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# Unusual ruthenium hydride complexes supported by the $[N(2-PPh_2-4-Me-C_6H_3)_2]$ pincer ligand

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Dedicated to Professor Arnold L. Rheingold on the occasion of his 70th birthday.

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# ABSTRACT

Complexes of Ru(II) containing the pincer ligand  $[^{N}(2-PPh_2-4-Me-C_6H_3)_2]$  (PNP<sup>Ph</sup>) were prepared. The complex (PNP<sup>Ph</sup>H)RuCl<sub>2</sub> (1) was treated with 2 equiv AgOTf to produce the triflate complex (PNP<sup>Ph</sup>H)Ru(OTf)<sub>2</sub> (2). Complex 1 was also treated with an excess of NaBH<sub>4</sub> to give a bimetallic complex [(PNP<sup>Ph</sup>)RuH<sub>3</sub>]<sub>2</sub> (3). A number of methods, including X-ray crystallography, NMR spectroscopy, and computational studies, were used to probe the structure of 3. Addition of Lewis bases to 3 resulted in octahedral complexes containing a hydride ligand *trans* to a dihydrogen ligand.

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#### 1. Introduction

Transition metal complexes supported by multiple hydride and dihydrogen ligands have been of considerable interest since stable non-classical hydrides were first isolated by Kubas et al. [1–6]. A number of such complexes have been synthesized, with a particular focus on the Group 8 metals [7]. The characterization of dihydrogen complexes can be based on a variety of experiments, including  $T_1$  measurements, determination of  $J_{H-D}$  coupling constants, and neutron diffraction [8–11]. However, a continuum of possible structures exist, ranging from dihydrogen ligands to dihydrides, making exact classification and determination both difficult and subjective [4,7]. Additionally, recent calculations suggest that many dihydrogen structures are nearly equal in energy to dihydride structures, with a very low energy barrier between the two, which can make it difficult to assign a definitive structure [12,13].

This group has long been interested in silyl and silylene ligands on transition metal complexes [14]. Recent success with PNP pincer ligands on Ir and Rh sparked an interest in exploration of related chemistry on Ru, a metal that has supported a number of interesting silylene complexes [15–17]. Within these contexts, we envisioned a (PNP<sup>Ph</sup>)RuH(H<sub>2</sub>) (PNP<sup>Ph</sup> = [ $^{-N}(2-PPh_2-4-Me-C_6H_3)_2$ ]) complex, analogous to the (PNP<sup>iPr</sup>)RuH(H<sub>2</sub>) complex reported by Ozerov and co-workers [18], to be a suitable starting material for reactions with organosilanes. However, we found that attempts to prepare a ruthenium hydride complex supported by PNP<sup>Ph</sup> resulted in an unusual bimetallic complex with non-classical H<sub>2</sub>/(H)<sub>2</sub> ligands. While a large number of H<sub>2</sub> complexes have been reported, a much smaller number of dinuclear species have been observed [19–24]. Herein we report the synthesis and characterization of this dimer and its reactions with Lewis bases.

### 2. Experimental section

### 2.1. General procedures

All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N<sub>2</sub>) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H<sub>2</sub>SO<sub>4</sub>, 0.5 N KMnO<sub>4</sub> in 3 M H<sub>2</sub>SO<sub>4</sub>, and NaHCO<sub>3</sub>. Pentane was then dried over MgSO<sub>4</sub> and stored over activated 4 Å molecular sieves, and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H<sub>2</sub>SO<sub>4</sub> and saturated NaHCO<sub>3</sub>. Benzene, toluene, tetrahydrofuran, diethyl ether, dichloromethane, hexanes, and pentane were dried using a VAC Atmospheres solvent purification system. Benzene-d<sub>6</sub> was dried by vacuum distillation from Na/K alloy. Dichloromethane-d<sub>2</sub> was dried by vacuum distillation from CaH<sub>2</sub>. PNP<sup>Ph</sup>H [25] and [(COD)RuCl]<sub>n</sub> [26] were prepared according to literature methods. All other chemicals were purchased from commercial sources, and used without further purification.

<sup>1</sup>H, <sup>2</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded using Bruker AVB 400, AV-500 or AV-600 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room temperature and referenced to the residual protonated solvent for <sup>1</sup>H. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced relative to 85% H<sub>3</sub>PO<sub>4</sub> external standard ( $\delta = 0$ ). <sup>13</sup>C{<sup>1</sup>H} NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For <sup>13</sup>C{<sup>1</sup>H}



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NMR spectra, resonances obscured by the solvent signal are omitted. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley. Infrared spectra were recorded on a Nicolet Nexus 6700 FTIR spectrometer with a liquid-nitrogen-cooled MCT-B detector. Measurements were made at a resolution of 4.0 cm<sup>-1</sup>. Solution molecular weights were obtained by the Signer method [27].

## 2.2. (PNP<sup>Ph</sup>H)RuCl<sub>2</sub> (1)

A Teflon-stopped flask was charged with PNP<sup>Ph</sup>H (1.00 g, 1.77 mmol) and [(COD)RuCl<sub>2</sub>]<sub>n</sub> (0.495 g, 1.77 mmol) followed by 25 mL of toluene. The reaction was heated at 110 °C for 24 h. The orange precipitate was collected by filtration and dried under vacuum to give **1** as an orange solid (1.10 g, 85% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500.0 MHz):  $\delta$  9.51 (s, 1H, NH), 8.16 (d, J<sub>HH</sub> = 8.2, 2H, ArH), 7.44 (br s, 4H, ArH), 7.37 (d, J<sub>HH</sub> = 8.2, 2H, ArH), 7.19 (t, J<sub>HH</sub> = 7.6, 2H, ArH), 7.04 (br s, 2H, ArH), 7.00–6.95 (ov m, 6H, ArH), 6.84 (br s, 4H, ArH), 6.66 (t, J<sub>HH</sub> = 7.6, 4H, ArH), 2.24 (s, 6H, ArCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.9 MHz):  $\delta$  154.9, 136.7, 135.3, 132.4, 131.8, 130.6, 128.9, 127.9, 127.2, 126.7, 20.5. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 161.9 MHz):  $\delta$  65.6. IR (cm<sup>-1</sup>): v(N-H) 3015. *Anal.* Calc. for C<sub>38</sub>H<sub>33</sub>NCl<sub>2</sub>P<sub>2</sub>Ru: C, 61.88; H, 4.51; N, 1.90. Found: C, 62.27; H, 4.72; N, 1.88%.

# 2.3. (PNP<sup>Ph</sup>H)Ru(OTf)<sub>2</sub> (2)

A flask covered with aluminum foil was charged with **1** (0.100 g, 0.136 mmol) and AgOTf (0.100 g, 2.64 mmol) followed by 10 mL of C<sub>6</sub>H<sub>6</sub>. The reaction was stirred at room temperature for 5 h, then the green-brown solution was filtered through Celite and evaporated to dryness. The resulting yellow residue was recrystallized from C<sub>6</sub>H<sub>6</sub> at room temperature to give **3** as a yellow solid (0.090 g, 65% yield).<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600.0 MHz):  $\delta$  11.72 (s, 1H, NH), 8.32 (d, J<sub>HH</sub> = 8.2, 2H, ArH), 7.47 (q, J<sub>HH</sub> = 7.0, 4H, ArH), 7.34 (t, J<sub>HH</sub> = 7.4, 4H, ArH), 7.08–7.00 (ov m, 8H, ArH), 6.92–6.91 (ov m, 6H, ArH), 6.74 (br s, 2H, ArH), 1.68 (s, 6H, ArCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150.9 MHz):  $\delta$  139.8, 134.5, 133.5, 132.3, 131.6, 131.4, 130.9, 129.6, 129.2, 19.9. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 161.9 MHz):  $\delta$  48.1. IR (cm<sup>-1</sup>):  $\nu$ (N–H) 3374. *Anal.* Calc. for C<sub>40</sub>H<sub>33</sub>NF<sub>6</sub>O<sub>6</sub>P<sub>2</sub>S<sub>2</sub>Ru: C, 49.79; H, 3.45; N, 1.45. Found: C, 50.07; H, 3.36; N, 1.18%.

## 2.4. [(PNP<sup>Ph</sup>)RuH<sub>3</sub>]<sub>2</sub> (3)

A flask was charged with 1 (0.100 g, 0.136 mmol) and NaBH<sub>4</sub> (0.100 g, 2.64 mmol) followed by 25 mL of THF. The reaction was stirred at 80 °C for 3 h, then the brown solution was reduced in vacuo and the resulting dark brown residue was dissolved in 10 mL of C<sub>6</sub>H<sub>6</sub>. The brown solution was filtered through Celite and the volatile material was removed under vacuum to give 2 as a red-brown solid (0.088 g, 96% yield).  $^1\text{H}$  NMR (C\_6D\_6, 400.0 MHz):  $\delta$  7.93–7.88 (ov m, 4H, ArH), 7.77 (dt, J<sub>HH</sub> = 8.4, J<sub>HP</sub> = 2.4, 2H, ArH), 7.84–7.45 (ov m, 6H, ArH), 7.33-7.26 (ov m, 6H, ArH), 7.20 (ov m, 6H, ArH), 7.15 (d, J<sub>HH</sub> = 8.4 Hz, 2H, ArH), 2.27 (s, 6H, ArCH<sub>3</sub>), -12.08 (s, 1H, Ru-H), -13.17 (s, 1H, Ru-H), -15.55 (s, 1H, Ru-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.9 MHz):  $\delta$  161.9 (t,  $J_{PC}$  = 8.8), 137.0, 136.7 (t,  $J_{PC}$  = 22.9), 136.3 (t,  $J_{PC}$  = 3.0), 135.9 (t,  $J_{PC}$  = 7.4), 135.5 (t,  $J_{PC}$  = 21.7), 135.1 (t,  $J_{PC} = 5.5$ ), 131.9, 131.8, 130.8, 130.1, 130.0 (t,  $J_{PC} = 5.0$ ), 129.4 (t,  $J_{PC}$  = 4.7), 124.0 (t,  $J_{PC}$  = 4.9), 21.9. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 161.9 MHz): δ 56.1. Anal. Calc. for C<sub>76</sub>H<sub>70</sub>N<sub>2</sub>P<sub>4</sub>Ru<sub>2</sub>: C, 68.25; H, 5.28; N, 2.09. Found: C, 69.16; H, 5.49; N, 1.89%. Molecular weight in CH<sub>2</sub>Cl<sub>2</sub>: 1450 g/mol. Calculated for the dimer: 1337 g/mol.

# 2.5. (PNP<sup>Ph</sup>)RuH(H<sub>2</sub>)(XyINC) (4)

A solution of xylylisocyanide (0.018 g, 0.14 mmol) in 1 mL of toluene was added to a solution of **3** (0.092 g, 0.07 mmol) in 1 mL of toluene and the resulting solution was stirred for 20 h. The reaction mixture was filtered and dried under vacuum to give **4** as a brown solid (0.096 g, 87% yield). <sup>1</sup>H NMR ( $C_6D_6$ , 400.0 MHz):  $\delta$  8.15 (m, 4H, ArH), 8.02 (m, 2H, ArH), 7.83 (d, 2H,  $J_{HH}$  = 8.5 Hz, ArH), 7.30 (m, 2H, ArH), 7.06 (ov m, 6H, ArH), 6.94 (m, 6H, ArH), 6.74 (d, 2H,  $J_{HH}$  = 8.5 Hz, ArH), 6.69 (m, 3H, ArH), 1.94 (s, 6H, ArCH<sub>3</sub>), 1.90 (s, 6H, ArCH<sub>3</sub>), -4.38 (br s, 2H, Ru-H<sub>2</sub>), -8.80 (t, 1H,  $J_{HP}$  = 20.6 Hz, Ru-H). <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , 125.9 MHz):  $\delta$  169.0, 136.6, 133.5, 131.8, 129.7, 129.1, 128.9, 124.6, 123.8, 123.0, 108.1, 19.9, 18.5. <sup>31</sup>P{<sup>1</sup>H} NMR ( $C_6D_6$ , 161.9 MHz):  $\delta$  55.6. IR (cm<sup>-1</sup>): v(Ru-H) 2040, 2010; v(Ru-H<sub>2</sub>) 1586. Anal. Calc. for C<sub>47</sub>H<sub>44</sub>N<sub>2</sub>P<sub>2</sub>Ru: C, 70.57; H, 5.54; N, 3.50. Found: C, 69.59; H, 5.56; N, 3.57%.

## 2.6. $(PNP^{Ph})RuH(H_2)(PPh_3)$ (5)

A solution of triphenylphosphine (0.037 g, 0.14 mmol) in 1 mL of toluene was added to a solution of **3** (0.092 g, 0.07 mmol) in 1 mL of toluene and the resulting solution was stirred for 24 h. The reaction mixture was filtered and dried under vacuum to give **5** as a brown solid (0.098 g, 76% yield). <sup>1</sup>H NMR ( $C_6D_6$ , 400.0 MHz): δ 7.86 (d, 2H, J<sub>HH</sub> = 8.3 Hz, ArH), 7.57 (m, 6H, ArH), 7.50 (t, 6H,  $J_{\rm HH}$  = 8.3 Hz, ArH), 6.97 (m, 6H, ArH), 6.90 (t, 10H, ArH), 6.81 (t, 5H, J<sub>HH</sub> = 7.0 Hz, ArH), 6.69 (m, 6H, ArH), 1.82 (s, 6H, ArCH<sub>3</sub>), -4.59 (s, 2H, Ru-H<sub>2</sub>), -9.73 (dt, 1H,  $J_{HP}$  = 21.7, 22.4 Hz, Ru-H).  $^{13}\text{C}\{^{1}\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 125.9 MHz):  $\delta$  160.7, 139.6, 139.3, 134.6, 134.5, 134.4, 133.7, 133.2, 133.0, 133.9, 131.1, 129.0, 128.4, 126.8, 126.7, 122.9, 67.4, 25.4.  ${}^{31}P{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 161.9 MHz):  $\delta$ 71.13 (t,  $J_{PP}$  = 29.4 Hz), 55.3 (d,  $J_{PP}$  = 29.4 Hz). IR (cm<sup>-1</sup>): v(Ru-H) 1957, 1913; v(Ru-H<sub>2</sub>) 1579. Anal. Calc. for C<sub>56</sub>H<sub>50</sub>NP<sub>3</sub>Ru: C, 72.25; H, 5.41; N, 1.50. Found: C, 69.62; H, 5.61; N, 1.49%. The low value observed for carbon may be due to incomplete combustion of the complex during analysis; alternatively, it may reflect a small amount of impurity that is not observed by NMR spectroscopy.

#### 2.7. X-ray Structure determination

The X-ray analysis of **3** was carried out at UC Berkeley CHEXRAY crystallographic facility. Measurements were made on an APEX-II CCD area detector with a HELIOS multilayer mirrors monochromating device using Cu K $\alpha$  radiation ( $\lambda$  = 1.54184 Å). Data was integrated and empirical absorption corrections were made using the APEX2 program package. The structure was solved by direct methods and expanded using Fourier techniques. All calculations were performed using the SHELXTL crystallographic package. Nonhydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions.

## 2.8. Computational details of **3**<sup>\*</sup>

All calculations were performed in the molecular graphics and computing facility of the College of Chemistry, University of California, Berkeley (NSF grant CHE-0233882). Calculations were performed using the Gaussian '03 suite of programs [28] at the B3LYP/LANL2DZ level of theory with LANL2DZdp ECP polarization functions for Ru [29]. Vibrational frequencies were calculated for all converged structures and confirm that these structures lie on a minimum. Graphical representations of the structures were generated using Mercury.

## 3. Results and discussion

## 3.1. Synthesis of Ru(II) complexes supported by PNP<sup>Ph</sup>H

The reaction of 1 equiv of  $PNP^{Ph}H$  with 1 equiv of  $[(COD)RuCl_2]_n$ in toluene at 110 °C for 24 h produced  $(PNP^{Ph}H)RuCl_2$  (1) as an orange solid in 85% yield (eq 1). The <sup>1</sup>H NMR spectrum displays a broad singlet at 9.51 ppm for the intact amine resonance and a single methyl resonance at 2.24 ppm for the ligand. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum possesses a single resonance for the PNP ligand at 65.6 ppm, indicating the presence of equivalent phosphorus groups. The infrared spectrum of the complex exhibits a broad v(N-H) band at 3015 cm<sup>-1</sup>. The analogous  $[(PNP^{iPT}H)RuCl_2]_n$  complex synthesized by Ozerov and co-workers was found to be an insoluble coordination polymer [18], while **1** was found to be soluble in halogenated solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and C<sub>6</sub>H<sub>5</sub>F. However, reactions of **1** with reagents such as MeLi, nBuLi, LiN(-SiMe<sub>3</sub>)<sub>2</sub>, and LDA in THF resulted in multiple unidentifiable products. Complex **1** did not react with silanes such as PhSiH<sub>3</sub>, Ph<sub>2</sub>SiH<sub>2</sub>, and Et<sub>3</sub>SiH at 80 °C for 2 days in C<sub>6</sub>D<sub>6</sub> or C<sub>6</sub>D<sub>5</sub>Br.



Treatment of **1** with 2 equiv of AgOTf in benzene in the absence of light resulted in the formation of  $(PNP^{Ph}H)Ru(OTf)_2(2)$  as a light yellow solid in 65% yield (eq 2). The <sup>1</sup>H NMR spectrum displays a broad singlet at a downfield resonance of 11.72 ppm for the amine, and a broad v(N-H) band at 3374 cm<sup>-1</sup> was observed by infrared spectroscopy. A single methyl resonance is observed for the ligand backbone at 1.68 ppm, indicating a symmetric arrangement of the ligand about the Ru center. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum reveals an upfield shift for the PNP<sup>Ph</sup> ligand to 48.1 ppm. In contrast to 1, complex 2 was found to be soluble in both polar and nonpolar solvents, allowing for reactivity studies with various alkylating reagents and silanes. Reactions to derivatize 2 with reagents like  $Bn_2Mg(Et_2O)_n$ , MeLi, or LDA were found to be unproductive due to rapid conversion of complex mixtures of unidentified products. Reactions of the organosilanes MesSiH<sub>3</sub> and Ph<sub>3</sub>SiH with 2 did not proceed even with heating at 80 °C for 3 days.



3.2. Synthesis and characterization of [(PNP<sup>Ph</sup>)RuH<sub>3</sub>]<sub>2</sub>

The reaction of **1** with an excess of NaBH<sub>4</sub> in THF at 80 °C for 3 h generated a new complex (**3**) in high yield as a red-brown solid (eq 3). Complex **3** exhibits good stability at room temperature under  $N_2$ 

in both the solid state and in solution. The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **3** indicate that the PNP<sup>Ph</sup> ligand lies on a plane of symmetry, with one methyl resonance observed at 2.27 ppm and only one phosphorus resonance appearing at 56.1 ppm. Interestingly, the <sup>1</sup>H NMR spectrum of **3** possesses three chemically inequivalent upfield hydride resonances at -12.08, -13.17, and -15.55 ppm, each of which integrate to one with respect to the methyl groups on the ligand. These hydride resonances are broad and exhibit no splitting due to coupling to phosphorus nuclei. Additionally, H-H coupling is not observed due to the broadness of the resonances (width at half height = 34 Hz). The inequivalent resonances are surprising because they seem to indicate that full oxidative addition of an H<sub>2</sub> ligand has taken place to give a Ru(IV) trihydride complex. In contrast, (PNP<sup>iPr</sup>)RuH(H<sub>2</sub>) displays a single broad resonance in the hydride region integrating to 3 and resulting from exchange of the hydride and H<sub>2</sub> ligand [25]. The <sup>1</sup>H NMR spectra of **3** (Fig. 1) observed at temperatures ranging from -90 °C to 80 °C exhibited neither sharpening nor coalescence of all three hydride resonances. Using the inversion recovery method, the average  $T_1$  relaxation times were found to be 115 ms for each hydride, which is longer than expected for a dihydrogen ligand [7]. <sup>11</sup>B NMR spectroscopy supports the absence of any borohydride ligands in 3.



The gross connectivity in **3** was determined by X-ray crystallography, with dark red needles grown by vapor diffusion of heptane into a toluene solution of **3** at room temperature over one week. Due to poor crystallinity, the X-ray data is not of sufficient quality to report accurate bond distances and angles: however, general comments on the structure of **3** can be made. Complex **3** is a dimeric species consisting of two Ru atoms, two PNP ligands, and therefore six hydride-like ligands (not located crystallographically). The Ru-Ru distance of 2.6 Å is typical of two Ru atoms bridged by hydride ligands. The pincer ligand is bound to the metal in a facial arrangement rather than the more common meridinal binding. The angles around the N atom of the ligand sum to 360°. An empty coordination site is located trans to the N atom of each PNP ligand, presumably filled by a hydride ligand. Complex **3** was found to have a molecular weight of 1450 g/mol in  $CH_2Cl_2$ , indicating that the dimer remains intact in solution [27].

DFT studies at the B3LYP/LANL2DZ level of theory were undertaken to provide further insight into the geometric structure of **3** and the optimized DFT structure is designated as **3**<sup>\*</sup>. The connectivity found via X-ray analysis was utilized as a starting point, and different arrangements of the hydride ligands were examined. No PNP<sup>Ph</sup> ligand simplifications were made. The geometries of a number of structures were optimized, and all converged to the





Fig. 2. Optimized geometry of 3.

**Table 1** Selected bond distances of  $\mathbf{3}^*$  (Å)

ciccica bolia distances	$OI J (\Lambda).$
Ru(1)-P(1)	2.3595
Ru(1)-P(2)	2.3249
Ru(1) - N(1)	2.1372
Ru(1)–H(1a)	1.7506
Ru(1)-H(1b)	1.7570
H(1a)–H(1b)	0.842
Ru(1)-H(3)	1.8073
Ru(1)-H(4)	1.8442
Ru(1)-Ru(2)	2.824
Ru(2)-P(3)	2.3590
Ru(2)-P(4)	2.3274
Ru(2)-N(2)	2.1380
Ru(2)-H(2a)	1.7564
Ru(2)-H(2b)	1.7501
H(2a)–H(2b)	0.842
Ru(2)-H(3)	1.8108
Ru(2)-H(4)	1.8398

same structure, represented by  $\mathbf{3}^*$  in Fig. 2. Rather than displaying three hydrides, a non-classical dihydrogen ligand with an H–H bond distance of 0.842 Å is observed. Other bond distances and bond angles of  $\mathbf{3}^*$  are consistent with the experimental data (Table 1).

Thus, the computational studies suggest a structure that seems inconsistent with the NMR data in that rapid exchange (e.g., by rotation about the Ru–H<sub>2</sub> bond) would be expected to give rise to one hydride resonance for the H<sub>2</sub> ligand. Although the detailed structure of **3** is yet to be determined, it seems reasonable to conclude that it is a dimeric hydride of the type  $[(PNP^{Ph})RuH_3]_2$ , involving bridging hydrogen ligands.

## 3.3. Addition of Lewis Bases to [(PNP<sup>Ph</sup>)RuH<sub>3</sub>]<sub>2</sub>

Reactions of **3** with Lewis bases resulted in  $(PNP^{Ph})Ru(H)(H_2)L$ , L = (xylyl)isocyanide (**4**) and triphenylphosphine (**5**) (eq 4). The

<sup>1</sup>H NMR spectra of **4** and **5** display two new characteristic upfield resonances: a broad peak integrating to two hydrogens (-4.38 and -4.59 ppm, respectively, for **4** and **5**) and a sharp peak at higher field corresponding to one hydrogen that exhibits fine coupling. In the case of **4**, this peak is a triplet ( $J_{HP} = 20.6 \text{ Hz}$ ) at -8.80 ppm. For complex **5**, a doublet of triplets ( $J_{HP} = 21.7$ , 22.4 Hz) is observed at -9.73 ppm. The small coupling constants to phosphorus indicate that this hydride ligand is *cis* to all P-atoms in each complex. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **4** displays a single resonance at 55.6 ppm, while the spectrum of **5** possesses two resonances: a triplet at 71.1 ppm for the PPh<sub>3</sub> ligand and a doublet at 55.3 ppm for the PNP ligand. The P–P coupling constant of 29.4 Hz is indicative of a *cis* arrangement of the two types of phosphorus donor atoms.



The  $T_1$  times were measured for **4** and **5**. In complex **4**, the resonance at -4.38 ppm has a  $T_1$  of 100 ms, while the resonance at -8.80 ppm has a  $T_1$  of 300 ms. The  $T_1$  times for **5** follow a similar pattern: 90 ms (-4.59 ppm) and 650 ms (-9.73 ppm). These times are consistent with the integrations, splitting patterns, and the assignment of the downfield resonance ( $\sim$ 4.5 ppm) to an H<sub>2</sub> ligand and the upfield resonance ( $\sim 9 \text{ ppm}$ ) to a classical hydride ligand. Both **4** and **5** react rapidly with 1 atm  $D_2$  gas at room temperature to give  $(PNP)Ru(D)(D_2)L$ . The <sup>1</sup>H NMR spectra were obtained from  $-30 \,^{\circ}\text{C}$  to 60  $^{\circ}\text{C}$ , but  $J_{\text{H-D}}$  was not observable for either complex. However, a number of ruthenium complexes with a classical hydride ligand trans to an H<sub>2</sub> ligand have been documented, with a narrow range of  $d_{H-H}$  values (0.84–0.94 Å) [7]. The shorter  $T_1$  times for **4** and **5**, as compared to **3**, indicate that the H–H distances in these complexes are similar to those described in the literature for related trans-(H<sub>2</sub>)(H) complexes.

## 4. Conclusion

New Ru hydride complexes supported by a PNP<sup>Ph</sup> pincer ligand have been obtained. The exact structural nature of the hydride **3** has yet to be determined, but it has been shown to behave as a synthon for the [(PNP<sup>Ph</sup>)RuH<sub>3</sub>] fragment. The Ru dimer undergoes attack by a Lewis base to give a monomeric species containing a non-classical H<sub>2</sub> ligand. These complexes represent the first Ru complexes supported by the PNP<sup>Ph</sup> ligand.

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