# Ruthenium(II) Hydrido Complexes of 2,6-(Diphenylphosphinomethyl)pyridine

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A series of PNP−ruthenium(II) complexes $Ru(OCOMe)_2(PNP)$ (**1**), $Ru(OCOMe)_2(PNP)(PPh_3)$ (**2**), the monohydrides $RuHX(PNP)(PPh_3)$ (X = OCOMe (**3**); X = Cl (**4**)), and dihydride $RuH_2(PNP)(PPh_3)$ (**5**) (PNP = 2,6-bis(diphenylphosphinomethyl)pyridine) were synthesized and characterized by microanalysis as well as NMR, IR, and mass spectroscopies. The solution dynamics of complex **1** were studied by variable-temperature $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopies. The crystal structure of $RuHCl(PNP)(PPh_3)$ (**4**) was determined by X-ray crystallography, showing that the PNP ligand coordinates the Ru atom in a meridional mode. The hydrido complexes $RuH(OCOMe)(PNP)(PPh_3)$ (**3**) and $RuH_2(PNP)(PPh_3)$ (**5**) undergo deuterium exchange reactions with $CD_3OD$ to give substitution of both the hydrides and PNP methylene protons by deuterium. The probable intermediates involved in these exchange processes are molecular dihydrogen complexes of Ru(II).



## Introduction

In recent years, chiral polydentate ligands have attracted much attention as ligands of transition-metal catalysts in a variety of asymmetric transformations.[1] Thus, several ruthenium diphosphine and triphosphine complexes have been shown to display rich catalytic behavior, including high enantioselectivity using chiral chelating diphosphine ligands[2] such as BINAP. We[3a,b] and others[5−9] have recently developed a new type of tridentate PNP ligand with an axial element of symmetry, and we have studied its coordination to a wide variety of transition metals (Ru, Pd, Rh, Ir). This PNP tridentate system is designed so as to allow meridional coordination to the metal center, where the $C_2$ symmetrical environment of the ligand may be preserved in octahedral catalytic intermediates. This arrangement allows the substrate to approach and bind along the $C_2$ axis, thus interacting directly with the substituents on the phosphorus donor atoms and experiencing the quadrant effect shown in Figure 1. Additionally, the nitrogen atom should modify the properties of the resulting complexes and their catalytic reactivities relative to that found for their triphosphine- or trinitrogen-based ligands.

We initially investigated the coordination chemistry of the simplest achiral member of this family, 2,6-bis(diphenylphosphinomethyl)pyridine (hereafter designated as PNP, Figure 1), and reported certain catalytic properties of the resultant complexes.[4] In this paper, we describe our results concerning the synthesis and characterization of a new series of ruthenium(II) hydrido complexes containing the PNP ligand, including a structural analysis by X-ray diffraction of one such hydrido complex.

## Experimental Section

**General Considerations.** All experiments were carried out under a nitrogen or argon atmosphere, using a vacuum line or Vacuum Atmospheres glovebox equipped with a Dri-Train HE-493 inert gas purifier. $^1H$ (300 MHz) and $^{31}P\{^1H\}$ (121.5 MHz, broadband decoupled) NMR spectra were recorded

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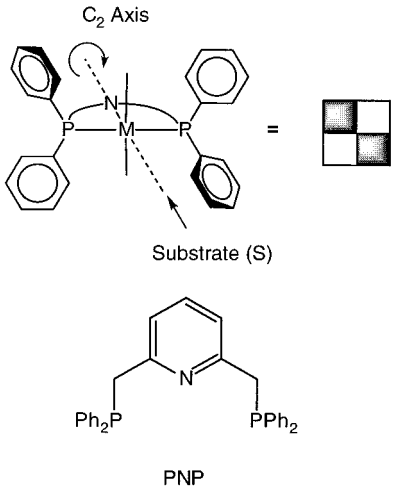


**Figure 1.** Quadrant effects of tridentate ligands and the PNP ligand.



on a Bruker AC300 instrument and referenced to $Me_4Si$ and 85% aqueous $H_3PO_4$, respectively. FT-IR spectra were recorded on a Perkin-Elmer 1600 Series spectrometer on KBr pellets or in Nujol. FAB-MS spectra and elemental analyses were carried out by the corresponding facilities at the Chemistry Research Centre at Université Louis Pasteur, Strasbourg. Methylene chloride and acetonitrile were distilled under nitrogen over calcium hydride; pentane, THF, and benzene over sodium and benzophenone. $Ru_2(OCOMe)_4$,[10] $RuCl_2(PPh_3)_3$,[11] $RuHCl(PPh_3)_3$,[12] $Ru(OCOMe)_2(PPh_3)_2$,[13] $RuH(OCOMe)(PPh_3)_3$,[14] $RuH_2(PPh_3)_4$,[15] and PNP[16] were prepared following the literature methods.

**Synthesis of $Ru(OCOMe)_2(PNP)$ (1).** A solution of PNP (200 mg, 0.420 mmol) and $Ru_2(OCOMe)_4$ (100 mg, 0.228 mmol) in 50 mL of $CH_3OH$ was refluxed for 6 h. After the mixture was cooled to room temperature, the green solution obtained was evaporated to dryness, the resulting solid was extracted with $CH_2Cl_2$, and the extracts were filtered to remove excess $Ru_2(OCOMe)_4$. The resulting green solution was concentrated in vacuo, and on addition of excess $Et_2O$, a crystalline green product precipitated, which was collected by filtration and dried under vacuum. Yield: 220 mg, 75%. Anal. Calcd for $C_{35}H_{33}NP_2O_4Ru$: C, 60.52; H, 4.79; N, 2.02; P, 8.92. Found: C, 60.47; H, 5.00; N, 2.27; P, 8.89. FAB-MS *m/z* (assignment, relative intensity): 636.0 ($[M - OAc]^+$, 90), 576.1 ($[M - 2OAc]^+$, 100). $^1H$ NMR $\delta$ (298 K, $CD_2Cl_2$, ppm): 8.20−6.4 (m, 23 H, H arom), 4.35 (s, 2 × 2H, $CH_2$), 1.89 (s, 2 × 3H, $CH_3CO_2$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, ppm): at 298 K $\delta$ 28.14 (s, PNP); at 200 K 2 broad singlets (relative intensities ca. 2:1) at $\delta$ 31.76 and 24.56. $^{31}P\{^1H\}$ NMR ($CD_3OD$, ppm): at 298 K $\delta$ 25.54 (s, PNP); at 200 K 2 broad singlets (relative intensities ca. 9:1) at $\delta$ 29.78 and 23.14.

**Synthesis of $Ru(OCOMe)_2(PNP)(PPh_3)\cdot CH_2Cl_2$ (2).** A solution of PNP (200 mg, 0.420 mmol) in 10 mL of THF was added dropwise to a solution of $Ru(OCOMe)_2(PPh_3)_2$ (313 mg, 0.420 mmol) in 20 mL of THF. The mixture was stirred for 4 h, and then the yellow-orange solution obtained was concentrated in vacuo and excess of pentane added. The resulting yellow precipitate was collected by filtration, washed with pentane, and dried in vacuo. Complex **2** was recrystallized from $CH_2Cl_2$/pentane, giving a yellow microcrystalline product. Yield: 360 mg, 90%. Anal. Calcd for $C_{54}H_{50}NP_3Cl_2O_4Ru$: C, 62.25; H, 4.84; N, 1.34; P, 8.92. Found: C, 61.61; H, 4.99; N, 1.19; P, 8.41. $^1H$ NMR $\delta$ (298 K, $CDCl_3$, ppm): 7.60−6.87 (m, 38 H, H arom), 4.48 (t, 2 × 2H, $CH_2$), 1.15 (s, 2 × 3H, $MeCO_2$), 5.28 (s, 2 H, $CH_2Cl_2$). $^{31}P\{^1H\}$ NMR (298 K, $CDCl_3$, ppm): MXX′ spectrum with ($\delta_X + \delta_{X'}$) at 40.18 (d, 2 P, PNP); $\delta_M$ 33.78 (t, 1 P, $PPh_3$); $J_{(M,X)} = 30$ Hz.

**Synthesis of $RuH(OCOMe)(PNP)(PPh_3)$ (3). Method I.** A solution of PNP (200 mg, 0.420 mmol) in 10 mL of THF was added dropwise to a solution of $RuH(OCOMe)(PPh_3)_3$ (400 mg, 0.421 mmol) in 15 mL of THF. The mixture was stirred for 3 h, and then the yellow solution obtained was concentrated in vacuo and excess pentane added. The resulting yellow precipitate was collected by filtration, washed with pentane and dried in vacuo. Yield: 320 mg, 80%. Anal. Calcd for $C_{51}H_{46}NP_3O_2Ru$: C, 68.14; H, 5.16; N, 1.56. Found: C, 67.24; H, 5.12; N, 1.58. FAB-MS *m/z* (assignment, relative intensity): 898.1 ($[M - H]^+$, 37), 838.1 ($[M - H - OCOMe]^+$, 25), 636.0 ($[M - H - PPh_3]^+$, 100), 576.0 ($[M - H - OCOMe - PPh_3]^+$, 40). IR (Nujol mull, $cm^{-1}$): $\nu$(Ru−H) 2064. $^1H$ NMR $\delta$ (298 K, $C_6D_6$, ppm): 7.87−6.37 (m, 38 H, H arom), 5.30 and 3.74 (2 dt, 2 × 2H, $CH_2$), 2.21 (s, 3H, $MeCO_2$), −18.47 (q, 1H, Ru−H, $J$(H,P) = 22 Hz). $^{31}P\{^1H\}$ NMR (298 K, $C_6D_6$, ppm): MXX′ spectrum, $\delta_M$ 59.12 (t, 1P, $PPh_3$); $\delta_X$ 30.46 (d, 2P, PNP); $J$(M,X) = 30 Hz.

**Method II.** A solution of $Ru(OCOMe)_2(PNP)(PPh_3)$ (40 mg, 0.042 mmol) in 10 mL of benzene was transferred in a 50 mL stainless steel autoclave. After degassing 3 times with $H_2$, the mixture was maintained at 25 °C under 20 bar of $H_2$ for 2 h. The resulting yellow solution obtained was concentrated under vacuo, and excess pentane was added. The resulting yellow precipitate was collected by filtration and dried in vacuo. Yield: 35 mg, 93%.

**Synthesis of $RuHCl(PNP)(PPh_3)\cdot CH_2Cl_2$ (4). Method I.** A solution of PNP (200 mg, 0.420 mmol) in 10 mL of THF was added dropwise to a solution of $RuHCl(PPh_3)_3$ (390 mg, 0.422 mmol) in 20 mL of THF. After being stirred for 4 h, the violet solution turned yellow. The solution was concentrated in vacuo, and excess pentane was added. The resulting yellow precipitate was collected by filtration, washed with pentane, and dried in vacuo. Complex **5** was recrystallized from $CH_2Cl_2$/pentane, giving an orange microcrystalline product. Yield: 310 mg, 84%. Anal. Calcd for $C_{50}H_{45}NP_3Cl_3Ru$: C, 62.54; H, 4.72; N, 1.46; P, 9.68. Found: C, 63.14; H, 4.73; N, 1.58; P, 9.14. IR (Nujol mull, $cm^{-1}$): $\nu$(Ru−H) 1987. $^1H$ NMR $\delta$ (298 K, $CDCl_3$, ppm): 7.76−7.70 and 7.34−6.78 (m, 38 H, H arom), 4.76 and 3.96 (2 dt, 2 × 2H, $CH_2$), −17.26 (q, 1H, Ru−H, $J$(H, P) = 21 Hz), 5.29 (s, 2H, $CH_2Cl_2$). $^{31}P\{^1H\}$ NMR (298 K, $CDCl_3$, ppm): $\delta_M$ 58.09 (t, 1P, $PPh_3$); $\delta_X$ 48.98 (d, 2P, PNP); $J$(M,X) = 30 Hz.

**Method II.** A suspension of $LiAlH_4$ (45 mg, 1.185 mmol) in 5 mL of THF was added dropwise to a solution of $RuCl_2(PNP)(PPh_3)$ (500 mg, 0.549 mmol) in 20 mL of THF. The mixture was stirred for 2 h at room temperature. After addition of ethanol (30 mL), the solution was concentrated and the resulting yellow solution cooled to −20 °C to give yellow-orange crystals. Yield: 390 mg, 81%.

**Synthesis of $RuH_2(PNP)(PPh_3)$ (5).** A solution of PNP (200 mg, 0.420 mmol) in 10 mL of THF was added dropwise to a solution of $RuH_2(PPh_3)_4$ (485 mg, 0.420 mmol) in 20 mL of THF with stirring. After 1 h, the yellow-orange solution obtained was concentrated in vacuo and excess pentane added. The resulting yellow precipitate was collected by filtration, washed with pentane and dried in vacuo. Yield: 240 mg, 68%. Anal. Calcd for $C_{49}H_{44}NP_3Ru$: C, 70.00; H, 5.27; N, 1.67. Found: C, 70.53; H, 4.63; N, 1.72. FAB-MS *m/z* (assignment, relative intensity): 839.1 ($[M - 2H]^+$, 100); 576.0 ($[M - 2H - PPh_3]^+$, 50). IR (Nujol mull, $cm^{-1}$): $\nu$(Ru−H) 1977. $^1H$ NMR $\delta$ (298 K, $C_6D_6$, ppm): 7.97−6.21 (m, 38H, H arom), 3.86 (t, 2

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× 2H, $CH_2$), −4.87 (q, 2H, Ru−H, $J$(H, P) = 19 Hz). $^{31}P\{^1H\}$ NMR (298 K, $C_6D_6$, ppm): MXX′ spectrum with $\delta_M$ 78.46 (t, 1P, $PPh_3$); $\delta_X$ 70.71 (d, 2P, PNP); $J$(M,X) = 31 Hz.

**Deuterium Exchange Reactions of 3 and 5 with $CD_3OD$.** For **3**: In an NMR tube complex **3** (0.01 g, 11.12 mmol) was dissolved in 0.5 mL of $CD_3OD$. The reaction was followed by $^1H$ and $^{31}P$ NMR spectroscopies. After 1 h, the $^1H$ NMR spectrum showed peaks at $\delta$ (298 K, $CD_3OD$, ppm) 7.68−6.90 (m, 38 H, $H_{arom}$), 4.57 and 3.94 (2 dt, 2 × 2H, $CH_2$), 1.84 (s, 3H, $CH_3CO_2$); the $^{31}P\{^1H\}$ NMR (298 K, $CD_3OD$, ppm) showed the following resonances: $\delta_M$ 61.41 (s (br), 1 P, $PPh_3$); $\delta_A$ 51.83 (s (br), 2 P, PNP). The spectra were taken at regular intervals, and after 144 h, no further changes were observed, i.e., the following spectra were obtained: $^1H$ NMR $\delta$ (298 K, $CD_3OD$, ppm) 7.68−6.90 (m, 38 H, H arom), 1.84 (s, 3 H, $CH_3CO_2$); $^{31}P\{^1H\}$ NMR (298 K, $CD_3OD$, ppm) $\delta_M$ 61.47 (s (br), 1 P, $PPh_3$); $\delta_X$ 51.74 (s (br), 2 P, PNP). The FAB-MS of the final product showed $m/z$ (assignment, relative intensity): 844.8 ($[M - OAc]^+$, 100), 579.8 ($[M - D - OAc - PPh_3]^+$, 25).

For **5**: **5** (0.01 g, 11.9 mmol) was dissolved in 0.5 mL of $CD_3OD$ and syringed into an NMR tube, and the reaction was followed by both $^1H$ and $^{31}P$ NMR spectroscopies. After ca. 5 min, the following spectra were obtained: $^1H$ NMR $\delta$ (298 K, $CD_3OD$, ppm) 7.60−6.70 (m, 38H, H arom); $^{31}P\{^1H\}$ NMR (298 K, $CD_3OD$, ppm): $\delta_M$ 61.89 (t, 1P, $PPh_3$); $\delta_X$ 56.08 (2P, d, PNP); $J$(M,X) = 27 Hz. The exchange reactions had already gone to completion. The FAB-MS spectrum of the product showed $m/z$ (assignment, relative intensity): 845.2 ($[M - D]^+$, 100).

**Crystallographic Data Collection and Structure Determination of $RuHCl(PNP)(PPh_3)\cdot CH_2Cl_2$ (4).** Single crystals of **4** ($C_{49}H_{43}NP_3ClRu\cdot CH_2Cl_2$, MW = 960.3) were obtained as described above. Data were collected at room temperature using Mo Kα graphite-monochromated radiation, $\lambda$ = 0.7107 Å, on a Nonius CAD4-F diffractometer. The orange compound crystallizes in the triclinic system, space group $P\bar{1}$, with $a$ = 10.525(3) Å, $b$ = 13.477(4) Å, $c$ = 18.350(5) Å, α = 69.56(2), $\beta$ = 79.12(2)°, $\gamma$ = 68.44(2)°, $V$ = 2262.9 Å$^3$, $d_{calcd}$ = 1.409 g cm$^{-3}$, $Z$ = 2, $\mu$ = 6.568 cm$^{-1}$. A total number of 13 526 reflections were collected over the range 2° < $\theta$ < 29°. Three standard reflections measured every hour during the data collection period showed no significant trend. The data were corrected for Lorentz, polarization, and absorption factors ($\psi$ scan of 4 reflections). There were 8862 reflections with $I > 3\sigma(I)$ used. The structure was solved using direct methods. The $CH_2Cl_2$ solvation molecule is disordered over two positions (ratio 0.7/0.3). Nonsolvent hydrogen-atom positions were calculated (C−H = 0.95 Å, B(H) = 1.3$B_{eqv}$($C$) Å$^2$), solvent protons were omitted and the proton attached to Ru was located from a difference map. All hydrogen atoms were introduced as fixed contributors. For all computations the Nonius MolEN package[17] was used. Crystal data and details on intensity collection parameters are indicated in Table 1. Full-matrix least-squares led to the final values of R(F) = 0.044, and Rw(F) = 0.66.

**Table 1. X-ray Experimental Data**

| | |
|---|---|
| formula | $C_{49}H_{43}NP_3ClRu\cdot CH_2Cl_2$ |
| mol wt | 960.27 |
| cryst system | triclinic |
| space group | $P\bar{1}$ |
| $a$ (Å) | 10.525(3) |
| $b$ (Å) | 13.477(4) |
| $c$ (Å) | 18.350(5) |
| α (deg) | 69.56(2) |
| $\beta$ (deg) | 79.12(2) |
| $\gamma$ (deg) | 68.44(2) |
| $V$ (Å$^3$) | 2262(1) |
| $Z$ | 2 |
| color | orange |
| cryst dimens (mm) | 0.46 × 0.28 × 0.22 |
| $D_{calc}$ (g cm$^{-3}$) | 1.41 |
| $F_{000}$ | 984 |
| $\mu$ (mm$^{-1}$) | 0.657 |
| trans min and max | 0.970/1.000 |
| temp (K) | 294 |
| wavelength (Å) | 0.710 73 |
| radiation | Mo Kα graphite-monochromated |
| diffractometer | Enraf Nonius CAD4 |
| scan mode | $\theta/2\theta$ |
| $hkl$ limits | −14,14; −18,17; −25,0 |
| $\theta$ limits (deg) | 2.5/29.97 |
| no. of data measd | 13 526 |
| no. of data with $I/3\sigma(I)$ | 8873 |
| weighting scheme | $4F_o^2/(\sigma^2(F_o^2) + 0.0064F_o^4$ |
| no. of variables | 520 |
| $R$(F) | 0.044 |
| $R_w$(F) | 0.066 |
| GOF | 1.286 |
| largest peak in final difference (e Å$^{-3}$) | 0.905 |

## Results and Discussion

The synthetic results described in this paper are shown in Scheme 1.

**Synthesis and NMR Studies on $Ru(OCOMe)_2$(PNP) (1).** Treatment of $Ru_2(OCOMe)_4$ with 1 equiv of PNP in refluxing methanol for 6 h produces **1** as green crystals after recrystallization from $CH_2Cl_2$/pentane. Microanalysis is in full agreement with the proposed formulation of $Ru(OCOMe)_2$(PNP).

The $^1H$ NMR spectrum of **1** in $CD_2Cl_2$ solution at room temperature exhibits a broad singlet for the methyl resonance at 1.89 ppm assigned to two acetate groups, which upon cooling to 200 K separates into two singlets at 2.11 and 1.86 ppm. The $^{31}P\{^1H\}$ NMR spectrum of this compound in $CD_2Cl_2$ solution at room temperature exhibits a broad singlet at $\delta$ 28.14 ppm, which at 200 K appears as two separate singlets at $\delta$ 31.76 and 24.56 ppm with relative intensities of approximately 2:1. At ambient temperature, the $^{31}P\{^1H\}$ NMR spectrum of **1** in a polar solvent, $CD_3OD$, exhibits a broad singlet at $\delta$ 25.54 ppm, which at 200 K separates again into two singlets at $\delta$ 29.78 and 23.14 ppm, which now have a relative intensity of ca. 9:1. The FAB MS spectrum shows $m/z$ at 636.0, $[M - OCOMe]^+$ (90), and 576.1, $[M - 2OCOMe]^+$ (100), indicating the presence of monomeric species. We propose that two isomers **1a** and **1b** exist in equilibrium in solution where the PNP ligand is coordinated to the metallic center in a tridentate *mer* fashion in both isomers. The octahedral isomer, **1a**, contains both monodentate and bidentate acetate ligands, whereas **1b** is a pentacoordinate cationic species with a chelating acetate ligand formed by the dissociation of one acetate ligand (Scheme 1) or perhaps a solvated hexacoordinate complex. This would account for the observation that in a polar solvent the equilibrium is shifted toward **1b**.

The variable-temperature $^1H$ and $^{31}P$ NMR data show that rapid exchange occurs between **1a** and **1b** even at low temperatures, thereby equilibrating the phosphorus environments. The high-temperature process observed in the $^1H$ spectra may involve an exchange between terminal and chelating acetate ligands in **1a** via an intermediate ($\eta^1$-$OCOMe)_2Ru$(PNP) species.

**Synthesis and Characterization of Complex $Ru(OCOMe)_2(PNP)(PPh_3)$ (2).** Complex **2** has been isolated by the reaction between PNP and $Ru(OCOMe)_2$-

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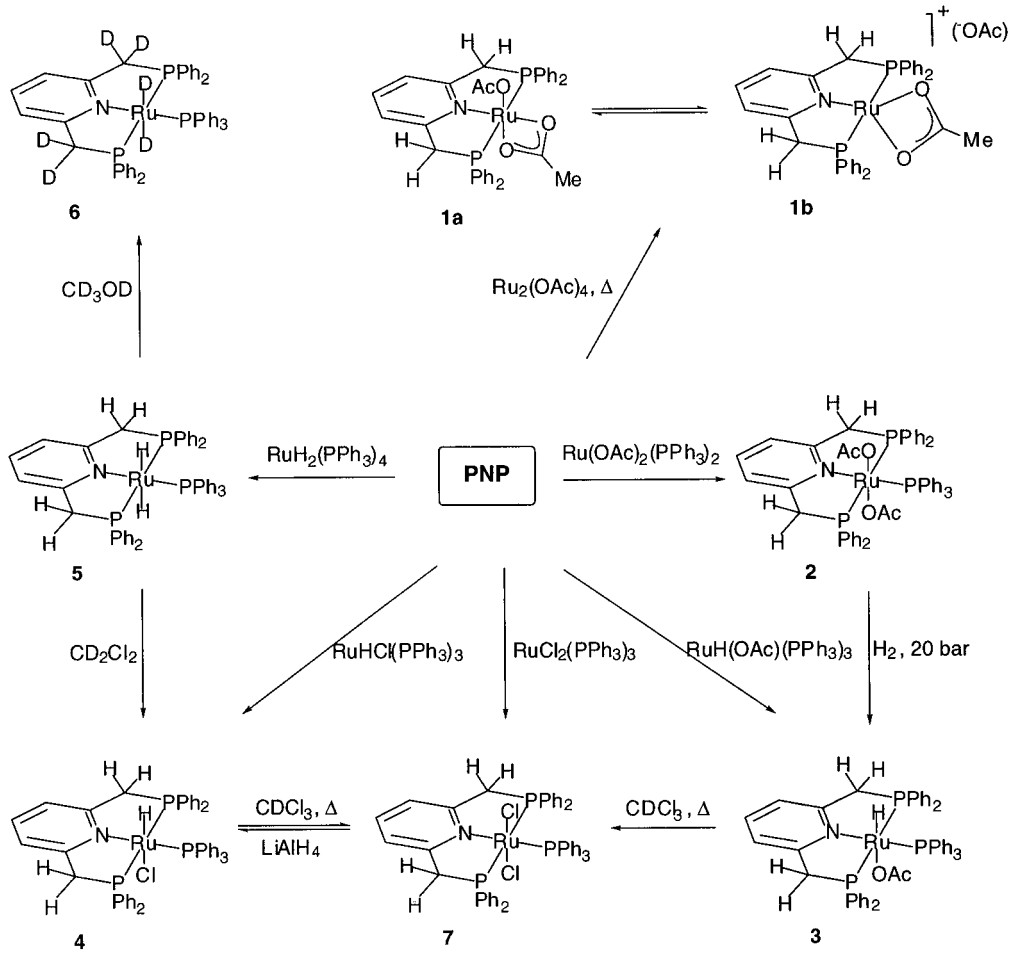
**Scheme 1**




$(PPh_3)_2$ in THF at room temperature and characterized by spectroscopic techniques.

The $^{31}P\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ solution shows an MXX′ system ($\delta_X$ = 40.18 ppm, 1P, PNP; $\delta_M$ = 33.78 ppm, 1P, $PPh_3$) with a $J$(M,X) coupling constant of 30 Hz, indicating that the triphenylphosphine is in a cis position to the two phosphorus atoms of the PNP ligand. The $^1H$ NMR spectrum exhibits a singlet at $\delta$ 1.15 ppm for the methyl groups of the two acetate ligands and a virtual triplet at $\delta$ 4.48 ppm attributed to the methylene protons on the PNP ligand. This triplet results from an AA′XX′ system where each proton is virtually coupled to the two equivalent phosphorus nuclei ($^2J_{HP} + {}^4J_{HP'}$ = 8.7 Hz). Such a situation has been frequently described in the literature concerning other PNP coordination compounds[7,8] and is characteristic of a meridional coordination, where the two protons of each $CH_2$ moiety are equivalent. Consequently, the molecule possesses a plane of symmetry that includes the three donor atoms of PNP, so that $PPh_3$ necessarily lies trans to the pyridine nitrogen.

The molecular structure of analogous complex $RuCl_2$-(PNP)($PPh_3$) has been previously determined by X-ray diffraction methods[4] and shows that the PNP ligand coordinates to the metallic center in a tridentate meridional mode with the triphenylphosphine ligand trans to the pyridine nitrogen, the two chlorides lying mutually trans; **2** clearly has an analogous structure.

**Synthesis and Characterization of Hydride Complex, RuH(OCOMe)(PNP)($PPh_3$) (3).** The monohydride complex RuH(OCOMe)(PNP)($PPh_3$) (**3**) can be synthesized by two methods: either by reaction of PNP ligand and 1 equiv of RuH(OCOMe)$(PPh_3)_3$ in THF at room temperature or by reaction of complex **2** in benzene under a $H_2$ pressure (20 bar) in a stainless steel autoclave. Complex **3** was isolated in good yield and characterized by spectroscopic techniques.

The IR spectrum exhibits an absorption with weak intensity at $\nu$(Ru−H) = 2064 $cm^{-1}$, assigned to a terminal hydride ligand. The $^{31}P\{^1H\}$ NMR spectrum in $C_6D_6$ solution of **3** shows an MXX′ system ($\delta_X$ = 30.46 ppm, 2P, PNP; $\delta_M$ = 59.12 ppm, 1P, $PPh_3$) with a $J$(M,X) coupling constant of 30 Hz, indicating that the $PPh_3$ ligand is cis to the PNP ligand. The $^1H$ NMR spectrum exhibits a singlet at $\delta$ 2.21 ppm attributed to the methyl of the acetate group and a high-field quartet at $\delta$ = −18.47 ppm, which confirms the presence of a terminal metal hydride. The observed multiplicity originates from the nearly identical $J$(H,P) coupling of 22 Hz to the cis phosphorus atoms of $PPh_3$ and to the two equivalent $PPh_2$ groups of the PNP ligand. However, the PNP methylene signals now appear in the $^1H$ NMR spectrum as a set of two doublets of triplets centered at $\delta$ 5.30 and 3.74 ppm, corresponding to an AA′BB′XX′ system. The two methylene protons borne by each carbon are now unequivalent, with a *gem* coupling constant of 15.9 Hz, and virtually coupled to the phosphorus atoms with different coupling constants ($^2J_{HP} + {}^4J_{HP'}$ = 8.6 and 9.4 Hz). Further, the reaction

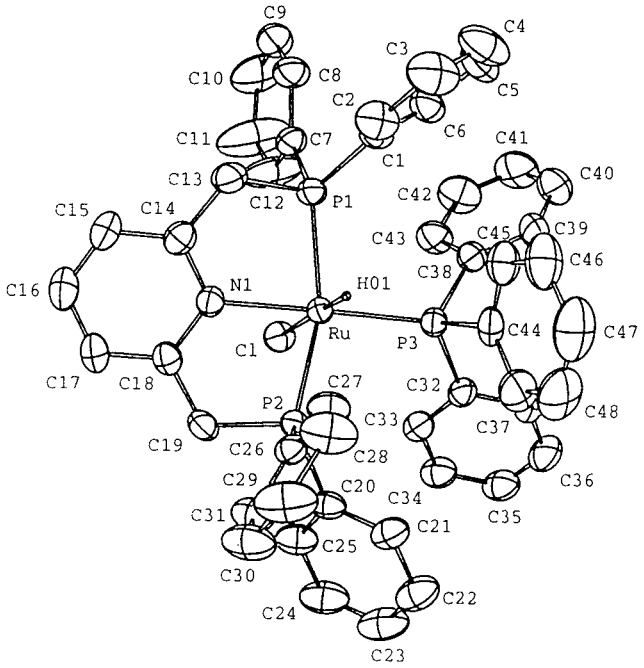



**Figure 2.** ORTEP drawing of $RuHCl(PNP)(PPh_3)\cdot CH_2Cl_2$. Hydrogen atoms and $CH_2Cl_2$ are omitted.

of **3** with $CDCl_3$ on heating for 2 h at 60 °C yields **7**, as confirmed by $^1H$ and $^{31}P$ NMR.

**Synthesis and Characterization of Hydride Complex RuHCl(PNP)($PPh_3$) (4).** The monohydride complex RuHCl(PNP)($PPh_3$) (**4**) was also synthesized by two methods: either by reaction directly between PNP and 1 equiv of $RuHCl(PPh_3)_3$ in THF at room temperature or by reacting $RuCl_2(PNP)(PPh_3)$ in THF at room temperature with excess $LiAlH_4$. An orange microcrystalline crop of **4** was obtained by recrystallization from $CH_2Cl_2$/pentane and characterized by spectroscopic techniques. The IR spectrum exhibits an absorption with weak intensity at $\nu(Ru-H) = 1987\ cm^{-1}$, assigned to a terminal hydride ligand. The $^{31}P\{^1H\}$ NMR spectrum of **4** in $CDCl_3$ solution shows an MXX′ system ($\delta_X$ = 48.98, 2P, PNP; $\delta_M$ = 58.09 ppm, 1P, $PPh_3$) with a $J$(M,X) coupling constant of 30 Hz, again indicating a *mer* coordination geometry for the PNP ligand with $PPh_3$ trans to pyridine. The $^1H$ NMR spectrum in high-field region shows a quartet at $\delta$ −17.26 ppm, which confirms the presence of a terminal hydride ($J$(H,P) = 21 Hz). The PNP methylene signals appear as a set of two doublets of triplets centered at 4.76 and 3.96 ppm, corresponding to an AA′BB′XX′ system. The two methylene protons borne by each carbon are not equivalent, and a *gem* coupling constant of 15.9 Hz is observed, each proton is virtually coupled to the phosphorus atoms with slighly different coupling constants ($^2J_{HP} + {}^4J_{HP'} = 7.2$ and 9.2 Hz).

**X-ray Diffraction Study of 4.** An ORTEP plot of **4** is shown in Figure 2. Selected bond distances and angles are given in Table 2. The monohydride **4** is monomeric with a distorted octahedral geometry around the ruthenium and confirms that the PNP ligand is coordinated to the metallic center in a tridentate meridional mode, with the triphenylphosphine ligand trans to the nitrogen atom of the pyridine group. The hydride ligand is trans to the chloride ligand with Ru−H = 1.46 Å. Ru−H was located in a difference map but not refined. Therefore, there are no standard deviations for bond distances and angles involving this proton (Table 2). In general, the bond lengths and angles are unexceptional, but it is interesting to compare the structure of **4** with that found for $RuCl_2(PNP)(PPh_3)$ which we have previously reported.[4] Although the two structures are very similar, some differences are apparent, in particular the Ru−Cl bond is considerably longer in **4**, being 2.579 Å (cf. 2.412 Å in the dichloride complex), as a result of a ground-state trans effect of the hydride ligand. Further, all Ru−P bonds are shorter in **4** by ca. 0.06 Å, and some of the bond angles are correspondingly larger, e.g., the P−Ru−Cl angles have increased by 5−12°. Little difference is found for the P−Ru−P angle of the PNP ligand in the two complexes (156° vs 157.9°). Intuitively, electrostatic considerations would lead to the prediction of shorter Ru−P bonds in the dichloride Ru complex, which is not observed. Apparently, the shorter Ru−Cl bonds found in this latter complex must provide greater steric repulsion and cause the lengthening of the Ru−P bonds. These results are similar to those obtained by Bianchini[18,19] in the closely related complexes *mer*-$RuCl_2[nPrN(CH_2CH_2PPh_2)_2](PPh_3)$ and *mer*-$RuHCl[(nPr)N(CH_2CH_2PPh_2)_2](PPh_3)$.

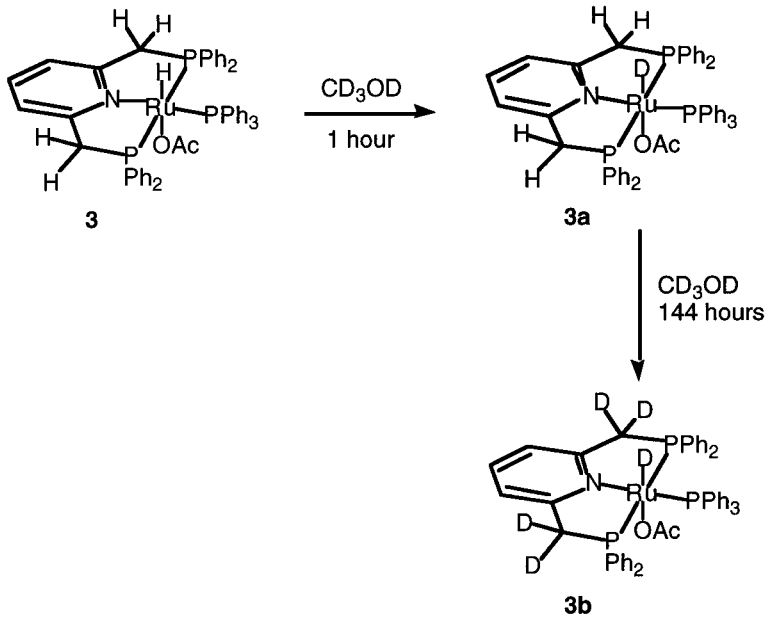
**Table 2. Selected Bond Distances (Å) and Bond Angles (deg)**

| | | | |
|---|---|---|---|
| Ru−H | 1.46 | Ru−N(1) | 2.150(2) |
| Ru−Cl | 2.5795(7) | C(14)−N(1) | 1.354(3) |
| Ru−P(1) | 2.3070(6) | C(18)−N(1) | 1.367(3) |
| Ru−P(2) | 2.3077(6) | C(19)−P(2) | 1.839(3) |
| Ru−P(3) | 2.2881(6) | C(13)−P(1) | 1.853(3) |
| Cl−Ru−H | 178 | C(1)−P(1)−H | 90 |
| P(1)−Ru−H | 80 | C(13)−P(1)−H1 | 90 |
| N(1)−Ru−H | 96 | Ru−P(3)−H1 | 34 |
| P(2)−Ru−H | 88 | C(32)−P(3)−H | 139 |
| P(3)−Ru−H | 81 | C(38)−P(3)−H | 123 |
| Ru−P(1)−H | 34 | C(44)−P(3)−H | 78 |
| Cl−Ru−P(1) | 101.32(2) | C(1)−P(1)−C(7) | 101.0(1) |
| Cl−Ru−N(1) | 84.55(6) | C(1)−P(1)−C(13) | 103.3(1) |
| Cl−Ru−P(2) | 90.08(2) | C(7)−P(1)−C(13) | 99.0(1) |
| Cl−Ru−P(3) | 98.34(2) | P(1)−C(1)−C(6) | 119.8(2) |
| P(1)−Ru−N(1) | 81.32(6) | P(1)−C(1)−C(2) | 121.3(2) |
| P(1)−Ru−P(2) | 155.97(3) | C(18)−C(19)−P(2) | 109.7(2) |
| P(1)−Ru−P(3) | 99.78(2) | C(19)−P(2)−C(20) | 102.1(1) |
| N(1)−Ru−P(2) | 78.77(6) | C(19)−P(2)−C(26) | 104.6(1) |
| N(1)−Ru−P(3) | 176.60(6) | C(20)−P(2)−C(26) | 98.1(1) |
| P(2)−Ru−P(3) | 99.38(2) | P(2)−C(20)−C(21) | 117.6(2) |

**Synthesis and Characterization of Dihydrido Complex $RuH_2(PNP)(PPh_3)$ (5).** The dihydride complex **5** was prepared by addition of 1 equiv of PNP to $RuH_2(PPh_3)_4$ in THF. The IR spectrum exhibits an absorption of medium intensity at $\nu(Ru-H) = 1977\ cm^{-1}$, which is assigned to the presence of terminal hydrides. $^{31}P\{^1H\}$ NMR of **5** in $C_6D_6$ solution shows an MXX′ system ($\delta_X$ = 70.71 ppm, 2P, PNP; $\delta_M$ = 78.46 ppm, 1P, $PPh_3$), and a $J$(M,X) coupling constant of 31 Hz indicates that the $PPh_3$ ligand is cis to the P atoms of the PNP ligand. The $^1H$ NMR spectrum exhibits a single resonance attributed to the methylene protons of the PNP ligand as a triplet at 3.86 ppm, with $^2J_{HP} + {}^4J_{HP'} = 6.5$ Hz. The quartet signal at high field $\delta$ −4.87 ppm ($J$(H,P) = 19 Hz), therefore, must result from the two hydride ligands being in a trans arrangement. The

(18) Bianchini, C.; Masi, D.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Acta Crystallogr.* **1995**, *C15*, 2514.
(19) Bianchini, C.; Innocenti, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Gaz. Chim. Ital.* **1992**, *122*, 461.

**Scheme 2**






possibility of a **5** being a molecular dihydrogen compound would seem to be excluded since the $CH_2$ resonances would not be equivalent. *trans*-Dihydrido complexes are rare but not unknown, and the pronounced reactivity of **5** may result from this rather rare stereochemical arrangement.

**Reactions of Hydride Complexes 4 and 5: Deuterium Exchange Reactions with $CD_3OD$.** The dihydride complex $RuH_2(PNP)(PPh_3)$ (**5**) reacts immediately in $CD_2Cl_2$ or $CDCl_3$, yielding the monohydride complex **4** by substitution of one hydride with a chloride ligand. Moreover, a very rapid reaction of **5** occurs at ambient temperature in a $CD_3OD$ solution. After a few minutes, $^1H$ NMR studies of the dihydride complex show the disappearance of the resonances due to the hydrides but more surprisingly the protons of the PNP methylenic groups have also been totally replaced by deuterons. No exchange with aromatic protons is detected. Growth of the $CD_3OH$ peak in the $^1H$ NMR confirms that exchange has occurred with the O−D function of the $CD_3OD$. The IR spectrum shows the disappearance of the $\nu$(Ru−H) vibration, but the resultant Ru−D absorption could not be observed due to it overlapping with strong pyridine vibrations. However, a FAB mass spectrum study of the resultant complex **6** shows a peak at $m/z = 845.2$ corresponding to $M - D^+$, where M is **5**-$d_6$, showing that the exchange of six hydrogens by deuterium has taken place.

The monohydride complex $RuH(OAc)(PNP)(PPh_3)$ (**3**) also displays a similar behavior in $CD_3OD$ but the H/D exchange is much slower (Scheme 2). Analysis by $^1H$ NMR (see Figure 3) shows the decrease of the hydride resonance over a few minutes to give $RuD(OAc)(PNP)(PPh_3)$, **3a**, but the total exchange of the $CH_2$ groups to yield $RuD(OAc)(PNP\text{-}d_4)(PPh_3)$, **3b**, is only complete after ca. 6 days, with a concomitant increase of the $^1H$ resonance of $CD_3OH$. The IR spectrum also showed the disappearance of the $\nu$(Ru−H) vibration.

The deuterium exchange reactions of $CD_3OD$ were only observed with the hydride complexes **3** and **5**, no exchange being detected for the other compounds described here. It is clear that two separate processes are involved: the exchange with the Ru−H function which is fast for both complexes and the slow exchange with the $CH_2$ groups which is considerably faster for the dihydrido species **5** than for the monohydrido species **3**.

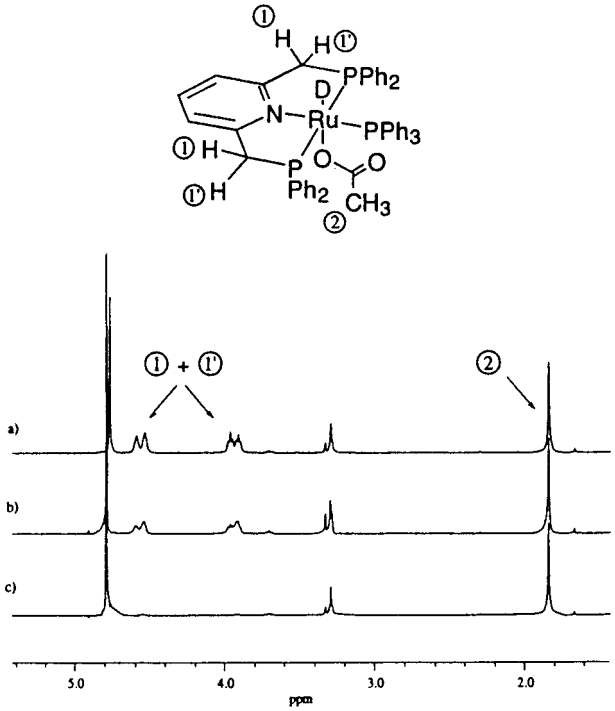
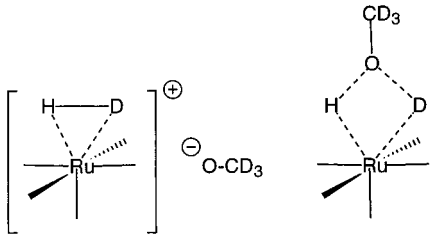



**Figure 3.** $^1H$ NMR signals of the PNP methylene protons of $RuH(OAc)(PNP)(PPh_3)$ in $CD_3OD$ at ambient temperature; (a) after 1 h; (b) after 30 h; (c) after 144 h.

In the exchange process involving the Ru−H function, it would seem highly unlikely that the hydride ligand would be removed as a proton in these electron-rich complexes, particularly by a relatively weak base such as methanol. It is known, however, that certain metal hydride complexes can be protonated by alcohols directly on the hydride ligand to form molecular dihydrogen




4a 4b

**Figure 4.**

complexes.[20] Such a dihydrogen intermediate is probably reversibly formed by the same mechanism in the exchange process observed here (Figure 4a), which would allow rapid exchange at the hydride ligand. Although we have not observed such an intermediate, very recently stable Ru(II) dihydrogen complexes closely similar to those suggested here have been reported.[21] An alternative mechanism where exchange takes place by a four-center interaction, equivalent to a $\sigma$-bond metathesis reaction, between the O−D bond of the alcohol and the Ru−H bond (Figure 4b), however, cannot be totally excluded. Such an intermediate or transition state would avoid the charge separation involved in the formation of $MeO^-$ and the intermediate cationic dihydrogen complex and may explain the rapidity of the exchange process. Labeling experiments and studies using more acidic and sterically encumbered alcohols will be necessary to clarify this point.

The methylene protons on the PNP ligand coordinated to Ru(II) are relatively acidic, since they are attached to a phosphonium center. Although we observe the deuterium incorporation in these methylene protons only with the hydrido complexes, direct exchange of the $CH_2$ groups with the Ru−D formed would appear unlikely for stereochemical reasons. The most feasible explanation for this exchange is that if a dihydrogen complex is formed in low concentration in solution as discussed above, the resultant $MeO^-$ present would then deprotonate (reversibly) the methylene protons. The deprotonation of a methylene group on PNP coordinated to Pt(II) and Pd(II) by $MeO^-$ has been observed.[7b] Since **5** is more basic than **3**, the methylene proton exchange would be expected to occur more readily for this dihydrido species **5** as more dihydrogen complex and $MeO^-$ would be formed in solution. In summation, these exchange processes would appear to be most reasonably explained by the formation of intermediate Ru(II) dihydrogen complexes but confirmation of this proposal must await further experimentation.

(20) See, for example: Bampos, N.; Field, L. D. *Inorg. Chem.* **1990**, *29*, 587.

(21) Jia, G.; Lee, H. M.; Williams, I. D.; Lau, C. P.; Chen, Y. *Organometallics* **1997**, *16*, 3941.

## Conclusions

The above complexes have been synthesized in order to test the activity of the Ru−PNP systems as catalysts in a variety of reactions, particularly in the hydrogenation of olefins, ketones, and imines. Our preliminary results using the hydrido complexes **3** and **5** are very promising. Such studies are the prelude to the synthesis and study of the analogue compounds containing chiral PNP ligands, which will be the subject of a forthcoming publication.

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**Supporting Information Available:** Tables of positional parameters, displacement parameters, bond distances, and bond angles (20 pages). Ordering information is given on any current masthead page.

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