10.4	9.4	−4.3
	β	10.4	7.5	−13.6
	γ	10.4	13.4	14.9
3-Picoline	*E/Z* Isomerization	11.7	16.1	22.1
3-Aminopyridine	E/*Z* Isomerization	11.2	14.4	15.8

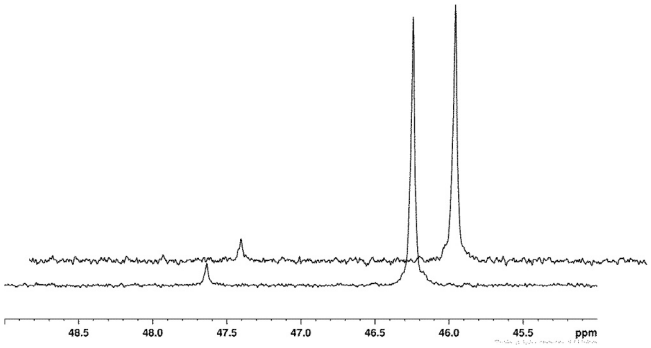

Fig. 12. Room temperature ^{31}P-{^{1}H} NMR spectra for solutions of $ReH_5(PPh_3)_2$(3-pic) (6.0 mg – lower trace, 3.0 mg – upper trace) both with 40 μL of en after 28 days. The resonances on the left of each trace arise from $ReH_5(PPh_3)_2$(en). The upper trace has been normalized by multiplying its intensity by a factor of two for comparison purposes. The upper trace is also offset for comparison purposes.

coalescence temperature of 330 K, the value of $\Delta G^{\ddagger}$ for the exchange of 3-picoline and 3-aminopyridine at the rhenium centers is 16.5 ± 0.3 kcal/mol. This value of $\Delta G^{\ddagger}$ for amine ligand exchange is considerably larger than the activation energies found for hydride ligand fluxionality, intermolecular hydrogen exchange, or *E* and *Z* isomer interconversions.

4. Discussion

4.1. Syntheses

A discussion of the above amine reactants versus other nitrogen-donor reactants in reactions with $ReH_7(PPh_3)_2$ is provided in the Supporting Material.

4.2. Fluxionality of the hydride ligands

A discussion of the fluxionality of the hydride ligands is found in the Supporting Material.

4.3. Activation parameters

Some activation parameters, primarily $\Delta G^{\ddagger}$ values, for isomer interconversions or hydride ligand fluxionality of eight-coordinate rhenium(V) pentahydride or tetrahydride complexes have been reported previously [14,25,26,28,32]. With the exception of the activation entropies for some rhenium(V) pentahydride complexes supported by a bidentate phosphite ligand that exhibit an unusual pattern of five independent low temperature ^{1}H NMR hydride resonances indicating a different low temperature structure [25], there is good agreement among the previously reported activation parameters and the activation parameters determined for the new complexes in this report. With regards to the free energy of activation for *E* and *Z* isomer interconversions or the coalescence of resonances for *meta* protons on the pyridine ligand of $ReH_5(PPh_3)_2$(py), previously reported values of $\Delta G^{\ddagger}$ ranged from 9.9 to 11.3 kcal/mol [14,32]. For the *E* and *Z* isomers containing 3-picoline or 3-aminopyridine, the values of $\Delta G^{\ddagger}$ for the isomer interconversion were found to be 11.7 and 11.2 kcal/mol respectively. These values of $\Delta G^{\ddagger}$ for isomer interconversions also fit well into the range of values (7.1 kcal/mol to 20 kcal/mol) found for isomer interconversions at square-planar Pt(II) centers with unsymmetrically substituted aromatic amine ligands [40–43]. With regards to the free energy of activation for Exchange α, the turnstile exchange of the two equivalent hydride ligands (H2 and H2′ in our labelling scheme) with the B site hydride ligand (H4), literature values for $\Delta G^{\ddagger}$ range from 8.4 to 10.2 kcal/mol [28,31] while the $\Delta G^{\ddagger}_{200K}$ values for the en, pn, and MET complexes were found to be 10.4, 8.5, and 10.4 kcal/mol respectively. For the free energy of activation for Exchange β of either the set of four A site hydride ligands or, in one case, the exchange of B site phosphorus atoms, literature values of $\Delta G^{\ddagger}$ ranged from 8.8 to 11.2 kcal/mol [25,26,28,32] while the $\Delta G^{\ddagger}_{200}$ values for the en, pn, and MET complexes were found to be 9.9, 10.2, and 10.4 kcal/mol respectively. The good agreement between literature values reported previously and the experimental results reported here supports the validity of the techniques and models used in this study.

Very little has been reported on activation enthalpies or activation entropies for the fluxional rearrangement of rhenium(V) polyhydride complexes [25,26,28]. In some cases, values for $\Delta G^{\ddagger}$ are relatively easily obtained from coalescence temperatures and low temperature frequency differences but those determinations do not result in reported values for the other activation parameters. Alternatively, Eyring plots can lead to significant errors for $\Delta S^{\ddagger}$ values due to extrapolation. With that stated, overlapping ranges of $\Delta G^{\ddagger}$ values for different fluxional or exchange mechanisms of these rhenium(V) polyhydride centers are not very informative about the underlying processes of topological rearrangements or atom exchanges. Examination of the values of $\Delta S^{\ddagger}$ for the new complexes from the Eyring equation, even with the potential for a sizable error, clearly indicates that Exchange β (average $\Delta S^{\ddagger} = -8.2$ cal/mol·K, st. dev. = 4.4) occurs through a different mechanism than either the *E* and Z isomer interconversion, pyridine proton coalescence, or Exchange γ (average $\Delta S^{\ddagger} = 17.1$ cal/mol·K, st. dev. = 3.2). Statistically, a *t* test for the mean value of $\Delta S^{\ddagger}$ for Exchange β values versus the mean value of $\Delta S^{\ddagger}$ for Exchange γ and the isomer interconversions suggests greater than 99% confidence that the two sets of activation entropies are not arising from the same underlying mechanism. Given the similarities between the activation entropies for Exchange γ, the hydride H4 exchange with hydrogen from adventitious water (average $\Delta S^{\ddagger} = 15.9$ cal/mol·K, st. dev. = 2.2), and the activation entropies for the isomer interconversions (average $\Delta S^{\ddagger} = 19.0$ cal/mol·K, st. dev. = 4.5) it is possible that both of these processes arise from a common mechanism.

4.4. Mechanisms

4.4.1. Exchanges α and β

Exchanges α and β likely proceed by unimolecular processes given their small positive or negative values of $\Delta S^{\ddagger}$. As has been suggested previously, Exchange α may proceed in a pairwise exchange of a single A site hydride ligand with H4 or may involve all three hydride ligands exchanging as the turnstile nickname indicates [32]. Exchange β may proceed through a pseudorotation or may rather proceed through another previously suggested mechanism, the exchange of dodechedral A sites for dodecahedral B sites [45,46]. Much theoretical work has been devoted to the rearrangement of dodecahedral complexes and the consensus of that work is that the lowest energy rearrangement involves small motions of two opposing sets of four inner sphere atoms that result in A site atoms being transformed into B site atoms and *vice versa* [45]. Multiple such A site – B site interconversions can effectively exchange all of the A site ligands through all three possible pairings of A site atoms within the trapezoids of the D_{2d} dodecahedron.

A good test of the A site – B site interconversion mechanism for Exchange β would seem to be the molecule $ReH_5(PPh_3)_3$. The B sites in $ReH_5(PPh_3)_3$ are occupied by an equivalent pair of PPh_3 ligands, a unique PPh_3 ligand, and a hydride ligand [47]. If an A site – B site inversion mechanism (Fig. 13) allows for the coalescence of the A site hydride ligands into a single chemically equivalent set at higher temperatures, that same mechanism should also allow for the coalescence of the chemically inequivalent set of B site phosphorus atoms of $ReH_5(PPh_3)_3$ into a single magnetically equivalent set as well and the activation parameters for that coalescence should be the same as the coalescence of the A site nuclei. One such report of the activation parameters for an A site hydride exchange and coalescence of B site inequivalent phosphorus atoms within the same compound has already appeared in the literature for the tetrahydride cation $[ReH_4(NP_3)]^+$ (NP_3 = tris[2-(*diphenylphosphanyl*)*ethyl*]amine). Values of $\Delta G^{\ddagger}$ for the A and the B site atom exchanges of the cation are 8.8 kcal/mol (203 K) and 9.1 kcal/mol (213 K), respectively, within the margins of error of

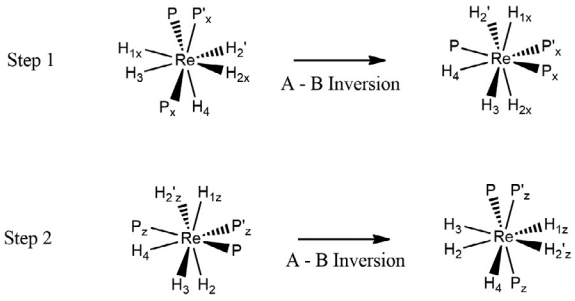

Fig. 13. A mechanism, based on inversion of dodecahedral A and B site identities, that can lead to the equivalence of all of the similar A site atoms or similar B site atoms on the NMR timescale.

being the same activation energy [28]. To the best of our knowledge, there have been no other reports of activation parameters for the exchange of B site atoms in similar rhenium(V) polyhydride complexes.

At room temperature, the $^{31}P\text{-}\{^{1}H\}$ NMR spectrum of $ReH_5(PPh_3)_3$ appears as a singlet which does not correspond to the structure of the complex in the solid state [47]. At low temperatures, the $^{31}P\text{-}\{^{1}H\}$ spectra consist of two broad resonances in a ratio of 1:2 which does correspond to the solid state structure of the complex. Simulation of the $^{31}P\text{-}\{^{1}H\}$ resonances at low temperatures results in a value for $\Delta G^{\ddagger}_{200}$ of 8.4 ± 0.3 kcal/mol, and values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 6.9 ± 0.3 kcal/mol and −9.2 ± 1.5 cal/mol·K respectively. The range of reported values for similar rhenium(V) pentahydride complexes of $\Delta G^{\ddagger}$ for Exchange β from Fig. 6 goes from 8.5 to 11.2 kcal/mol while the average value of $\Delta S^{\ddagger}$ is −7.3 cal/mol.K for that same atom exchange [25–29]. Similar barriers to A site – B site interconversions, $\Delta G^{\ddagger}$ = 10–12 kcal/mol, were found for eight-coordinate, dodecahedral, complexes of niobium and tantalum supported by dithiocarbamate ligands [48]. These activation parameters suggest that a single mechanism, the A site – B site inversion may explain the A site pairwise exchange of four hydride ligands at eight-coordinate rhenium(V) tetra- and penta- hydride complexes and also account for the observed coalescence of resonances for atoms residing in B sites in similar complexes and does so while allowing for a separate mechanism to account for the interconversion of *E* and *Z* isomers. A pseudorotation, as described in the literature of rhenium(V) polyhydride complexes, does not provide a mechanism for the coalescence of signals from two equivalent and one inequivalent phosphorus atom in B sites on the NMR time scale. The Supporting Material includes a detailed description of the mechanism depicted in Fig. 13.

4.4.2. Exchange γ and isomer interconversions

Exchange γ and the *E* and *Z* isomer interconversions have similar activation parameters including a significantly positive entropy of activation. The significantly positive entropy of activation for Exchange γ is consistent with an increase in the number of particles in the barrier step of that exchange while the significantly positive entropy of activation for the *E* and *Z* isomer interconversions is inconsistent with a simple rotation about the Re-N bond as the route to those interconversions. The similar positive entropies of activation may indicate a common mechanism for the two processes. Exchange γ, the exchange of hydrogen between the unique B site hydride ligands, H4, of the rhenium complexes and water, hinges on the presence of adventitious water in the sample at low temperatures in d_8-toluene. Water has been used previously at low temperatures in nonpolar solvents for investigations of hydrogen exchange by NMR spectroscopy [49]. Also, D_2O has been used effectively as a deuterium source in a catalytic H/D exchange even in a two phase solvent system where the catalyst and substrate were both in the organic phase and D_2O was the second phase [50]. In the current report, the ^{1}H resonances that occur near 6 ppm at temperatures near 250 K arise from water (see Section 3.2.2 above). The EXSY exchange of water protons that resonate near 6 ppm with protons that give rise to the coalescence resonance near 0.45 ppm, and the exchange of the protons that resonate near 6 ppm with hydride ligand H4 along with the positive entropy of activation may provide insight into the mechanism for both the intermolecular hydrogen exchange and the isomer interconversion. Sufficient electrostatic attraction between an electron pair on water and hydride ligand H4 on rhenium and between the electron pair on rhenium and a hydrogen atom on water can lead to a close association between the rhenium complex and a water molecule in toluene. (An association between water and a zinc complex, in solution, leads to a complex with a variable ^{19}F NMR chemical shift that depends upon the concentration of water in solution [51].) Such an associated molecular couple of water and rhenium pentahydride could provide a route to hydrogen exchange involving water and hydride H4 (Fig. 6, Exchange γ). The small value of $\Delta G^{\ddagger}$ would mean nearly equal sharing of the two hydrogen atoms between the two sets of electron pairs of the associated molecules resulting in only a small activation energy for the loss of water from the molecular couple. The exchange of hydrogen occurs upon the loss of water from the molecular couple. Loss of water from the molecular couple should have a positive entropy of activation. Loss of water from the molecular couple should also result in an excited state rhenium(V) center with the rhenium lone electron pair in an orbital other than its ground state $d_{x2\text{-}y2}$ orbital. This change in electronic structure should briefly disrupt the pi donation from rhenium towards the aromatic amine. The disruption of the pi donation will result in loss of partial double bond character between rhenium and nitrogen and free rotation about the Re-N bond should result. Thus the proposed exchange mechanism explains how the intermolecular hydrogen exchange between water and hydride H4 may be coupled with the interconversion of E and Z isomers.

4.4.3. Amine ligand exchange

The chemical properties of amine ligands on rhenium(V) pentahydride complexes have not been widely explored. Acidolysis reactions of rhenium(V) pentahydride complexes that include an amine ligand, in nitrile solvents, produce the cations $[ReH(NCR)_3(PPh_3)_2(amine)]^{2+}$ [38,52]. Reactions of complexes where the amine is pyrazine or 4-phenylpyrimidine with $ReH_7(PPh_3)_2$ result in dirhenium complexes in which the metal centers are bridged by the bidentate amine ligand [14,47]. Reactions of $ReH_5(PPh_3)_2$(amine) complexes that result in the loss of the amine ligand from the coordination sphere have not been reported for mononuclear complexes.

The mechanism of amine exchange for the complexes reported here is clearly separate from the mechanisms described above for Exchanges α, β, and γ, as well as for *E* and *Z* isomer interconversion due to the significantly larger activation barrier ($\Delta G^{\ddagger}$ = 16.5 kcal/mol versus a range of values from 8.5 to 11.7 kcal/mol for the remaining processes described above). The rate law for an amine substitution reaction indicates that the rate determining step corresponds to amine ligand dissociation. Amine ligand dissociation is consistent with the behavior observed for similar osmium(IV) tetrahydride complexes that include a single amine ligand [52,53].

5. Concluding remarks

This work highlights and clarifies several important physical and chemical aspects of rhenium(V) pentahydride complexes supported by an amine ligand. First, the mechanism for the fluxional exchange of hydride ligands in A sites likely involves distortions of the dodecahedral ligands that invert the locations of A site ligands with B site ligands. The mechanism for the fluxional exchange of hydride ligands also means that B site ligands are as fluxional as the A site hydride ligands are. Even at low temperatures, hydride ligands in these complexes are being exchanged with hydrogen from adventitious water if it is available in the sample matrix. Only the unique B site hydride ligand (the hydride ligand that is situated adjacent to the rhenium lone electron pair), H4, participates in hydrogen exchange with water. The amine ligands of the complexes exchange with free amine in solution through a process that is first order in the concentration of the rhenium complex. Finally, the entropy of activation can be useful for distinguishing among the various rearrangements that occur in such fluxional complexes.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://

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