### Supporting Information

### Phosphine-Imine and -Enamido Ligands for Acceptorless Dehydrogenation Catalysis

James M. Stubbs<sup>†</sup>, Kelly F. Firth<sup>†</sup>, Benjamin J. Bridge, Kathleen J. Berger, Richard J. Hazlehurst, Paul D. Boyle and Johanna M. Blacquiere\*

Department of Chemistry University of Western Ontario London, Ontario, Canada, N6A 5B7

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### **I** General Considerations

Reactions were conducted in a nitrogen atmosphere glove box or using standard Schlenk line techniques under a nitrogen atmosphere, unless otherwise indicated. Flasks, vials, and tubes were oven dried and cooled under nitrogen atmosphere prior to use. All reagents used were obtained from commercially available sources and used without further purification, unless otherwise indicated. All reaction solvents were obtained from an Innovative Technology 400-5 Solvent Purification system, dry and degassed, and stored over 4 Å molecular sieves under N<sub>2</sub> prior to use unless stated otherwise. Deuterated NMR solvents were obtained from commercial sources and stored over sieves. Solvents were removed under reduced pressure using a rotary evaporator or high vacuum line. RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> was synthesized following literature procedure.<sup>1</sup>

All NMR spectra were obtained on 400 or 600 MHz Varian spectrometers. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra were referenced internally to residual solvent values to TMS at 0 ppm as follows: benzene- $d_6$  (<sup>1</sup>H, 7.16 ppm; <sup>13</sup>C{<sup>1</sup>H}, 128.06 ppm), CDCl<sub>3</sub> (<sup>1</sup>H, 7.26 ppm), acetone- $d_6$  (<sup>1</sup>H, 2.05 ppm), CD<sub>3</sub>CN (<sup>1</sup>H, 1.94 ppm), toluene- $d_8$  (<sup>1</sup>H, 2.08 ppm). <sup>31</sup>P{<sup>1</sup>H} spectra obtained in deuterated solvents were referenced internally. <sup>31</sup>P{<sup>1</sup>H} spectra obtained in non-deuterated solvents were externally referenced to an 85% H<sub>3</sub>PO<sub>4</sub> sample. Multiplicities are described as s

(singlet), d (doublet), t (triplet), sept (septet), m (multiplet), br (broad) and ov (overlapping). Xray diffractometry measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K. Infrared spectra were collected on solid samples using a PerkinElmer UATR TWO FTIR spectrometer. Elemental analysis was performed by Laboratoire d'Analyse Élémentaire de l'Université de Montréal. Quantification of catalytic reactivity was achieved using an Agilent 7890a gas chromatography with a flame ionization detector (GC-FID), fitted with a HP-5 column. Calibration curves for benzyl alcohol, benzaldehyde, benzyl benzoate, benzyl amine, phenyl-N-(phenylmethyl)-methanimine, benzonitrile, and dibenzylamine were prepared to determine the response factors for each of the latter three species relative to benzylamine. The amount of each species was quantified, relative to the internal standard (tetrahydronaphthlene), using area counts corrected with the response factors.

### **II Synthetic Procedures**

### Synthesis of 2-diphenylphosphinoaniline

PPh<sub>2</sub> NH<sub>2</sub>

2-Diphenylphosphinoaniline was synthesized as per literature procedure,<sup>2</sup> with the exception of the KPPh<sub>2</sub> source. Instead of starting from commercially available KPPh<sub>2</sub>, the salt was generated in situ. In the glovebox, a solution of HPPh<sub>2</sub> (1.86 g, 10.0 mmol) in THF was added dropwise to a suspension of KH (0.40 g, 10.0 mmol) in THF. The resulting solution was dark orange, and the mixture was stirred for 10 min until H<sub>2</sub> evolution ceased. Fluoroaniline (1.03 g, 9.26 mmol) was added directly to this solution, and the synthesis was continued as per literature procedure. Compound **2** was obtained in 66% yield. The <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra matched the literature values.<sup>2</sup>

### Synthesis of H(1)



In a Schlenk flask, solid 2-diphenylphosphoaniline (0.250 g, 0.9 mmol) and liquid isobutyraldehyde (0.083 g, 1.15 mmol) were dissolved in 10 mL of toluene with 4 Å sieves. Formic acid (1.7  $\mu$ l, 0.045 mmol) was added, and the solution was stirred at room temperature for 24 h. Under ambient atmosphere, the reaction mixture was filtered to remove sieves. The solvent and excess isobutyraldehyde were removed by rotary evaporation, and 15 mL of hexanes was added to the resulting crude oil to form a solid precipitate. Without filtration, the solvent was removed by rotary evaporation to yield a white solid. Yield: 0.270 g (90%). Average Yield of

different iterations: 72% <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 599 MHz):  $\delta = 7.41 - 7.36$  (m, *m*-*H*(Ph), 4H), 7.29 (d, J = 3.8 Hz,  $H^{l}$ , 1H), 7.14 – 7.10 (m,  $H^{\delta}$ , 1H), 7.07 – 7.03 (m, *o*- and *p*-*H*(Ph), 6H), 7.01 (ddd, J = 7.8 Hz, 4.2, 1.8 Hz,  $H^{7}$ , 1H), 6.92 – 6.87 (m,  $H^{6}$ , 1H), 6.67 (ddd, J = 7.8, 4.2, 0.6 Hz,  $H^{4}$ , 1H), 2.15 (septdd, J = 6.6, 4.2, 0.6 Hz,  $H^{2}$ , 1H), 0.80 (d, J = 6.9 Hz,  $H^{3}$ , 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 151 MHz):  $\delta = 170.0$  (d,  $J_{CP} = 1.5$  Hz,  $C^{l}$ ), 155.7 (d,  $J_{CP} = 19.0$  Hz,  $C^{9}$ ), 138.2 (d,  $J_{CP} = 12.7$  Hz, *ipso-C*(Ph)<sub>2</sub>P), 134.7 (d,  $J_{CP} = 20.7$  Hz, *m*-C(Ph)<sub>2</sub>P), 133.0 (s,  $C^{7}$ ), 131.8 (d,  $J_{CP} = 15.0$  Hz,  $C^{8}$ ), 129.9 (s,  $C^{5}$ ), 128.7 (s, *p*-C(Ph)<sub>2</sub>P), 128.6 (d,  $J_{CP} = 2.9$  Hz, *o*-C(Ph)<sub>2</sub>P), 125.5 (s,  $C^{6}$ ), 117.9 (d,  $J_{CP} = 2.0$  Hz,  $C^{4}$ ), 34.8 (s,  $C^{2}$ ), 18.6 (s,  $C^{3}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 243 MHz):  $\delta = -14.4$  (s, *P*ArPh<sub>2</sub>). Anal. Calc. for C<sub>22</sub>H<sub>22</sub>NP: C, 79.74; H, 6.69; N, 4.23. Found: C, 79.74; H, 7.03; N, 4.12.



Solid RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (0.434 g, 0.453 mmol) was dissolved in 2 mL of THF. A solution of compound H(1) (0.150 g, 0.453 mmol) in 5 mL of THF was added, which resulted in an immediate colour change from purple to green. The reaction mixture was stirred for 2 h at room temperature. The solvent was reduced to approximately 1 mL on a high vacuum line, and hexanes (4 mL) was added to afford a green precipitate. The precipitate was collected by filtration, washed with ca. 15 mL hexanes, and dried. Yield: 0.241 g (70%). <sup>1</sup>H NMR ( $C_6D_6$ , 400 MHz):  $\delta$  8.26 (t, J = 16.0 Hz,  $H^{1}$ , 1H), 7.87 - 7.82 (m, ortho H of PPh<sub>3</sub>, 6H), 7.70 - 7.65 (m, ortho H of PPh<sub>2</sub>, 4H), 7.27 - 7.21 (m,  $H^4$  and  $H^7$ , 2H), 7.06 - 6.98 (m, meta H of PPh<sub>3</sub> and para H of PPh<sub>2</sub> and *para H* of PPh<sub>3</sub>, 11H), 6.90 - 6.85 (m, *meta H* of PPh<sub>2</sub> and H<sup>5</sup>, 4H), 6.80 - 6.77 (m,  $H^{6}$ , 1H), 2.79 (m,  $H^{2}$ , 1H), 1.18 (d, J = 8.0 Hz,  $H^{3}$ , 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 151 MHz):  $\delta$  171.7 ( $C^{1}$ ), 152.4 (d, <sup>2</sup> $J_{CP} = 13.6$  Hz,  $C^{9}$ ), 138.5 (d, <sup>1</sup> $J_{CP} = 43.8$  Hz,  $C^{8}$ ), 135.3 (d, <sup>2</sup> $J_{CP} = 10.6$  Hz, ortho C of PPh<sub>3</sub>), 134.7 - 134.6 (m, ortho C of PPh<sub>2</sub> and ipso C of PPh<sub>3</sub> and ipso C of PPh<sub>2</sub>), 132.0 ( $C^7$ ), 130.5 ( $C^5$ ), 129.9 (d,  ${}^4J_{CP}$  = 1.5 Hz, para C of PPh<sub>2</sub>), 129.4 (d,  ${}^5J_{CP}$  = 1.5 Hz, para C of PPh<sub>3</sub>), 128.0 ( $C^6$ ), 128.1 (meta C of PPh<sub>3</sub>), 127.90 (meta C of PPh<sub>2</sub>), 116.5 ( $C^4$ ), 37.2 ( $C^2$ ), 19.25 (C<sup>3</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 162 MHz):  $\delta = 89.0$  (d, <sup>2</sup>J<sub>PP</sub> = 35.6 Hz, PArPh<sub>2</sub>), 46.0 (d, <sup>2</sup>J<sub>PP</sub> = 35.6 Hz, Ru(PPh<sub>3</sub>)). Single crystals were obtained by vapour diffusion of diethyl ether into a solution of **2** in acetone. Anal. Calc. for C<sub>40</sub>H<sub>37</sub>Cl<sub>2</sub>NP<sub>2</sub>Ru: C, 62.75; H, 4.87; N, 1.83. Found: C, 62.37; H, 4.99; N, 1.76.



In a glove box, solid green 2 (0.150 g, 0.200 mmol) was dissolved in 3 mL of pyridine to give an amber solution. A solution of Li[N(SiMe<sub>3</sub>)<sub>2</sub>] (0.039 g, 0.23 mmol) in 2 mL of pyridine was added, resulting in an immediate colour change to red. The reaction mixture was stirred for 2 h, after which the solvent was reduced to approximately 1 mL, and ca. 5 mL cold hexanes were added to form a red precipitate. The precipitate was collected by filtration, washed with ca. 15 mL cold hexanes, and dried to yield a red solid. Despite multiple washings, <sup>1</sup>H NMR analysis reveals that ca. 2 molecules of pyridine remains relative to 3. Yield for 3: 120 mg (85%, 95%) purity). Free pyridine (py\*) signals are indicated in the listed NMR spectroscopy data. <sup>1</sup>H NMR  $(599 \text{ MHz}, C_6D_6)$ :  $\delta = 8.95-8.87$  (br, py-H, 2H), 8.70-8.59 (br, py-H, 2H), 8.53-8.48 (ov m, py\* and Ar-H), 8.43 (d, J = 4.8 Hz, Ar-H 2H), 7.70 (t, J = 7.8 Hz,  $H^7$ , 1H), 7.50 (t, J = 8.4 Hz, Ar-H, 2H), 7.31-7.30 (m, H<sup>5</sup> and H<sup>4</sup>, 2H), 6.98-6.95 (ov m, py\* and Ar-H, 2H), 6.93-6.90 (m, Ar-H, 2H), 6.86 (t, J = 7.8 Hz, Ar-H, 1H), 6.82-6.79 (m, Ar-H, 2H), 6.66 (py\*), 6.60 (t, J = 7.8 Hz,  $H^6$ , 1H), 6.55-6.52 (m, Ar-H, 2H), 6.47-6.45 (m, Ar-H, 2H), 6.12-6.08 (m, Ar-H, 3H), 5.83 (s, H<sup>1</sup>, 1H), 1.61 (s,  $H^3$  or  $H^3$ , 3H), 1.54 (s,  $H^3$  or  $H^3'$ , 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  168.3 (d,  $^{2}J_{CP} = 23.6 \text{ Hz}, C^{9}$ , 159.1 (Ar-C), 156.4 (Ar-C), 155.2 (Ar-C), 150.3 (py\*), 137.6 (Ar-C), 137.3 (Ar-C), 137.1 (Ar-C), 137.0 (Ar-C), 136.8 (C<sup>1</sup>), 135.8 (C<sup>7</sup>), 135.2 (py\*), 135.1 (Ar-C), 134.2 (d,  $J_{CP} = 9.2$  Hz, Ar-C), 133.1 (Ar-C), 132.7 (Ar-C), 132.6 (Ar-C), 130.7 (C<sup>5</sup>), 123.5 (py\*), 123.2 (År-*C*), 123.0 (År-*C*), 122.0 (År-*C*), 118.8 (*C*<sup>2</sup>), 116.9 (d, J = 11.5 Hz, *C*<sup>4</sup>), 112.0 (d,  $J_{CP} = 48.5$  Hz, *C*<sup>8</sup>), 111.4 (d,  $J_{CP} = 6.3$  Hz, *C*<sup>6</sup>), 67.8, 22.3 (*C*<sup>3'</sup> or *C*<sup>3</sup>), 20.1 (*C*<sup>3</sup> or *C*<sup>3'</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (162) MHz, C<sub>6</sub>D<sub>6</sub>): δ 71.6.

### General Procedure for Acceptorless Dehydrogenation of Benzyl Alcohol/Benzyl Amine

In a glovebox, the following stock solutions were prepared: Benzyl alcohol (57 mg, 0.53 mmol, 0.50 M) and tetrahydronaphthalene (28 mg, 0.21 mmol, 0.24 M) in toluene (1.05 mL); 3 (10 mg, 0.014 mmol, 0.038 M) in toluene (0.38 mL); 2 (12 mg, 0.015 mmol, 0.0375 mM) in toluene (0.40 mL); pyridine (10 mg, 0.13 mmol, 0.450 M) in toluene (0.28 mL); KPF<sub>6</sub> (10 mg, 0.054 mmol, 0.150 M) in CHCl<sub>3</sub> (0.36 mL). Four vials (A-D) were set up containing stir bars. Vial A was charged with catalyst **3** stock solution (100  $\mu$ L), additional toluene (50  $\mu$ L) and benzyl alcohol stock solution (150  $\mu$ L). Vial B and D were charged with the KPF<sub>6</sub> stock solution (25  $\mu$ L) and the solvent was then removed by vacuum. The catalyst 2 stock solution (100  $\mu$ L), additional toluene (25 µL) and benzyl alcohol stock solution (150 µL) were added to B and D. Vial C was charged with catalyst 2 stock solution (100  $\mu$ L), additional toluene (25  $\mu$ L) and benzyl alcohol stock solution (150 µL). Vials C and D were then charged with pyridine stock solution (25 µL). The final concentrations were 0.25 M in benzyl alcohol with 5 mol % loading of [Ru]. A final vial was charged with substrate/internal standard stock solution (150 µL) for use as the initial time = 0 (T0) sample for quantification of substrate and products by GC-FID analysis. The vials (except T0 sample) were capped, taped and removed from the glove box and heated to 100 °C with stirring. At 48 h a vial was removed from heat, cooled, and exposed to air

to quench. An aliquot (40  $\mu L)$  was diluted to 10 mM benzylamine with MeCN (960  $\mu L$ ) and analyzed by GC-FID. An aliquot (20  $\mu L$ ) of the T0 sample was diluted with MeCN (980  $\mu L$ ) and analyzed by GC-FID.

# General Procedure for Acceptorless Dehydrogenative Coupling of Benzyl Alcohol and Benzyl amine

In a glovebox, the following stock solutions were prepared: Benzyl alcohol (57 mg, 0.53 mmol, 1.000 M) and tetrahydronaphthalene (28 mg, 0.21 mmol, 0.480 M) in toluene (53 mL); benzyl amine (54 mg, 0.5 mmol, 1.00 mM) in toluene (0.50 mL); 3 (10 mg, 0.014 mmol, 0.038 M) in toluene (0.38 mL); 2 (12 mg, 0.015 mmol, 0.0375 mM) in toluene (0.40 mL); pyridine (10 mg, 0.13 mmol, 0.450 M) in toluene (0.28 mL); KPF<sub>6</sub> (10 mg, 0.054 mmol, 0.150 M) in CHCl<sub>3</sub> (0.36 mL). To the stock solution of benzyl amine, the stock solution of benzyl alcohol was added (0.50 mL) resulting in concentrations of 0.5 M for both substrates. Four vials (A-D) were set up containing stir bars. Vial A was charged with catalyst 3 stock solution (100  $\mu$ L), additional toluene (50  $\mu$ L) and combined benzyl alcohol and benzyl amine stock solution (150  $\mu$ L). Vial B and D were charged with the KPF<sub>6</sub> stock solution (25  $\mu$ L) and the solvent was then removed by vacuum. The catalyst **2** stock solution (100  $\mu$ L), additional toluene (25  $\mu$ L) and combined benzyl alcohol and benzyl amine stock solution (150 µL) were added to B and D. Vial C was charged with catalyst **2** stock solution (100  $\mu$ L), additional toluene (25  $\mu$ L) and combined benzyl alcohol and benzyl amine stock solution (150 µL). Vials C and D were then charged with pyridine stock solution (25 µL). The final concentrations were 0.25 M of benzyl alcohol and 0.25 M of benzyl amine with 5 mol% loading of [Ru]. A final vial was charged with substrate/internal standard stock solution (150  $\mu$ L) for use as the initial time = 0 (T0) sample for quantification of substrate and products by GC-FID analysis. The vials (except T0 sample) were capped, taped and removed from the glove box and heated to 100 °C with stirring. At 48 h a vial was removed from heat, cooled, and exposed to air to quench. An aliquot (40 µL) was diluted to 10 mM benzylamine with MeCN (960 µL) and analyzed by GC-FID. An aliquot (20 µL) of the T0 sample was diluted with MeCN (980 µL) and analyzed by GC-FID.

#### General Procedure for Stoichiometric Reactions with 3 and H<sub>2</sub>

Complex **3** (10 mg, mmol) was dissolved in benzene (0.8 mL) and added to a J. Young NMR tube. An initial <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectrum were obtained. The NMR tube was attached to the Schlenk line and the solution was degassed by three cycles of freeze, pump and thaw. The tube was filled with H<sub>2</sub> (ca. 1-2 atm). <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectrum was obtained immediately, after which the tube was heated to 75 °C in an oil bath. The reaction was analyzed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy at the time points [T = 0, 10 min, 3 h, 24 h]. No reactivity was observed.



Figure S1. <sup>1</sup>H NMR spectrum of H(1) in C<sub>6</sub>D<sub>6</sub> (600 MHz).



Figure S2. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of H(1) in C<sub>6</sub>D<sub>6</sub> (151 MHz).



Figure S4. <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of H(1) in C<sub>6</sub>D<sub>6</sub> (600 MHz).



Figure S5.<sup>1</sup>H- $^{13}$ C HSQC NMR spectrum of H(1) in C<sub>6</sub>D<sub>6</sub>.



Figure S6.  $^{1}H^{-13}C$  HMBC NMR spectrum of H(1) in C<sub>6</sub>D<sub>6</sub>.



Figure S7. <sup>1</sup>H NMR spectrum of 2 in  $C_6D_6$  (600 MHz)



Figure S8.  ${}^{13}C{}^{1}H$  NMR spectrum of 2 in C<sub>6</sub>D<sub>6</sub> (151 MHz).



Figure S10. <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of 2 in  $C_6D_6$ .



Figure S12.  $^{1}$ H- $^{13}$ C HMBC NMR spectrum of 2 in C<sub>6</sub>D<sub>6</sub>.



**Figure S13.** <sup>1</sup>H NMR spectrum of **3** in  $C_6D_6$  (600 MHz).



Figure S14. <sup>13</sup>C $\{^{1}H\}$  NMR spectrum of 3 in C<sub>6</sub>D<sub>6</sub>(151 MHz).



Figure S16. <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of 3 in C<sub>6</sub>D<sub>6</sub>.



Figure S17.  $^{1}$ H- $^{13}$ C HSQC NMR spectrum of 3 in C<sub>6</sub>D<sub>6</sub>.



Figure S18. <sup>1</sup>H-<sup>13</sup>C HMBC NMR spectrum of 3 in  $C_6D_6$ .

	$\mathrm{H}^{1}$	$H^2$	$C^1$	$C^2$	$\mathbf{P}^1$
H(1)	7.29	2.15 (m)	170.0	34.8	-14.4 (s)
2	8.26	2.79 (m)	171.8	37.2	$89.0 (d, {}^{2}J_{PP})$ = 35 Hz)
3	5.83	_	137.1	118.8	71.6 (s)
$\kappa^{1}$ -N M(1-azaallyl) <sup>b</sup>	7.28 <sup>c</sup>	_	149.8 – 187.5 <sup>d</sup>	$66.3 - 114.8^d$	
η <sup>3</sup> -NCC M(1- azaallyl) <sup>b</sup>	N/A	_	151.9 – 184.9 <sup>e</sup>	$42.0 - 64.5^{e}$	_

Table S1. Diagnostic NMR data for H(1), 2 and 3.<sup>a</sup>

<sup>*a*</sup>Spectra recorded in C<sub>6</sub>D<sub>6</sub> and field strengths are <sup>1</sup>H = 600 MHz; <sup>13</sup>C{<sup>1</sup>H} = 151 MHz; <sup>31</sup>P{<sup>1</sup>H} = 243 MHz. <sup>*b*</sup>Reported  $\delta$  values for known compounds. <sup>*c*</sup>One compound.<sup>3</sup> <sup>*d*</sup>Range for 7 compounds (Table S3).<sup>3-7</sup> <sup>*e*</sup>Range for a selection of 10  $\eta^3$ -NCC M(1-azallyl) compounds (Table S3).<sup>4,8</sup>

**Table S2.** Diagnostic <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR signals for known  $\kappa^{1}$ -N and  $\eta^{3}$ -NCC 1-azaallyl complexes.

Complex	$H^1$ (ppm)	$C^{1}$ (ppm)	$C^{2}$ (ppm)	Ref.
$\kappa^{1}$ -N				
$ \underbrace{ \begin{array}{c} \stackrel{i Pr_2}{\bigcirc} \stackrel{H}{\bigcirc} \stackrel{H}{\longrightarrow} \stackrel{H}{\bigcirc} \stackrel{H}{\longrightarrow} \stackrel{H}{\bigcirc} \stackrel{H}{\bigcirc} \stackrel{H}{\longrightarrow} \stackrel{H}{\bigcirc} \stackrel{H}{\longrightarrow} \stackrel{H}{\bigcirc} \stackrel{H}{\longrightarrow} \stackrel{H}{\rightarrow$	_	$187.5 (dd, {}^{3}J_{PC} = 4.3 Hz^{2} Lz = 4.3$	$\begin{array}{rcl} 84.4 \\ (^{1}J_{\rm PC} &=& 41.6 \\ \text{Hz} \end{array}$	5
Ar		33.3 Hz)	112)	
$ \begin{array}{c} H \\                                   $	7.28 (ddt, ${}^{3}J_{HP} =$ 38.2 Hz, ${}^{3}J_{HH}/{}^{4}J_{HP} = 4.9$ Hz, ${}^{4}J_{HP} = 1.4$ Hz)	$\begin{array}{c} 161.9 \\ (d, {}^{2}J_{\rm CP} = 20.9 \\ \text{Hz}) \end{array}$	$\begin{array}{l} 66.3 \\ (dd, {}^{1}J_{CP} = \\ 40.3 \text{ Hz}, {}^{3}J_{CP} \\ = 5.2 \text{ Hz})) \end{array}$	3
$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\$	_	156.4 (s)	114.8 (s)	6
$ \begin{array}{c c} Me_{3}Si \underbrace{\overset{Bu}{\underset{{}}{\overset{{}}}{\overset{{}}{\overset{{}}{\overset{{}}}{\overset{{}}{\overset{{}}}{\overset{{}}{\overset{{}}}{\overset{{}}{\overset{{}}}{\overset{{}}{\overset{{}}{\overset{{}}}{\overset{{}}{\overset{{}}}{\overset{{}}{\overset{{}}}{\overset{{}}{\overset{{}}}{\overset{{}}{\overset{{}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}{\overset{{}}}{\overset{{}}}{\overset{{}}{\overset{{}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}{\overset{{}}}{\overset{{}}}{\overset{{}}}{\overset{{}}}}}}$	_	<b>A</b> : 149.8 (s) <b>B</b> : 150.7 (s)	<b>A</b> : 108.4 (s) <b>B</b> : 109.4 (s)	4
(2 isomers: A and B)				



<sup>t</sup> Bu	-	184.9 (s)	48.8 (s)	8
$Me_3Si \sim N \xrightarrow{c^1} c^2 SiMe_3$				
Pd				
/				
<sup>t</sup> Bu	-	183.2 (s)	60.8	8
$Me_3Si \sim N \xrightarrow{c^1} c^2 SiMe_3$			$(d, {}^{2}J_{CP} = 5.3$	
Pd			Hz)	
۱ PPh <sub>3</sub>				

## **IV IR Spectra**



Figure S19. FT-IR spectrum of solid H(1).



Figure S20. FT-IR spectrum of solid 2.



Figure S21. FT-IR spectrum of solid 3.

### V Catalysis and Calibration Curves



**Figure S22.** Catalysis curve of benzyl alcohol (**A**) at 250 mM using **3** (5 mol%) at 100 °C over 72 h. The amount of each species was quantified, relative to the internal standard (tetrahydronaphthlene), using area counts corrected with the response factors. Data points are an average of two or three runs and the error bars represent the span of the obtained data.



**Figure S23.** Catalysis curve of benzyl alcohol (**A**) using  $2 + \text{KPF}_6$  (5 mol%) at 100 °C over 72 h. The amount of each species was quantified, relative to the internal standard (tetrahydronaphthlene), using area counts corrected with the response factors. Data points are an average of two or three runs and the error bars represent the span of the obtained data.



**Figure S24.** Catalysis curve of benzyl alcohol (A) using 2 + LiHMDS (5 mol%) at 100 °C over 72 h. The amount of each species was quantified, relative to the internal standard (tetrahydronaphthlene), using area counts corrected with the response factors. Data points are an average of two or three runs and the error bars represent the span of the obtained data.



Figure S25. Catalysis curve of benzyl amine using 3 (5 mol%) at 100  $^{\circ}$ C over 72 h. The amount of each species was quantified, relative to the internal standard (tetrahydronaphthlene), using area counts corrected with the response factors. Data points are an average of two or three runs and the error bars represent the span of the obtained data.



**Figure S26.** Catalysis curve of benzyl amine using  $2 + \text{KPF}_6$  (5 mol%) at 100 °C over 72 h. The amount of each species was quantified, relative to the internal standard (tetrahydronaphthlene), using area counts corrected with the response factors. Data points are an average of two or three runs and the error bars represent the span of the obtained data.



**Figure S27.** Catalysis curve of benzyl amine using 2 + LiHMDS (5 mol%) at 100 °C over 72 h. The amount of each species was quantified, relative to the internal standard (tetrahydronaphthlene), using area counts corrected with the response factors. Data points are an average of two or three runs and the error bars represent the span of the obtained data.



**Figure S28.** Calibration curve of benzyl alcohol (A) with a slope of 253  $\text{mM}^{-1}$ .



Figure S29. Calibration curve of benzaldehyde (B) with a slope of 228 mM<sup>-1</sup>.



Figure S30. Calibration curve of benzyl benzoate (C) with a slope of  $1060 \text{ mM}^{-1}$ .



**Figure S31.** Calibration curve of benzyl amine (**D**) with a slope of 240 m $M^{-1}$ .



**Figure S32.** Calibration curve of N-benzyl-phenylmethanimine (E) with a slope of 750 m $M^{-1}$ .



**Figure S33.** Calibration curve of benzonitrile (F) with a slope of  $162 \text{ mM}^{-1}$ .



**Figure S34.** Calibration curve of dibenzylamine (G) with a slope of 668  $\text{mM}^{-1}$ .

### VI Crystallographic Data

### Crystallographic Details for 2 and 3

*Data Collection and Processing*. The samples of **2** and **3** were mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K. The frame integration was performed using SAINT.<sup>9</sup> The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.<sup>10</sup>

Structure Solution and Refinement. The structure was solved by using a dual space methodology using the SHELXT program.<sup>11</sup> For **2**, there was disorder of the isopropyl group was disordered over two conformations. The normalized occupancy of the dominant conformer was refined to a value of 0.759(6). Disordered atom positions denoted with an asterisk. All non-hydrogen atoms for **2** and **3** were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural models were fit to the data using full matrix least-squares based on  $F^2$ . The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structures were refined using the SHELXL-2014 program from the SHELX suite of crystallographic software.<sup>11</sup> Graphic plots were produced using the XP program or the NRCVAX implementation of ORTEP.<sup>12,13</sup>



**Figure S35.** ORTEP drawing of **2** showing naming and numbering scheme. Ellipsoids are shown at a 50% probability level. Only one of the conformers of the iso-propyl groups is shown. Hydrogen atoms and the non-coordinating co-crystallized DMF molecule are removed for clarity.



**Figure S36.** ORTEP drawing of **3** showing naming and numbering scheme. Ellipsoids are shown at a 50% probability level. Hydrogen atoms and the co-crystallized THF molecule are removed for clarity.

**Table S3.** Summary of Crystal Data for **2** and **3** 

Compound number	2	3
CCDC	1470534	1470535
Formula	$C_{46}H_{51}Cl_2N_3O_2P_2Ru$	C41H44ClN4OPRu
Formula Weight (g/mol)	911.81	776.29
Crystal Dimensions (mm)	$0.387\times0.056\times0.037$	$0.234\times0.060\times0.032$
Crystal Color and Habit	orange needle	red plate
Crystal System	monoclinic	monoclinic
Space Group	P 2 <sub>1</sub> /n	C c
Temperature, K	110	110
<i>a</i> , Å	19.730(8)	9.445(4)
<i>b</i> , Å	10.286(4)	25.327(9)
<i>c</i> , Å	22.226(10)	16.190(6)
α,°	90	90
β,°	90.131(11)	106.706(19)
γ,°	90	90
V, $Å^3$	4511(3)	3710(3)

Number of reflections to determine final unit cell	9856	9891
Min and Max 2θ for cell determination, °	4.46, 52.54	4.8, 59.86
Ζ	4	4
F(000)	1888	1608
$\rho(g/cm)$	1.343	1.390
λ, Å, (ΜοΚα)	0.71073	0.71073
$\mu, (cm^{-1})$	0.576	0.576
Diffractometer Type	Bruker Kappa Axis Apex2	Bruker Kappa Axis Apex2
Scan Type(s)	$\phi$ and $\omega$ scans	$\phi$ and $\omega$ scans
Max 2 $\theta$ for data collection, °	52.828	63.038
Measured fraction of data	0.998	0.997
Number of reflections measured	86325	52911
Unique reflections measured	9234	10918
R <sub>merge</sub>	0.0765	0.0791
Number of reflections included in refinement	9234	10918
Cut off Threshold Expression	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Structure refined using	full matrix least-squares using F <sup>2</sup>	full matrix least-squares using $F^2$
Weighting Scheme	w=1/[ $\sigma^{2}(Fo^{2})+(0.0386P)^{2}+1$ . 3894P] where P=(Fo^{2}+2Fc^{2})/3	w=1/[ $\sigma^{2}(Fo^{2})+(0.0375P)^{2}$ ] where P=(Fo <sup>2</sup> +2Fc <sup>2</sup> )/3
Number of parameters in least-squares	528	444
R <sub>1</sub>	0.0402	0.0471
wR <sub>2</sub>	0.0789	0.0810
R <sub>1</sub> (all data)	0.0779	0.0782
wR <sub>2</sub> (all data)	0.0901	0.0906
GOF	1.024	1.032
Maximum shift/error	0.008	0.002
Min & Max peak heights on final $\Delta F$ Map ( $e^{-}/\text{Å}$ )	-0.521, 0.461	-0.948, 0.701

Where:
$\mathbf{R}_1 = \boldsymbol{\Sigma} ( \mathbf{F}_{o}  -  \mathbf{F}_{c} ) / \boldsymbol{\Sigma} \mathbf{F}_{o}$
$wR_{2} = \left[ \Sigma (w(F_{o}^{2} - F_{c}^{2})^{2}) / \Sigma (wF_{o}^{4}) \right]^{\frac{1}{2}}$
GOF = $[\Sigma(w(F_0^2 - F_c^2)^2) / (No. of reflues No. of parameters.)]^{\frac{1}{2}}$

Table S4. Bon	d lengths for 2		
Ru1-N1	2.087(2)	C13-C14	1.366(5)
Ru1-O1S	2.189(2)	С13-Н13	0.9500
Ru1-P1	2.2403(10)	C14-C15	1.370(5)
Ru1-P2	2.2909(11)	C14-H14	0.9500
Ru1-Cl2	2.4293(10)	C15-C16	1.372(5)
Ru1-Cl1	2.4802(10)	С15-Н15	0.9500
P1-C11	1.817(3)	C16-H16	0.9500
P1-C10	1.826(3)	C17-C22	1.377(4)
P1-C17	1.831(3)	C17-C18	1.384(4)
P2-C35	1.839(3)	C18-C19	1.380(5)
P2-C29	1.839(3)	C18-H18	0.9500
P2-C23	1.849(3)	C19-C20	1.367(5)
O1S-C1S	1.241(3)	С19-Н19	0.9500
N1S-C1S	1.321(4)	C20-C21	1.369(6)
N1S-C2S	1.445(5)	С20-Н20	0.9500
N1S-C3S	1.460(4)	C21-C22	1.385(5)
C1S-H1S	0.9500	C21-H21	0.9500
C2S-H2S1	0.9800	C22-H22	0.9500
C2S-H2S2	0.9800	C23-C24	1.384(4)
C2S-H2S3	0.9800	C23-C28	1.390(4)
C3S-H3S1	0.9800	C24-C25	1.385(5)
C3S-H3S2	0.9800	C24-H24	0.9500
C3S-H3S3	0.9800	C25-C26	1.366(6)
N1-C1'	1.285(4)	С25-Н25	0.9500
N1-C1	1.285(4)	C26-C27	1.376(5)
N1-C5	1.442(4)	C26-H26	0.9500
C1-C2	1.396(5)	C27-C28	1.389(4)
C1-H1	0.9500	С27-Н27	0.9500

C2-C4	1.531(6)	C28-H28	0.9500
C2-C3	1.610(6)	C29-C30	1.389(4)
С2-Н2	1.0000	C29-C34	1.389(4)
С3-НЗА	0.9800	C30-C31	1.379(4)
С3-Н3В	0.9800	С30-Н30	0.9500
С3-НЗС	0.9800	C31-C32	1.359(5)
C4-H4A	0.9800	С31-Н31	0.9500
C4-H4B	0.9800	C32-C33	1.376(5)
C4-H4C	0.9800	С32-Н32	0.9500
C1'-C2'	1.293(10)	C33-C34	1.389(4)
С1'-Н1'	0.9500	С33-Н33	0.9500
C2'-C4'	1.530(13)	С34-Н34	0.9500
C2'-C3'	1.645(11)	C35-C36	1.387(4)
С2'-Н2'	1.0000	C35-C40	1.395(4)
С3'-Н3'1	0.9800	C36-C37	1.389(5)
С3'-Н3'2	0.9800	С36-Н36	0.9500
С3'-Н3'3	0.9800	C37-C38	1.365(6)
C4'-H4'1	0.9800	С37-Н37	0.9500
C4'-H4'2	0.9800	C38-C39	1.361(6)
C4'-H4'3	0.9800	С38-Н38	0.9500
C5-C6	1.383(4)	C39-C40	1.380(5)
C5-C10	1.391(4)	С39-Н39	0.9500
C6-C7	1.369(5)	C40-H40	0.9500
С6-Н6	0.9500	O2S-C4S	1.205(5)
C7-C8	1.374(5)	N2S-C4S	1.310(5)
С7-Н7	0.9500	N2S-C5S	1.433(5)
C8-C9	1.382(5)	N2S-C6S	1.443(5)
С8-Н8	0.9500	C4S-H4S	0.9500
C9-C10	1.398(4)	C5S-H5S1	0.9800
С9-Н9	0.9500	C5S-H5S2	0.9800
C11-C12	1.379(4)	С5S-Н5S3	0.9800
C11-C16	1.397(4)	C6S-H6S1	0.9800
C12-C13	1.382(5)	C6S-H6S2	0.9800

Table S5. Bond angl	es for 2		
N1-Ru1-O1S	85.05(9)	C9-C10-P1	128.5(3)
N1-Ru1-P1	79.48(7)	C12-C11-C16	118.5(3)
O1S-Ru1-P1	88.67(6)	C12-C11-P1	120.4(2)
N1-Ru1-P2	93.76(7)	C16-C11-P1	121.1(2)
O1S-Ru1-P2	171.37(6)	C11-C12-C13	120.1(3)
P1-Ru1-P2	99.53(4)	С11-С12-Н12	120.0
N1-Ru1-Cl2	168.82(7)	С13-С12-Н12	120.0
O1S-Ru1-Cl2	85.88(6)	C14-C13-C12	120.8(3)
P1-Ru1-Cl2	93.79(4)	С14-С13-Н13	119.6
P2-Ru1-Cl2	96.18(4)	С12-С13-Н13	119.6
N1-Ru1-Cl1	91.90(7)	C13-C14-C15	119.7(3)
O1S-Ru1-Cl1	83.66(6)	C13-C14-H14	120.1
P1-Ru1-Cl1	168.95(3)	C15-C14-H14	120.1
P2-Ru1-Cl1	87.85(4)	C14-C15-C16	120.2(3)
Cl2-Ru1-Cl1	93.58(4)	C14-C15-H15	119.9
C11-P1-C10	108.33(14)	С16-С15-Н15	119.9
C11-P1-C17	100.38(14)	C15-C16-C11	120.7(3)
C10-P1-C17	102.15(14)	С15-С16-Н16	119.7
C11-P1-Ru1	128.39(10)	С11-С16-Н16	119.7
C10-P1-Ru1	101.19(10)	C22-C17-C18	118.2(3)
C17-P1-Ru1	113.72(10)	C22-C17-P1	122.1(2)
C35-P2-C29	100.31(14)	C18-C17-P1	119.7(2)
C35-P2-C23	102.78(15)	C19-C18-C17	120.7(3)
C29-P2-C23	99.52(14)	С19-С18-Н18	119.6
C35-P2-Ru1	123.10(10)	C17-C18-H18	119.6
C29-P2-Ru1	114.70(10)	C20-C19-C18	120.4(4)
C23-P2-Ru1	113.12(10)	С20-С19-Н19	119.8
C1S-O1S-Ru1	119.17(19)	С18-С19-Н19	119.8
C1S-N1S-C2S	121.1(3)	C19-C20-C21	119.7(4)
C1S-N1S-C3S	120.5(3)	С19-С20-Н20	120.2

C6S-H6S3

0.9800

C12-H12

0.9500

C2S-N1S-C3S	118.4(3)	С21-С20-Н20	120.2
O1S-C1S-N1S	124.1(3)	C20-C21-C22	120.1(4)
O1S-C1S-H1S	118.0	C20-C21-H21	119.9
N1S-C1S-H1S	118.0	С22-С21-Н21	119.9
N1S-C2S-H2S1	109.5	C17-C22-C21	120.9(4)
N1S-C2S-H2S2	109.5	С17-С22-Н22	119.6
H2S1-C2S-H2S2	109.5	С21-С22-Н22	119.6
N1S-C2S-H2S3	109.5	C24-C23-C28	118.1(3)
H2S1-C2S-H2S3	109.5	C24-C23-P2	125.6(3)
H2S2-C2S-H2S3	109.5	C28-C23-P2	116.3(2)
N1S-C3S-H3S1	109.5	C23-C24-C25	120.4(4)
N1S-C3S-H3S2	109.5	С23-С24-Н24	119.8
H3S1-C3S-H3S2	109.5	С25-С24-Н24	119.8
N1S-C3S-H3S3	109.5	C26-C25-C24	121.0(3)
H3S1-C3S-H3S3	109.5	С26-С25-Н25	119.5
H3S2-C3S-H3S3	109.5	С24-С25-Н25	119.5
C1'-N1-C5	121.4(3)	C25-C26-C27	119.6(4)
C1-N1-C5	121.4(3)	С25-С26-Н26	120.2
C1'-N1-Ru1	121.1(2)	С27-С26-Н26	120.2
C1-N1-Ru1	121.1(2)	C26-C27-C28	119.7(4)
C5-N1-Ru1	116.30(18)	С26-С27-Н27	120.2
N1-C1-C2	136.2(4)	С28-С27-Н27	120.2
N1-C1-H1	111.9	C27-C28-C23	121.1(3)
С2-С1-Н1	111.9	С27-С28-Н28	119.5
C1-C2-C4	111.2(4)	С23-С28-Н28	119.5
C1-C2-C3	104.9(4)	C30-C29-C34	117.8(3)
C4-C2-C3	108.2(4)	C30-C29-P2	122.0(2)
С1-С2-Н2	110.8	C34-C29-P2	120.2(2)
С4-С2-Н2	110.8	C31-C30-C29	120.9(3)
С3-С2-Н2	110.8	С31-С30-Н30	119.6
С2-С3-НЗА	109.5	С29-С30-Н30	119.6
С2-С3-Н3В	109.5	C32-C31-C30	120.6(3)
НЗА-СЗ-НЗВ	109.5	C32-C31-H31	119.7

С2-С3-Н3С	109.5	С30-С31-Н31	119.7
НЗА-СЗ-НЗС	109.5	C31-C32-C33	120.2(3)
НЗВ-СЗ-НЗС	109.5	С31-С32-Н32	119.9
С2-С4-Н4А	109.5	С33-С32-Н32	119.9
С2-С4-Н4В	109.5	C32-C33-C34	119.6(3)
Н4А-С4-Н4В	109.5	С32-С33-Н33	120.2
С2-С4-Н4С	109.5	С34-С33-Н33	120.2
Н4А-С4-Н4С	109.5	C33-C34-C29	121.0(3)
Н4В-С4-Н4С	109.5	С33-С34-Н34	119.5
N1-C1'-C2'	159.9(6)	С29-С34-Н34	119.5
N1-C1'-H1'	100.0	C36-C35-C40	117.9(3)
С2'-С1'-Н1'	100.0	C36-C35-P2	122.2(2)
C1'-C2'-C4'	110.5(9)	C40-C35-P2	120.0(3)
C1'-C2'-C3'	108.1(7)	C35-C36-C37	120.4(3)
C4'-C2'-C3'	108.0(9)	С35-С36-Н36	119.8
С1'-С2'-Н2'	110.1	С37-С36-Н36	119.8
C4'-C2'-H2'	110.1	C38-C37-C36	120.6(4)
С3'-С2'-Н2'	110.1	С38-С37-Н37	119.7
С2'-С3'-Н3'1	109.5	С36-С37-Н37	119.7
C2'-C3'-H3'2	109.5	C39-C38-C37	119.8(4)
H3'1-C3'-H3'2	109.5	С39-С38-Н38	120.1
С2'-С3'-Н3'3	109.5	С37-С38-Н38	120.1
H3'1-C3'-H3'3	109.5	C38-C39-C40	120.7(4)
H3'2-C3'-H3'3	109.5	С38-С39-Н39	119.7
C2'-C4'-H4'1	109.5	С40-С39-Н39	119.7
C2'-C4'-H4'2	109.5	C39-C40-C35	120.6(4)
H4'1-C4'-H4'2	109.5	С39-С40-Н40	119.7
C2'-C4'-H4'3	109.5	С35-С40-Н40	119.7
H4'1-C4'-H4'3	109.5	C4S-N2S-C5S	121.9(4)
H4'2-C4'-H4'3	109.5	C4S-N2S-C6S	120.4(4)
C6-C5-C10	120.7(3)	C5S-N2S-C6S	117.5(4)
C6-C5-N1	122.8(3)	O2S-C4S-N2S	127.3(4)
C10-C5-N1	116.4(2)	O2S-C4S-H4S	116.4

119.6(3)	N2S-C4S-H4S	116.4
120.2	N2S-C5S-H5S1	109.5
120.2	N2S-C5S-H5S2	109.5
121.0(3)	H5S1-C5S-H5S2	109.5
119.5	N2S-C5S-H5S3	109.5
119.5	H5S1-C5S-H5S3	109.5
119.8(3)	H5S2-C5S-H5S3	109.5
120.1	N2S-C6S-H6S1	109.5
120.1	N2S-C6S-H6S2	109.5
120.2(3)	H6S1-C6S-H6S2	109.5
119.9	N2S-C6S-H6S3	109.5
119.9	H6S1-C6S-H6S3	109.5
118.6(3)	H6S2-C6S-H6S3	109.5
112.8(2)		
	119.6(3) 120.2 120.2 121.0(3) 119.5 119.5 119.8(3) 120.1 120.2(3) 119.9 119.9 118.6(3) 112.8(2)	119.6(3)N2S-C4S-H4S120.2N2S-C5S-H5S1120.2N2S-C5S-H5S2121.0(3)H5S1-C5S-H5S2119.5N2S-C5S-H5S3119.5H5S1-C5S-H5S3119.8(3)H5S2-C5S-H5S3120.1N2S-C6S-H6S1120.1N2S-C6S-H6S2120.2(3)H6S1-C6S-H6S2119.9N2S-C6S-H6S3119.9H6S1-C6S-H6S3118.6(3)H6S2-C6S-H6S3112.8(2)H6S2-C6S-H6S3

# Table S6. Bond lengths for 3

Ru1-N3	2.086(4)	C18-C19	1.394(8)
Ru1-N1	2.091(4)	C18-H18	0.9500
Ru1-N4	2.135(4)	C19-C20	1.373(9)
Ru1-N2	2.181(4)	С19-Н19	0.9500
Ru1-P1	2.2406(14)	C20-C21	1.396(8)
Ru1-Cl1	2.4623(14)	С20-Н20	0.9500
P1-C10	1.811(6)	C21-C22	1.384(7)
P1-C17	1.825(5)	С21-Н21	0.9500
P1-C11	1.834(5)	С22-Н22	0.9500
N1-C5	1.349(6)	C23-C24	1.376(7)
N1-C1	1.400(6)	С23-Н23	0.9500
N2-C27	1.340(6)	C24-C25	1.400(8)
N2-C23	1.343(6)	C24-H24	0.9500
N3-C32	1.342(6)	C25-C26	1.372(8)
N3-C28	1.349(6)	С25-Н25	0.9500
N4-C37	1.332(7)	C26-C27	1.386(7)
N4-C33	1.358(7)	С26-Н26	0.9500

C1-C2	1.332(7)	С27-Н27	0.9500
С1-Н1	0.9500	C28-C29	1.405(7)
C2-C3	1.498(9)	С28-Н28	0.9500
C2-C4	1.507(10)	C29-C30	1.374(8)
СЗ-НЗА	0.9800	С29-Н29	0.9500
С3-Н3В	0.9800	C30-C31	1.374(8)
С3-НЗС	0.9800	С30-Н30	0.9500
C4-H4A	0.9800	C31-C32	1.394(7)
C4-H4B	0.9800	С31-Н31	0.9500
C4-H4C	0.9800	С32-Н32	0.9500
C5-C10	1.428(7)	C33-C34	1.382(8)
C5-C6	1.436(7)	С33-Н33	0.9500
C6-C7	1.380(7)	C34-C35	1.365(9)
С6-Н6	0.9500	С34-Н34	0.9500
C7-C8	1.373(9)	C35-C36	1.376(9)
С7-Н7	0.9500	С35-Н35	0.9500
C8-C9	1.372(9)	C36-C37	1.385(7)
С8-Н8	0.9500	С36-Н36	0.9500
C9-C10	1.406(7)	С37-Н37	0.9500
С9-Н9	0.9500	O1S-C1S	1.422(5)
C11-C12	1.375(8)	O1S-C4S	1.431(6)
C11-C16	1.391(7)	C1S-C2S	1.502(6)
C12-C13	1.402(8)	C1S-H1S1	0.9900
С12-Н12	0.9500	C1S-H1S2	0.9900
C13-C14	1.357(11)	C2S-C3S	1.510(7)
С13-Н13	0.9500	C2S-H2S1	0.9900
C14-C15	1.356(11)	C2S-H2S2	0.9900
C14-H14	0.9500	C3S-C4S	1.486(6)
C15-C16	1.377(9)	C3S-H3S1	0.9900
С15-Н15	0.9500	C3S-H3S2	0.9900
С16-Н16	0.9500	C4S-H4S1	0.9900
C17-C18	1.394(7)	C4S-H4S2	0.9900
C17-C22	1.404(8)		

 Table S7. Bond angles for 3

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N3-Ru1-N1	89.26(16)	C18-C17-P1	121.7(4)
N3-Ru1-N4	177.30(19)	C22-C17-P1	119.9(4)
N1-Ru1-N4	90.15(16)	C19-C18-C17	120.3(6)
N3-Ru1-N2	86.57(15)	С19-С18-Н18	119.9
N1-Ru1-N2	95.00(15)	C17-C18-H18	119.9
N4-Ru1-N2	90.86(15)	C20-C19-C18	121.3(6)
N3-Ru1-P1	94.19(12)	С20-С19-Н19	119.4
N1-Ru1-P1	82.45(12)	С18-С19-Н19	119.4
N4-Ru1-P1	88.34(12)	C19-C20-C21	119.1(5)
N2-Ru1-P1	177.33(11)	С19-С20-Н20	120.5
N3-Ru1-Cl1	88.44(13)	С21-С20-Н20	120.5
N1-Ru1-Cl1	177.34(11)	C22-C21-C20	120.3(6)
N4-Ru1-Cl1	92.21(12)	C22-C21-H21	119.9
N2-Ru1-Cl1	86.19(11)	C20-C21-H21	119.9
P1-Ru1-Cl1	96.39(5)	C21-C22-C17	120.9(5)
C10-P1-C17	106.3(2)	С21-С22-Н22	119.6
C10-P1-C11	108.8(2)	С17-С22-Н22	119.6
C17-P1-C11	100.6(2)	N2-C23-C24	123.4(5)
C10-P1-Ru1	103.25(17)	N2-C23-H23	118.3
C17-P1-Ru1	117.51(17)	С24-С23-Н23	118.3
C11-P1-Ru1	119.69(18)	C23-C24-C25	119.2(5)
C5-N1-C1	120.7(4)	C23-C24-H24	120.4
C5-N1-Ru1	121.1(3)	C25-C24-H24	120.4
C1-N1-Ru1	117.8(3)	C26-C25-C24	118.0(5)
C27-N2-C23	116.5(4)	С26-С25-Н25	121.0
C27-N2-Ru1	124.0(3)	С24-С25-Н25	121.0
C23-N2-Ru1	119.3(3)	C25-C26-C27	118.8(5)
C32-N3-C28	117.3(4)	С25-С26-Н26	120.6
C32-N3-Ru1	122.1(3)	С27-С26-Н26	120.6
C28-N3-Ru1	120.6(4)	N2-C27-C26	124.1(5)
C37-N4-C33	116.8(5)	N2-C27-H27	118.0
C37-N4-Ru1	122.0(3)	С26-С27-Н27	118.0

C33-N4-Ru1	121.1(4)	N3-C28-C29	122.0(5)
C2-C1-N1	128.4(5)	N3-C28-H28	119.0
С2-С1-Н1	115.8	С29-С28-Н28	119.0
N1-C1-H1	115.8	C30-C29-C28	119.7(5)
C1-C2-C3	119.8(6)	С30-С29-Н29	120.2
C1-C2-C4	123.4(6)	С28-С29-Н29	120.2
C3-C2-C4	116.8(6)	C29-C30-C31	118.5(5)
С2-С3-НЗА	109.5	С29-С30-Н30	120.8
С2-С3-Н3В	109.5	С31-С30-Н30	120.8
НЗА-СЗ-НЗВ	109.5	C30-C31-C32	119.3(5)
С2-С3-НЗС	109.5	С30-С31-Н31	120.3
НЗА-СЗ-НЗС	109.5	С32-С31-Н31	120.3
НЗВ-СЗ-НЗС	109.5	N3-C32-C31	123.1(5)
С2-С4-Н4А	109.5	N3-C32-H32	118.4
C2-C4-H4B	109.5	С31-С32-Н32	118.4
Н4А-С4-Н4В	109.5	N4-C33-C34	122.8(6)
С2-С4-Н4С	109.5	N4-C33-H33	118.6
Н4А-С4-Н4С	109.5	С34-С33-Н33	118.6
Н4В-С4-Н4С	109.5	C35-C34-C33	119.0(6)
N1-C5-C10	119.8(5)	С35-С34-Н34	120.5
N1-C5-C6	123.8(5)	С33-С34-Н34	120.5
C10-C5-C6	116.4(5)	C34-C35-C36	119.4(5)
C7-C6-C5	120.5(6)	С34-С35-Н35	120.3
С7-С6-Н6	119.7	С36-С35-Н35	120.3
С5-С6-Н6	119.7	C35-C36-C37	118.5(6)
C8-C7-C6	122.1(6)	С35-С36-Н36	120.8
С8-С7-Н7	118.9	С37-С36-Н36	120.8
С6-С7-Н7	118.9	N4-C37-C36	123.6(5)
C9-C8-C7	119.3(5)	N4-C37-H37	118.2
С9-С8-Н8	120.4	С36-С37-Н37	118.2
С7-С8-Н8	120.4	C1S-O1S-C4S	103.6(5)
C8-C9-C10	121.3(6)	O1S-C1S-C2S	104.9(6)
С8-С9-Н9	119.4	O1S-C1S-H1S1	110.8

С10-С9-Н9	119.4	C2S-C1S-H1S1	110.8
C9-C10-C5	120.3(5)	O1S-C1S-H1S2	110.8
C9-C10-P1	126.3(5)	C2S-C1S-H1S2	110.8
C5-C10-P1	113.3(4)	H1S1-C1S-H1S2	108.8
C12-C11-C16	117.2(5)	C1S-C2S-C3S	101.0(6)
C12-C11-P1	119.5(4)	C1S-C2S-H2S1	111.6
C16-C11-P1	123.3(4)	C3S-C2S-H2S1	111.6
C11-C12-C13	120.6(6)	C1S-C2S-H2S2	111.6
С11-С12-Н12	119.7	C3S-C2S-H2S2	111.6
С13-С12-Н12	119.7	H2S1-C2S-H2S2	109.4
C14-C13-C12	120.5(7)	C4S-C3S-C2S	106.3(6)
С14-С13-Н13	119.7	C4S-C3S-H3S1	110.5
С12-С13-Н13	119.8	C2S-C3S-H3S1	110.5
C15-C14-C13	119.7(6)	C4S-C3S-H3S2	110.5
С15-С14-Н14	120.2	C2S-C3S-H3S2	110.5
С13-С14-Н14	120.2	H3S1-C3S-H3S2	108.7
C14-C15-C16	120.3(7)	O1S-C4S-C3S	105.9(6)
С14-С15-Н15	119.8	O1S-C4S-H4S1	110.6
С16-С15-Н15	119.8	C3S-C4S-H4S1	110.6
C15-C16-C11	121.6(7)	O1S-C4S-H4S2	110.6
С15-С16-Н16	119.2	C3S-C4S-H4S2	110.6
С11-С16-Н16	119.2	H4S1-C4S-H4S2	108.7
C18-C17-C22	118.2(5)		

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