# Synthesis and Characterization of Ruthenium(II) Hydrido and Hydroxo Complexes Bearing the 2,6-Bis(di-*tert*-butylphosphinomethyl)pyridine Ligand

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*Summary: The reaction of [Ru(CO)$_2$Cl$_2$]$_n$ with 2,6-bis-(di-tert-butylphosphinomethyl)pyridine) (PNP) and then anion exchange yields [Ru(PNP)(CO)$_2$Cl]PF$_6$ (**1**). Reaction of **1** with AgBF$_4$, in acetone, followed by acetonitrile and then anion exchange gave [Ru(PNP)(CO)$_2$(CH$_3$CN)]-(PF$_6$)$_2$ (**2**); reaction of **2** with water gave [Ru(PNP)-(CO)$_2$OH]PF$_6$ (**3**), whereas reaction of **2** with aqueous KOH led to [Ru(PNP)(CO)(CH$_3$CN)H]PF$_6$ (**4**). Complexes **3** and **4** have been structurally characterized.*

## Introduction

Ruthenium(II) hydrido and hydroxo complexes have attracted increasing attention because of their occurrence as key intermediates in stoichiometric and catalytic transformations of organic molecules.[1] However, the number of well-characterized, monomeric ruthenium hydroxo complexes, in particular, remains few. As part of a continuing study of ruthenium(II) complexes bearing polydentate ligands,[2] we now describe the preparation of ruthenium hydrido and hydroxo complexes that incorporate a terdentate 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine (PNP) ligand. This ligand has been reported recently by the groups of Milstein[3] and Hartwig[4] and is highly electron donating with an axial element of symmetry that includes the nitrogen and carbon three of the pyridyl group.

## Results and Discussion

As shown in Scheme 1, reaction of the PNP ligand with [Ru(CO)$_2$Cl$_2$]$_n$ in refluxing methanol followed by anion exchange leads to [*cis*-Ru(PNP)(CO)$_2$Cl]PF$_6$ (**1**), in moderate yield; the compound was characterized by spectral data and elemental analysis. The assignment of cis stereochemistry to the two carbonyl groups is suggested after structural characterization of compounds derived from **1**, *vide infra*. The $^{31}$P NMR spectrum of **1** exhibits a singlet at 82.28 ppm, indicating that the two phosphorus atoms are chemically equivalent and that the complex may have a plane of sym-

## Scheme 1



## Scheme 2
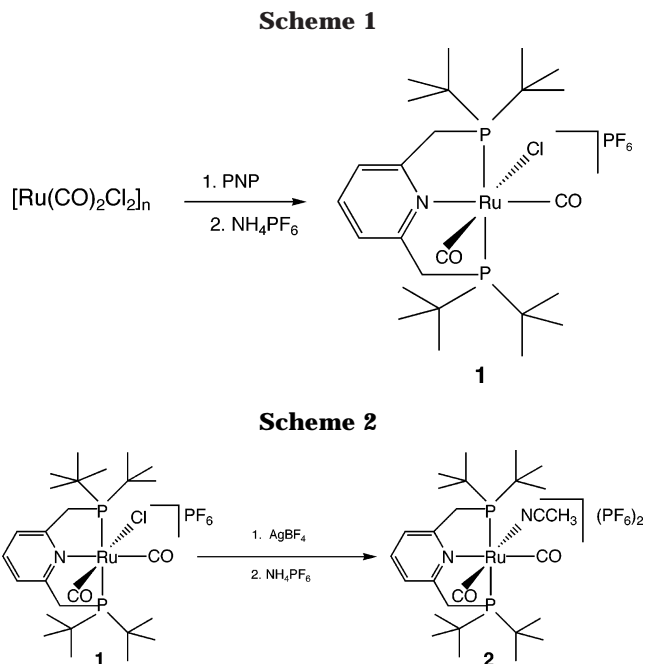


metry. However, the $^1$H NMR spectrum shows a doublet of doublets, with splitting of each line into a virtual triplet, for the four CH$_2$P protons (two pairs of diastereotopic protons), at 4.14 ppm due to coupling with both phosphorus atoms; thus the complex is not symmetrical.

Preparation of **1** gave us the necessary starting material to initiate the syntheses of additional compounds bearing the PNP ligand in the manner we used previously with the terpyridine analogue of **1**.[2b] As shown in Scheme 2, reaction of **1** with AgBF$_4$ in acetone followed by treatment with acetonitrile, then anion exchange, afforded a compound that we have characterized as the result of spectral data and elemental analysis as [*cis*-Ru(PNP)(CO)$_2$(CH$_3$CN)](PF$_6$)$_2$·0.5 acetone (**2**). Again, the assignment of cis stereochemistry results from structural data obtained on a derivative of this compound as discussed below. Complex **2** is an air-stable white solid. The $^{31}$P NMR spectrum of **2** exhibits a singlet at 82.08 ppm, indicating that the two phosphorus atoms are chemically equivalent as in **1**. As with **1**, the $^1$H NMR spectrum again shows a doublet of doublets, further split into virtual triplets, centered at 4.11 ppm for the CH$_2$P protons.

We had planned to prepare the aquo analogue of **2** by treating the product resulting from chloride ion extraction from **1** with water instead of acetonitrile.

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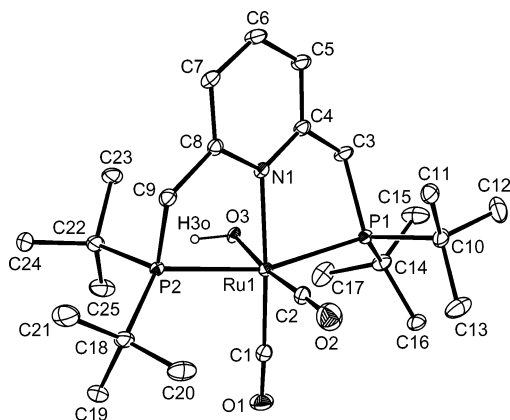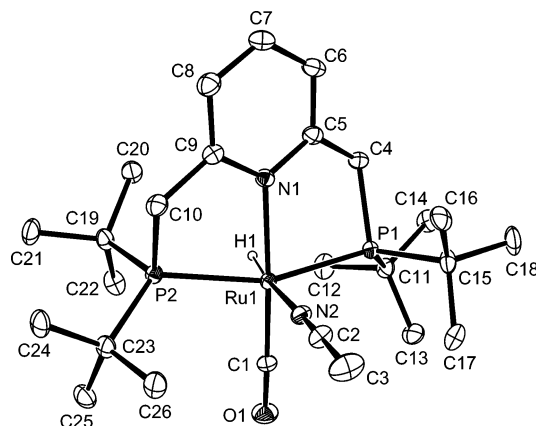
**Figure 1.** ORTEP drawing of **3** with thermal ellipsoids shown at the 50% level.



**Figure 2.** ORTEP drawing of **4** with thermal ellipsoids shown at the 50% level.

**Table 1. Crystal Data and Structure Refinement for 3 and 4**

|  | **3** | **4** |
|---|---|---|
| empirical formula | $C_{25}H_{44}NF_6O_3P_3Ru$ | $C_{26}H_{47}N_2F_6OP_3Ru \cdot 0.75CH_3OH$ |
| fw | 714.59 | 735.92 |
| cryst syst | triclinic | orthorhombic |
| space group | $P\bar{1}$ | $P2_12_12_1$ |
| unit cell dimens | $a = 8.2883(6)$ Å | $a = 13.3421(8)$ Å |
|  | $b = 12.7436(10)$ Å | $b = 15.5510(9)$ Å |
|  | $c = 15.7252(12)$ Å | $c = 16.4447(10)$ Å |
|  | $\alpha = 106.437(1)°$ | $\alpha = 90°$ |
|  | $\beta = 104.999(1)°$ | $\beta = 90°$ |
|  | $\gamma = 92.173(1)°$ | $\gamma = 90°$ |
| volume | $1527.7(2)$ Å$^3$ | $3412.0(4)$ Å$^3$ |
| $Z$ | 2 | 4 |
| density (calcd) | 1.553 Mg/m$^3$ | 1.433 Mg/m$^3$ |
| abs coeff | 0.735 mm$^{-1}$ | 0.658 mm$^{-1}$ |
| $\theta$ range, deg | 1.41 to 28.26° | 1.80 to 28.22° |
| no. of reflns measd | 13 395 | 29 086 |
| no. of unique reflns ($R_{int}$) | 6835 (0.0189) | 7910 (0.0255) |
| no. of variables | 364 | 391 |
| GOF | 1.074 | 1.073 |
| R1, wR2 $(I > 2\sigma I)^a$ | 0.0402, 0.0967 | 0.0393, 0.1159 |
| R1, wR2 (all data) | 0.0458, 0.0986 | 0.0416, 0.1171 |

$^a$ R1 $= \Sigma||F_o| - |F_c||/\Sigma|F_o|$; wR2 $= \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

**Table 2. Selected Bond Distances (Å) and Angles (deg) for 3**

| | | | |
|---|---|---|---|
| **Bond Distances** | | | |
| Ru(1)−C(1) | 1.884(3) | Ru(1)−P(1) | 2.4079(8) |
| Ru(1)−C(2) | 1.873(3) | Ru(1)−P(2) | 2.4000(8) |
| Ru(1)−O(3) | 1.918(19) | C(1)−O(1) | 1.140(4) |
| Ru(1)−N(1) | 2.125(2) | C(2)−O(2) | 1.160(4) |
| **Bond Angles** | | | |
| C(1)−Ru(1)−C(2) | 93.16(14) | C(2)−Ru(1)−N(1) | 91.45(13) |
| C(1)−Ru(1)−P(1) | 98.96(10) | C(2)−Ru(1)−O(3) | 173.52(12) |
| C(1)−Ru(1)−P(2) | 97.15(10) | P(1)−Ru(1)−N(1) | 82.26(7) |
| C(1)−Ru(1)−O(3) | 92.75(11) | P(1)−Ru(1)−P(2) | 162.95(3) |
| C(1)−Ru(1)−N(1) | 175.14(12) | N(1)−Ru(1)−P(2) | 81.22(7) |
| C(2)−Ru(1)−P(1) | 93.80(9) | N(1)−Ru(1)−O(3) | 82.73(9) |
| C(2)−Ru(1)−P(2) | 90.80(9) | O(3)−Ru(1)−P(2) | 91.11(6) |

However, that reaction afforded a product that has been characterized as [*cis*-Ru(PNP)(CO)$_2$OH]PF$_6$ (**3**) after analysis of the X-ray structural data in addition to spectral and elemental analysis data. Although deprotonation of aquo complexes usually requires mild base,[5] the expected intermediate aquo complex is not observable in this case. The ORTEP[6] diagram for **3** (cation only) is shown in Figure 1; the X-ray data collection parameters are shown in Table 1, and selected bond distances and bond angles are shown in Table 2. Compound **3** has distorted octahedral geometry about the ruthenium center and shows cis carbonyl ligands. The similarity in the spectral properties of **1** and **3** suggests that **1** also has cis carbonyl groups. Furthermore, it seems likely that cis geometry is maintained in the conversion of **1** to **2** and that water displaces the acetonitrile ligand without changing the stereochemistry of other ligands. The steric demands of the PNP ligand are such that the P−Ru−P bond angle (162.95-

(3)°) deviates from linearity and is bent toward the hydroxyl ligand. With **3**, the $^{31}$P NMR spectrum shows two resonances, at 82.34 and 82.25 ppm, indicating slightly inequivalent phosphorus atoms. The $^1$H NMR spectrum for **3** shows a doublet at 4.11 ppm with each line further split into virtual triplets and a doublet at 3.88 ppm with broadened lines for the CH$_2$P protons. Compound **3** can also be prepared by treating **2** with water; the reaction requires several days for completion (see Experimental Section).

In an effort to find an alternative way to prepare compound **3**, we treated the acetonitrile complex **2** with aqueous KOH solution. This afforded a new compound, [Ru(PNP)(CO)(CH$_3$CN)H]PF$_6$ (**4**), which has been characterized with spectral data, elemental analysis, and X-ray structure determination. The $^{31}$P NMR spectrum of **3** exhibits resonances at 82.34 and 82.25 ppm, indicating two slightly different phosphorus atoms. The $^1$H NMR spectrum shows a doublet of doublets, with each line further split into virtual triplets, at 3.84 ppm for the CH$_2$P protons. The ORTEP diagram for **4** is shown in Figure 2. X-ray data collection parameters for **4** are shown in Table 1; selected bond distances and bond angles are shown in Table 3. Compound **4** has distorted octahedral geometry about the ruthenium center. The hydride ligand was isotropically refined. The Ru−H bond in **4** is unusually short at 1.23(2) Å and comparable to that (1.25(4) Å) in RuHCl(PPr$_3$)(C$_6$H$_9$NO) reported by Caulton et al.[7] Also, the H−Ru−P$_1$ bond angle in **4** is distorted away from 90° at 76(3)°. The

(5) See, for example: Kelly, J. M.; O'Connell, C. M.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1986**, 253.
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**Scheme 3**



**Scheme 4**
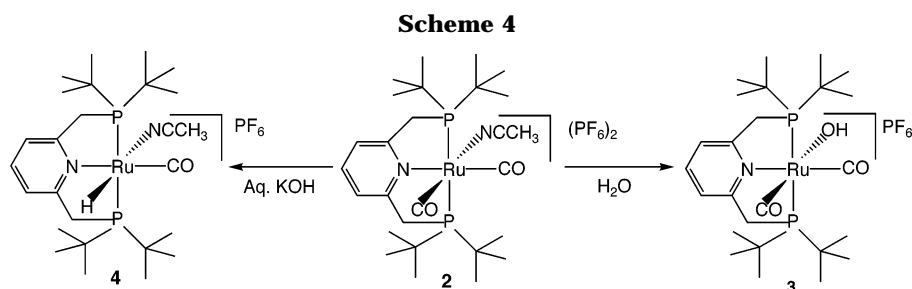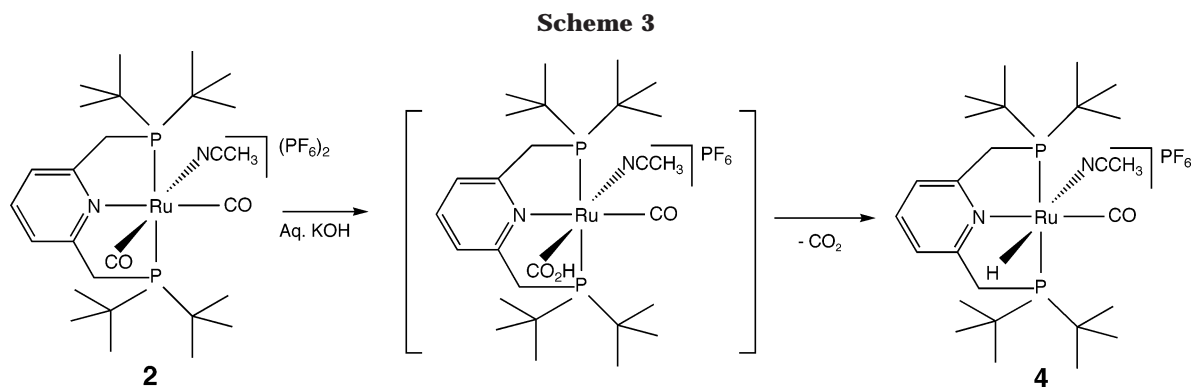


**Table 3.  Selected Bond Distances (Å) and Angles (deg) for 4**

| Bond Distances | | | |
|---|---|---|---|
| Ru(1)−H(1) | 1.23(2) | Ru(1)−P(1) | 2.3413(10) |
| Ru(1)−C(1) | 1.836(4) | Ru(1)−P(2) | 2.3449(10) |
| Ru(1)−N(1) | 2.158(3) | C(1)−O(1) | 1.157(5) |
| Ru(1)−N(2) | 2.161(4) | C(2)−N(2) | 1.135(5) |

| Bond Angles | | | |
|---|---|---|---|
| C(1)−Ru(1)−P(1) | 97.60(13) | N(1)−Ru(1)−P(2) | 80.83(10) |
| C(1)−Ru(1)−P(2) | 97.50(13) | N(1)−Ru(1)−H(1) | 93(4) |
| C(1)−Ru(1)−N(1) | 174.90(15) | P(1)−Ru(1)−P(2) | 159.43(4) |
| C(1)−Ru(1)−N(2) | 94.83(15) | P(1)−Ru(1)−N(2) | 97.53(10) |
| C(1)−Ru(1)−H(1) | 83(4) | P(1)−Ru(1)−H(1) | 76(3) |
| N(1)−Ru(1)−N(2) | 90.12(13) | H(1)−Ru(1)−N(2) | 172(3) |
| N(1)−Ru(1)−P(1) | 82.91(10) | H(1)−Ru(1)−P(2) | 93(3) |

P−Ru−P bond angle (159.43(4)°) is distorted from linearity even more than in **3** and is bent toward the hydride ligand. Although **4** was obtained in low yield, the reaction does not provide **3** as a competing product. It is likely that **4** is generated by hydroxide ion addition to a carbonyl ligand followed by decarboxylation of the intermediate metallocarboxylic acid as illustrated in Scheme 3. This method of synthesis and subsequent decarboxylation of a metalloacid to a metal hydride is a well-known process.[8] However, the addition of water to a carbonyl ligand in other cationic complexes is also well-known.[8a] Interestingly, **2** reacts with water by ligand displacement only. The two pathways are summarized in Scheme 4.

## Experimental Section

**General Data.** Reagent grade solvents dichloromethane, acetone, and acetonitrile were used as received. Diethyl ether and methanol were distilled over sodium benzophenone and $P_2O_5$, respectively. $CD_3CN$ was obtained from Cambridge Isotope Laboratories. Ammonium hexafluorophosphate, triethylamine, di-*tert*-butylphosphine, di-*tert*-butylchlorophosphine, 2,6-lutidine, 2,6-bis(chloromethyl)pyridine, and silver

tetrafluoroborate were obtained from Aldrich. $RuCl_3 \cdot 3H_2O$ was purchased from Pressure Chemical Co. $[Ru(CO)_2Cl_2]_n$[9] and 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine[3] (PNP) were prepared according to literature procedures. Spectral data were obtained on the following instruments: NMR, Varian Unity Inova 500 MHz; FTIR, Mattson RS1. Diffuse reflectance data were obtained on the Mattson instrument with a DRIFTS accessory (Graseby-Specac Inc., "Mini-Diff") as KCl dispersions. All spectra were recorded at 25 °C. ^{1}H NMR chemical shifts were referenced to residual protons in the deuterated solvent, acetonitrile (1.93 ppm). In ^{13}C NMR measurements the signal of $CD_3CN$ at 1.30 ppm was used as a reference. ^{31}P NMR chemical shifts are reported in parts per million downfield from $H_3PO_4$ and referenced to external 85% phosphoric acid in $D_2O$. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

**[Ru(PNP)(CO)$_2$Cl]PF$_6$ (1).** PNP ligand (2.28 g, 5.76 mmol) was added to a suspension of $[Ru(CO)_2Cl_2]_n$ (1.20 g, 5.26 mmol) in dry methanol (40 mL). The mixture was refluxed for 2 h, then the clear yellow solution was cooled to room temperature. A solution of 1.10 g (6.75 mmol) of $NH_4PF_6$ dissolved in a minimum amount of methanol was added, and this mixture was stirred for 15 min. During this period a white solid precipitated. It was collected by vacuum filtration and then dried under vacuum to give a white solid, mp > 250 °C, yield 2.31 g (60%). The product was recrystallized from acetone/diethyl ether. Anal. Calcd for $C_{25}H_{43}NClF_6O_2P_3Ru$: C, 40.96; H, 5.91. Found: C, 40.94; H, 6.11. IR (DRIFTS, KCl): $\nu_{CO}$ 2054 and 1990 cm$^{-1}$. ^{1}H NMR (CD$_3$CN): δ 7.94 (t, 1H, pyridine-H4), 7.63 (d, 2H, pyridine-H3,5), 4.14 (dd with splitting of each line into vt, 4H, CH$_2$P), 1.42 and 1.39 (vt, 18 H each, *tert*-butyl methyls). ^{31}P NMR (CD$_3$CN): δ 82.27.

**[Ru(PNP)(CO)$_2$(CH$_3$CN)](PF6)$_2$·0.5CH$_3$COCH$_3$ (2).** To a solution of 1.00 g (1.36 mmol) of **1** in acetone (20 mL) was added AgBF$_4$ (0.32 g, 1.63 mmol) in the minimum amount of acetone. The solution was stirred at room temperature for 30 min under nitrogen, and then the solvent was evaporated. The resulting white solid was triturated with CH$_3$CN and stirred for 15 min, and then the mixture was filtered to remove AgCl. An aqueous solution of NH$_4$PF$_6$ (0.28 g, 1.70 mmol) was added,

(8) (a) See: Bennett, M. A. *J. Mol. Catal.* **1987**, *41*, 1, and references therein. (b) Gibson, D. H.; Mehta, J. M.; Ye, M.; Richardson, J. F.; Mashuta, M. S. *Organometallics* **1994**, *13*, 1070.

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and the mixture was stirred for 15 min. The solvents were evaporated and the product was collected and washed with water to remove excess ammonium salt; the product yield was 1.2 g (93%), mp > 250 °C. The product was recrystallized from acetone/hexane and then dried under vacuum. Anal. Calcd for $C_{27}H_{46}N_2F_{12}O_2P_4Ru \cdot 0.5CH_3COCH_3$: C, 37.51; H, 5.41. Found: C, 37.24; H, 5.23. IR (DRIFTS, KCl): $\nu_{CN}$ 2357 and 2330 cm$^{-1}$, $\nu_{CO}$ 2085 and 2038 cm$^{-1}$. $^1$H NMR (CD$_3$CN): $\delta$ 8.09 (t, 1H, pyridine-H4), 7.75 (d, 2H, pyridine-H3,5), 4.11 (dd with splitting of each line into a vt, 4H, CH$_2$P), 2.41 [s, 3H (0.5 acetone)], 2.07 (CH$_3$CN), 1.43 and 1.40 vt, 18H each, *tert*-butyl methyls). $^{31}$P NMR (CD$_3$CN): $\delta$ 82.08.

**[Ru(PNP)(CO)$_2$OH]PF$_6$ (3).** (a) To a solution of 0.25 g (0.26 mmol) of **2** in 15 mL of acetone was added 4 mL of water. The colorless solution was stirred at room temperature. During the next 7 days, aliquots of the solution were monitored by $^1$H NMR spectroscopy. Slow transformation of **2** to **3** took place. After this time, the solution was evaporated to dryness and the crude product collected (0.18 g, 91% yield). The product was recrystallized from acetone; it had the same spectral properties as the product obtained from method b.

(b) To a solution of 1.20 g (1.64 mmol) of **1** in acetone (15 mL) was slowly added AgBF$_4$ (0.39 g, 2.00 mmol) in the minimum amount of acetone. The solution was stirred at room temperature for 40 min under nitrogen, and then solvent was evaporated. The resulting white solid was treated with H$_2$O (20 mL) and stirred overnight, and then the mixture was filtered to remove AgCl. An aqueous solution (5 mL) of NH$_4$-PF$_6$ (0.33 g, 2.02 mmol) was added and the mixture stirred for 20 min. Then CH$_2$Cl$_2$ (25 mL) was added, and the mixture was stirred for 30 min. The organic layer was separated, dried with anhydrous MgSO$_4$, and then evaporated to dryness. After drying, 1.10 g of crude product was collected (94% yield; mp > 250 °C). The product was recrystallized from acetone and hexane and then dried under vacuum over P$_2$O$_5$. Anal. Calcd for $C_{25}H_{44}NF_6O_3P_3Ru$: C, 42.02; H, 6.21. Found: C, 41.60; H, 5.91. IR (DRIFTS, KCl): $\nu_{CO}$ 2034 and 1973 cm$^{-1}$. $^1$H NMR (CD$_3$CN): $\delta$ 7.97 (t, 1H, pyridine-H4), 7.64 (d, 2H, pyridine-H3,5), 4.11 (d with both lines split into virtual triplets, 2H, CH$_2$P), 3.88 (d with broadened lines, 2H, CH$_2$P), 1.40 and 1.34 (vt, 18H each, *tert*-butyl methyls). $^{31}$P NMR (CD$_3$CN): $\delta$ 82.34 and 82.25.

**[Ru(PNP)(CO)(CH$_3$CN)H]PF$_6$ (4).** To a colorless solution of 0.50 g (0.52 mmol) of **2** in acetone (10 mL) was added 0.5 mL of 0.5 M KOH solution dropwise. The color of the solution changed to yellow immediately. The solution was stirred for 10 min at room temperature and solvents were evaporated. The yellow residue was redissolved in a mixture of H$_2$O (10 mL) and CHCl$_2$ (10 mL). After 10 min stirring, the organic layer was collected, dried with anhydrous MgSO$_4$, and then evaporated to dryness. After drying, 0.11 g (27% yield; mp 220 °C) of crude product was obtained. The product was recrystallized from acetone and water. Anal. Calcd for $C_{26}H_{47}N_2F_6OP_3$-Ru: C, 43.88; H, 6.66. Found: C, 44.16; H, 6.73. IR (DRIFTS, KCl): $\nu_{CN}$ 2105 cm$^{-1}$, $\nu_{Ru-H}$ 2078 cm$^{-1}$, $\nu_{CO}$ 1915 cm$^{-1}$. $^1$H NMR (CD$_3$CN): $\delta$ 7.73 (t, 1H, pyridine-H4), 7.40 (d, 2H, pyridine-H3,5), 3.84 (dd with splitting of each line into a vt, 4H, CH$_2$P), 2.13 (s, 3H, CH$_3$CN) 1.37 and 1.22 (vt, 18H each, *tert*-butyl methyls), $-13.80$ (t, $J_{PH}$ = 18.5 Hz, 1H, Ru−H). $^{31}$P NMR (CD$_3$-CN): $\delta$ 88.14.

**X-ray Crystal Structures of 3 and 4.** Crystals of **3** suitable for X-ray analysis were grown by slow evaporation of an acetone solution. A $0.23 \times 0.16 \times 0.04$ mm$^3$ colorless single crystal of **3** was mounted on a 0.05 mm CryoLoop with Paratone oil for collection of X-ray data on a Bruker SMART APEX CCD diffractometer. The SMART[10] software package (v 5.628) was used to acquire a total of 1868 30-s frame $\omega$-scan exposures of data at 100 K to a $2\theta$ max = 56.52° using

monochromated Mo K$\alpha$ radiation (0.71073 Å) from a sealed tube and a monocapillary. Frame data were processed using SAINT[11] (v 6.36) to determine final unit cell parameters: $a$ = 8.2883(6) Å, $b$ = 12.7436(10) Å, $c$ = 15.7252(12) Å, $\alpha$ = 106.437-(1)°, $\beta$ = 104.999(1)°, $\gamma$ = 92.173(1)°, $V$ = 1527.7(2) Å$^3$ and to produce raw *hkl* data that were then corrected for absorption (transmission min./max. = 0.833/0.986; $\mu$ = 0.735 mm$^{-1}$) using SADABS[12] (v 2.05). The structure was solved by direct methods in the space group $P\bar{1}$ using SHELXS-90[13] and refined by least-squares methods on $F^2$ using SHELXL-97[14] incorporated into the SHELXTL[15] (v 6.12) suite of programs. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their geometrically generated positions and refined as a riding model. The hydroxyl H atom was located by a difference map and was included as a fixed contribution with $U$(H) = 1.5 $U_{eq}$ (attached O atom). Methylene and phenyl H's were included as fixed contributions with $U$(H) = 1.2 $U_{eq}$ (attached C atom), while methyl groups were allowed to ride (the torsion angle which defines its orientation was allowed to refine) on the attached C atom, and these atoms were assigned $U$(H) = 1.5 $U_{eq}$. For all 6835 unique reflections ($R_{int}$ = 0.0189) the final anisotropic full matrix least-squares refinement on $F^2$ for 364 variables converged at R1 = 0.0458 and wR2 = 0.0986 with a GOF of 1.074.

Crystals of **4** suitable for X-ray analysis were grown by slow evaporation from a methanol solution. X-ray structural analysis for **4** was performed on a $0.17 \times 0.16 \times 0.09$ mm$^3$ colorless plate using an identical data acquisition strategy described above for **3** at 100 K to a $2\theta_{max}$ = 56.440. Compound **4** crystallizes in the non-centrocemetric orthorhombic space group $P2_12_12_1$ with unit cell parameters $a$ = 13.3421(8) Å, $b$ = 15.5510(9) Å, $c$ = 16.4447(10) Å, $V$ = 3412.0(4) Å$^3$, $Z$ = 4, and $r_{calcd}$ = 1.433 Mg m$^{-3}$. The 7910 raw independent reflections were corrected for absorption (transmission min./max. = 0.906/0.989; $\mu$ = 0.658 mm$^{-1}$) using SADABS[12] (v 2.05). The structure was solved by direct methods and refined on $F^2$ using SHELX-TL.[14] A partial occupancy (75%) methanol solvate was present. All non-hydrogen atoms were refined anisotropically. The hydride H atom was located from an electron difference map and refined isotropically. Methyl, methylene, and phenyl H's were included as fixed contributions as described above for **1**. For all 7910 unique reflections ($R$(int) = 0.0255) the final anisotropic full matrix least-squares refinement on $F^2$ for 391 variables converged at R1 = 0.0416 and wR2 = 0.1171 with a GOF of 1.073. The absolute structure was determined by refinement of the Flack parameter (0.09(3)).

**Supporting Information Available:** Tables giving full details of the crystallographic data and data collection parameters, atomic coordinates, anisotropic displacement parameters, bond distances, bond angles, and torsion angles for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030659O

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