Supporting Information

Intermolecular Coupling Reaction of Cyclic Amines and Alkenes Catalyzed by a Ruthenium-Hydride Complex $(\text{PCy}_3)_2(\text{CO})\text{RuHCl}$

Chae S. Yi* and Sang Young Yun

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53201-1881

Ilia A. Guzei

Molecular Structure Laboratory, Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706-1396

General Information. All operations were carried out in an inert-atmosphere glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Tetrahydrofuran, benzene, hexanes and Et₂O were distilled from purple solutions of sodium and benzophenone immediately prior to use. The NMR solvents were dried from activated molecular sieves (4 Å). All amine and alkene substrates were received from commercial sources and used without further purification. The ¹H, ¹³C and ³¹P NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer. Mass spectra were recorded from a Hewlett-Packard HP 5970 GC/MS spectrometer. The organic products were isolated from COW-MAC 350 GC spectrometer equipped with Chromoborb P column (AW DMCS 80/100; 4' × 0.25" O.D., 20% DC 200) using He as the carrier gas (flow rate 60 mL/min). High resolution FAB mass spectra were obtained at the Center of Mass Spectrometry, Washington University, St. Louis, MO. Elemental analyses were performed at the Midwest Microlab, Indianapolis, IN.

Synthesis of Na[(PCy₃)₂(CO)(Cl)Ru(NC₄H₈)H] (5). In a glove box, complex **1** (200 mg, 0.28 mmol), pyrrolidine (100 mg, 1.4 mmol) and NaOH (10 mg) in 4 mL of THF were charged in a 25 mL Schlenk tube equipped with a Teflon screw joint and a magnetic stirring bar. The tube was brought out of the box, and was evacuated under vacuum while it was cooled in a liquid nitrogen bath. Excess ethylene (6 mmol) was condensed into the tube via a vacuum line. The reaction tube was gradually warmed to room temperature and stirred in an oil bath at 80 °C for 12 h. The reaction tube was cooled to room temperature and the reaction mixture was concentrated to ~2 mL under vacuum. The resulting solids were filtered on a frit, washed with Et₂O (20 mL), and dried under vacuum to give **5** as a white solid (175 mg, 75% yield). Single crystals of **5** suitable for X-ray crystallographic analysis were obtained from benzene/CH₂Cl₂/hexane solution.

Selected characterization data for **5**: ¹H NMR (CD₂Cl₂, 300 MHz) δ 3.63 and 2.47 (m, CH₂ amide), 2.2-1.2 (m, PCy₃), -15.73 (t, *J*_{PH} = 20.1 Hz, Ru-H); ¹³C{¹H} NMR (CD₂Cl₂, 75 MHz; 35 °C) δ 202.2 (t, *J*_{PC} = 25.2 Hz, CO), 61.5 and 37.6 (CH₂ amide), 35.3 (pseudo t, *J*_{PC} = 9.2 Hz, C_{ipso} of cyclohexyl), 30.5 (C_{meta} of cyclohexyl), 28.5 (m, C_{ortho} of cyclohexyl), 27.7 (C_{para} of cyclohexyl); ³¹P{¹H} NMR (CD₂Cl₂, 125 MHz) δ 37.2 (PCy₃); IR (KBr) ν_{CO} = 1900 cm⁻¹; Anal Calcd for C₄₁H₇₅NOP₂RuNa: C, 60.01; H, 9.23; N, 1.71. Found C,

60.82; H, 9.10; N, 1.71.

Kinetic Study of the Catalytic Reaction. To a C_6D_6 (0.35 mL) solution of the complex **1** or **5** (10 mg, 14 μ mol), pyrrolidine (12.0 μ L, 0.14 mmol) was added via a micro syringe in a Wilmad J-Young NMR tube with a Teflon screw cap. The tube was cooled in a liquid nitrogen bath, and excess ethylene (1.2 mmol) was condensed via a vacuum line transfer. The tube was gradually warmed to room temperature. The sample tube was inserted into the NMR probe which was preset at 80 °C. The rate was measured by monitoring the 1H integration of pyrrolidine (CH_2NCH_2 (δ 2.63 ppm)) and **2a** ($CH_2N=C$ (δ 3.74 ppm)) signals, and these were normalized against an internal standard (solvent resonance). The k_{obs} was estimated from a first-order plot of $\ln[2a]$ vs time. A sample plot is shown below.

Typical Procedure of the Catalytic Reaction. In a glove box, complex **1** (5-15 mol %) was charged with an amine (1.4 mmol) and 5 mL THF solution in a thick-walled 25 mL Schlenk tube equipped with a magnetic stirring bar. The tube was brought out of the box, and cooled in a liquid nitrogen bath. Excess ethylene (8 mmol) was condensed into the tube via a vacuum line. The reaction tube was gradually warmed to room temperature and stirred in an oil bath at 80-120 °C for 16-24 h. The tube was opened to air at room temperature, and the crude product mixture was analyzed by GC. The solvent was removed under a rotary aspirator and the

organic product was isolated by trap-to-trap vacuum distillation (95% pure by ^1H NMR). The analytically pure products were obtained from a preparatory GC (flow rate at 60 mL/min).

Selected Spectroscopic Data of Organic Products.

For **2a**: ^1H NMR (C_6D_6 , 300 MHz) δ 3.74 (m, CH_2N), 2.10 (q, $J = 7.5$ Hz, CH_2CH_3), 1.99 (t, $J = 8.7$ Hz, $\text{CH}_2\text{C}=\text{N}$), 1.47 (m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.09 (t, $J = 7.2$ Hz, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz) δ 177.2 ($\text{C}=\text{N}$), 61.7 (CH_2N), 37.5 ($\text{CH}_2\text{C}=\text{N}$), 27.5 ($\text{CH}_2\text{CH}_2\text{N}$), 23.5 (CH_2CH_3), 11.4 (CH_3); GC-MS ($\text{M}^+ = 97$); IR (neat) $\nu_{\text{C}=\text{N}} = 1645\text{ cm}^{-1}$.

For **2b**: ^1H NMR (C_6D_6 , 300 MHz) δ 3.76 (m, CH_2N), 2.12 (t, $J = 6.9$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.01 (t, $J = 7.8$ Hz, $\text{CH}_2\text{C}=\text{N}$), 1.58 (t, $J = 8.1$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.46 (m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.87 (t, $J = 7.2$ Hz, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz) δ 176.4 ($\text{C}=\text{N}$), 61.7 (CH_2N), 37.7 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 36.3 ($\text{CH}_2\text{C}=\text{N}$), 23.4 ($\text{CH}_2\text{CH}_2\text{N}$), 20.5 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 14.8 (CH_3); GC-MS ($\text{M}^+ = 111$).

For **2c**: ^1H NMR (C_6D_6 , 300 MHz) δ 3.78 (m, CH_2N), 2.18 (t, $J = 7.8$ Hz, $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$), 2.03 (t, $J = 7.5$ Hz, $\text{CH}_2\text{C}=\text{N}$), 1.57 (m, $\text{CH}_2\text{C}(\text{CH}_3)_3$), 1.50 (m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.86 (s, $\text{C}(\text{CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz) δ 176.9 ($\text{C}=\text{N}$), 61.7 (CH_2N), 40.9 ($\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$), 37.8 ($\text{CH}_2\text{C}=\text{N}$), 30.7 ($\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$), 30.2 ($\text{CH}_2\text{C}(\text{CH}_3)_3$), 29.9 ($\text{CH}_2\text{C}(\text{CH}_3)_3$), 23.4 ($\text{CH}_2\text{CH}_2\text{CH}_2$); GC-MS ($\text{M}^+ = 153$).

For **2d**: ^1H NMR (C_6D_6 , 300 MHz) δ 3.59 (t, $J = 4.5$ Hz, CH_2N), 2.15 (q, $J = 7.2$ Hz, CH_2CH_3), 1.95 (t, $J = 5.7$ Hz, $\text{CH}_2\text{C}=\text{N}$), 1.47 (m, $\text{CH}_2\text{CH}_2\text{N}$), 1.39 (m, $\text{CH}_2\text{CH}_2\text{C}=\text{N}$), 1.14 (m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.13 (t, $J = 7.2$ Hz, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz) δ 177.2 ($\text{C}=\text{N}$), 52.4 (CH_2N), 35.9 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 33.9 ($\text{CH}_2\text{CH}_2\text{N}$), 32.4 ($\text{CH}_2\text{C}=\text{N}$), 27.5 (CH_2CH_3), 24.5 ($\text{CH}_2\text{CH}_2\text{C}=\text{N}$), 11.2 (CH_2CH_3); GC-MS ($\text{M}^+ = 125$); IR (neat) $\nu_{\text{C}=\text{N}} = 1666\text{ cm}^{-1}$.

For **2e**: ^1H NMR (C_6D_6 , 300 MHz) δ 3.56 (t, $J = 6.0$ Hz, CH_2N), 2.16 (q, $J = 7.5$ Hz, CH_2CH_3), 1.95 (t, $J = 6.6$ Hz, $\text{CH}_2\text{C}=\text{N}$), 1.64 – 1.23 (m, 8 H), 1.18 (t, $J = 7.2$ Hz, CH_2CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz) δ 173.8 ($\text{C}=\text{N}$), 49.5 (CH_2N), 33.9 (CH_2CH_3), 30.9, 29.9, 28.9, 27.0 and 25.5 (CH_2), 11.3 (CH_2CH_3); GC-MS ($\text{M}^+ = 139$); IR (neat) $\nu_{\text{C}=\text{N}} = 1660\text{ cm}^{-1}$.

For **2f**: ^1H NMR (C_6D_6 , 300 MHz) δ 3.99 (m, CH_2N), 2.06 (m, CH_2CH_3), 1.97 (m, $\text{CH}_2\text{C}=\text{N}$), 1.74 ($\text{CH}_2\text{CH}_2\text{C}=\text{N}$), 1.26 (d, $J = 6.9$ Hz, CHCH_3), 1.10 (t, $J = 7.8$ Hz, CH_2CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz) δ

175.5 (C=N), 68.0 (CHN), 37.3 (CH₂C=N), 31.0 (CH₂CHN), 26.9 (CH₂CH₃), 22.6 (CHCH₃), 10.9 (CH₂CH₃); GC-MS (M⁺ = 111); IR (neat) $\nu_{\text{C=N}}$ = 1650 cm⁻¹.

For **2g**: ¹H NMR (C₆D₆, 300 MHz) δ 3.99 (m, CH_{eq}HN), 3.05 (m, CH_{ax}HN), 2.07 (q, *J* = 7.5 Hz, CH₂CH₃), 1.78 (m, CH₂C=N), 1.45 (d, *J* = 12.6 Hz, CH₂C=N), 1.59 (m, CH₂CH₂CH), 1.39–1.08 (m, CH₂CH), 1.17 (t, *J* = 7.8 Hz, CH₃), 0.91 (m, CH), 0.68 (m, CH₂CH₂CH); ¹³C{¹H} NMR (C₆D₆, 75 MHz) δ 169.4 (C=N), 57.4 (CH₂N), 38.6 (CHCH₂N), 37.5 (CH₂C=N), 36.7 (CHCH₂C=N), 34.1 (CH₂CH₃), 33.9 (CH₂CH), 31.0 (CH₂CH), 27.1 and 27.0 (CH₂), 11.3 (CH₃); GC-MS (M⁺ = 165); IR (neat) $\nu_{\text{C=N}}$ = 1667 cm⁻¹.

For **3c**: ¹H NMR (C₆D₆, 300 MHz) δ 2.88 (m, CHN), 2.69 (m, CH₂N), 1.74 – 1.00 (m, 8 H), 0.90 (C(CH₃)₃); ¹³C{¹H} NMR (C₆D₆, 75 MHz) δ 60.6 (CHN), 47.4 (CH₂N), 42.6, 32.8, 32.5 and 30.7 (CH₂), 30.1 (C(CH₃)₃), 26.3 (CH₂CH₂CH₂); GC-MS (M⁺ = 155).

For **3d**: ¹H NMR (C₆D₆, 300 MHz) δ 2.83 and 2.56 (m, CH₂N), 2.35 (m, CHN), 1.6 – 0.94 (m, 6 H, cyclohexyl), 1.27 (m, CH₂CH₃), 0.89 (t, *J* = 7.8 Hz, CH₃); ¹³C{¹H} NMR (C₆D₆, 75 MHz) δ 60.8 (CHN), 47.6 (CH₂N), 36.9 (CH₂CH₃), 32.2 (CH₂CH), 31.1 (CH₂CH₂N), 27.9 (CH₂CH₂CH), 26.1 (CH₂CH₂CH₂N), 11.4 (CH₃); GC-MS (M⁺ = 127).

For **4a**: ¹H NMR (C₆D₆, 300 MHz) δ 3.85 (m, Si(OCH₂CH₃)₃), 2.65 (t, *J* = 6.3 Hz, CH₂N), 1.54 (m, NCH₂CH₂), 1.18 (m, Si(OCH₂CH₃)₃); ¹³C{¹H} NMR (C₆D₆, 75 MHz) δ 59.8 (Si(OCH₂CH₃)₃), 47.2 (CH₂N), 27.5 (NCH₂CH₂), 19.2 (Si(OCH₂CH₃)₃); GC-MS (M⁺ = 233).

For **4g**: ¹H NMR (C₆D₆, 300 MHz) δ 2.89 (m, NCH_{eq}HCH₂CH), 2.75 (ddd, *J* = 10.8, 3.3 and 1.5 Hz, CHCH_{eq}HN), 2.28 (q, *J* = 6.9 Hz, NCH₂CH₃), 1.18 (ddd, *J* = 10.8, 10.8 and 4.2 Hz, NCH_{ax}HCH₂CH), 1.49 (t, *J* = 10.5 Hz, CHCH_{ax}HN), 1.69 – 0.72 (m, 10 H), 1.05 (t, *J* = 6.9 Hz, NCH₂CH₃); ¹³C{¹H} NMR (C₆D₆, 75 MHz) δ 62.1 (CHCH₂N), 54.9 (NCH₂CH₂CH), 53.4 (NCH₂CH₃), 42.9 (CH), 42.8 (CH), 34.2, 34.9, 31.0, 27.5 and 27.1 (CH₂), 13.4 (CH₃); GC-MS (M⁺ = 167).

X-Ray Crystallographic Determination of 5. *Data Collection:* A yellow air-sensitive crystal with approximate dimensions 0.43 x 0.32 x 0.26 mm³ was selected under oil at ambient conditions and attached to the tip of a nylon loop. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker CCD-1000

diffractometer with MoK $_{\alpha}$ ($\lambda = 0.71073$ Å) radiation and the diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 10 seconds per frame. A total of 67 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 15878 strong reflections from the actual data collection. The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of 0.80 Å. A total of 31686 data were harvested by collecting three sets of frames with 0.25° scans in ω with an exposure time 60 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.

Structure Solution and Refinement: The systematic absences in the diffraction data were consistent for space groups *Cc* and *C2/c* but only the latter, centrosymmetric space group *C2/c* yielded chemically reasonable and computationally stable results of refinement. A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms except N2 were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The Ru complex occupies a crystallographic twofold axis. The hydride H, carbonyl, chloride and pyrrolidine ligands as well as the sodium counterion are equally disordered over two positions and were refined with restraints and constraints. The presence of sodium cation and hydride ligand was confirmed by spectroscopic means. The final least-squares refinement of 257 parameters against 4146 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.1219 and 0.2832, respectively. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI).

Table 1. Crystal data and structure refinement for **5**.

Identification code	yi0008	
Empirical formula	C ₄₁ H ₇₅ Cl N Na O P ₂ Ru	
Formula weight	819.47	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 16.7232(9) Å	$\alpha = 90^\circ$
	b = 9.9985(6) Å	$\beta = 102.7770(10)^\circ$
	c = 24.6961(14) Å	$\gamma = 90^\circ$
Volume	4027.1(4) Å ³	
Z	4	
Density (calculated)	1.352 Mg/m ³	
Absorption coefficient	0.579 mm ⁻¹	
F(000)	1752	
Crystal size	0.43 x 0.32 x 0.26 mm ³	
Theta range for data collection	2.39 to 26.43°	
Index ranges	-20 ≤ h ≤ 20, -12 ≤ k ≤ 12, -30 ≤ l ≤ 30	
Reflections collected	31645	
Independent reflections	4141 [R(int) = 0.0506]	
Completeness to theta = 26.43°	99.8 %	
Absorption correction	Multi-scan with SADABS	
Max. and min. transmission	0.8641 and 0.7890	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4141 / 31 / 250	
Goodness-of-fit on F ²	1.259	
Final R indices [I > 2σ(I)]	R1 = 0.1215, wR2 = 0.2745	
R indices (all data)	R1 = 0.1233, wR2 = 0.2753	
Largest diff. peak and hole	3.012 and -2.381 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru	10000	3225(1)	2500	22(1)
P(1)	10225(1)	2807(2)	3470(1)	14(1)
Cl(1)	8618(3)	3722(6)	2425(2)	35(1)
Na(1)	11649(10)	8117(13)	2515(6)	81(4)
C(1)	8912(9)	2920(20)	2473(9)	35(1)
O(1)	8202(8)	2787(16)	2439(6)	35(1)
N(1)	9619(7)	5403(11)	2462(5)	21(3)
C(20)	8846(11)	5984(16)	2394(8)	26(4)
C(21)	8883(10)	7448(15)	2234(8)	25(4)
C(22)	9781(7)	7775(14)	2468(8)	17(4)
C(23)	10202(8)	6419(13)	2518(8)	15(4)
C(2)	10304(5)	4232(9)	3965(3)	18(2)
C(3)	9531(6)	5098(9)	3819(4)	21(2)
C(4)	9564(6)	6266(9)	4219(4)	25(2)
C(5)	10323(6)	7099(9)	4246(4)	25(2)
C(6)	11105(7)	6259(9)	4392(4)	29(2)
C(7)	11069(5)	5067(9)	3993(4)	22(2)
C(8)	11195(5)	1900(9)	3741(4)	20(2)
C(9)	11392(6)	1527(9)	4364(4)	22(2)
C(10)	12279(6)	1062(9)	4539(4)	23(2)
C(11)	12444(6)	-137(10)	4197(4)	27(2)
C(12)	12237(6)	198(11)	3581(4)	32(2)
C(13)	11346(6)	642(10)	3412(4)	27(2)
C(14)	9357(6)	1863(9)	3642(4)	22(2)
C(15)	9249(7)	1813(11)	4246(4)	31(2)
C(16)	8463(8)	1144(10)	4300(5)	38(3)
C(17)	8421(7)	-270(10)	4067(5)	37(3)
C(18)	8526(6)	-285(11)	3470(5)	32(2)
C(19)	9315(5)	404(8)	3415(4)	18(2)

Table 3. Bond lengths [Å] and angles [°] for **5**.

Ru-C(1)#1	1.832(14)	C(12)-C(13)	1.522(12)
Ru-C(1)	1.832(14)	C(12)-H(12A)	0.9900
Ru-N(1)#1	2.264(11)	C(12)-H(12B)	0.9900
Ru-N(1)	2.264(11)	C(13)-H(13A)	0.9900
Ru-Cl(1)#1	2.331(6)	C(13)-H(13B)	0.9900
Ru-Cl(1)	2.331(6)	C(14)-C(15)	1.542(13)
Ru-P(1)#1	2.378(2)	C(14)-C(19)	1.558(12)
Ru-P(1)	2.378(2)	C(14)-H(14)	1.0000
Ru-H	1.5800(11)	C(15)-C(16)	1.508(15)
P(1)-C(8)	1.850(9)	C(15)-H(15A)	0.9900
P(1)-C(14)	1.857(9)	C(15)-H(15B)	0.9900
P(1)-C(2)	1.862(9)	C(16)-C(17)	1.522(14)
Na(1)-C(18)#2	2.872(19)	C(16)-H(16A)	0.9900
C(1)-O(1)	1.179(2)	C(16)-H(16B)	0.9900
N(1)-C(23)	1.393(13)	C(17)-C(18)	1.522(16)
N(1)-C(20)	1.394(13)	C(17)-H(17A)	0.9900
C(20)-C(21)	1.521(13)	C(17)-H(17B)	0.9900
C(20)-H(20A)	0.9900	C(18)-C(19)	1.521(12)
C(20)-H(20B)	0.9900	C(18)-Na(1)#3	2.872(19)
C(21)-C(22)	1.521(13)	C(18)-H(18A)	0.9900
C(21)-H(21A)	0.9900	C(18)-H(18B)	0.9900
C(21)-H(21B)	0.9900	C(19)-H(19A)	0.9900
C(22)-C(23)	1.520(13)	C(19)-H(19B)	0.9900
C(22)-H(22A)	0.9900	C(1)#1-Ru-C(1)	160.6(15)
C(22)-H(22B)	0.9900	C(1)#1-Ru-N(1)#1	83.8(8)
C(23)-H(23A)	0.9900	C(1)-Ru-N(1)#1	115.5(8)
C(23)-H(23B)	0.9900	C(1)#1-Ru-N(1)	115.5(8)
C(2)-C(7)	1.517(12)	C(1)-Ru-N(1)	83.8(8)
C(2)-C(3)	1.531(12)	N(1)#1-Ru-N(1)	31.9(5)
C(2)-H(2)	1.0000	C(1)#1-Ru-Cl(1)#1	22.1(8)
C(3)-C(4)	1.522(13)	C(1)-Ru-Cl(1)#1	176.4(7)
C(3)-H(3A)	0.9900	N(1)#1-Ru-Cl(1)#1	61.8(3)
C(3)-H(3B)	0.9900	N(1)-Ru-Cl(1)#1	93.6(3)
C(4)-C(5)	1.507(14)	C(1)#1-Ru-Cl(1)	176.4(7)
C(4)-H(4A)	0.9900	C(1)-Ru-Cl(1)	22.1(8)
C(4)-H(4B)	0.9900	N(1)#1-Ru-Cl(1)	93.6(3)
C(5)-C(6)	1.528(13)	N(1)-Ru-Cl(1)	61.8(3)
C(5)-H(5A)	0.9900	Cl(1)#1-Ru-Cl(1)	155.4(3)
C(5)-H(5B)	0.9900	C(1)#1-Ru-P(1)#1	86.7(7)
C(6)-C(7)	1.539(12)	C(1)-Ru-P(1)#1	90.0(7)
C(6)-H(6A)	0.9900	N(1)#1-Ru-P(1)#1	101.0(3)
C(6)-H(6B)	0.9900	N(1)-Ru-P(1)#1	98.5(3)
C(7)-H(7A)	0.9900	Cl(1)#1-Ru-P(1)#1	92.88(14)
C(7)-H(7B)	0.9900	Cl(1)-Ru-P(1)#1	91.42(13)
C(8)-C(13)	1.547(12)	C(1)#1-Ru-P(1)	90.0(7)
C(8)-C(9)	1.548(12)	C(1)-Ru-P(1)	86.7(7)
C(8)-H(8)	1.0000	N(1)#1-Ru-P(1)	98.5(3)
C(9)-C(10)	1.523(13)	N(1)-Ru-P(1)	101.0(3)
C(9)-H(9A)	0.9900	Cl(1)#1-Ru-P(1)	91.42(13)
C(9)-H(9B)	0.9900	Cl(1)-Ru-P(1)	92.88(14)
C(10)-C(11)	1.526(14)	P(1)#1-Ru-P(1)	159.77(11)
C(10)-H(10A)	0.9900	C(1)#1-Ru-H	65(5)
C(10)-H(10B)	0.9900	C(1)-Ru-H	95(5)
C(11)-C(12)	1.521(14)	N(1)#1-Ru-H	147(5)
C(11)-H(11A)	0.9900	N(1)-Ru-H	173(5)
C(11)-H(11B)	0.9900	Cl(1)#1-Ru-H	87(5)

Cl(1)-Ru-H	118(5)	C(4)-C(5)-H(5B)	109.2
P(1)#1-Ru-H	88(5)	C(6)-C(5)-H(5B)	109.2
P(1)-Ru-H	72(5)	H(5A)-C(5)-H(5B)	107.9
C(8)-P(1)-C(14)	109.6(4)	C(5)-C(6)-C(7)	111.3(8)
C(8)-P(1)-C(2)	102.0(4)	C(5)-C(6)-H(6A)	109.4
C(14)-P(1)-C(2)	100.7(4)	C(7)-C(6)-H(6A)	109.4
C(8)-P(1)-Ru	112.4(3)	C(5)-C(6)-H(6B)	109.4
C(14)-P(1)-Ru	111.2(3)	C(7)-C(6)-H(6B)	109.4
C(2)-P(1)-Ru	119.9(3)	H(6A)-C(6)-H(6B)	108.0
O(1)-C(1)-Ru	176(2)	C(2)-C(7)-C(6)	111.6(8)
C(23)-N(1)-C(20)	108.5(12)	C(2)-C(7)-H(7A)	109.3
C(23)-N(1)-Ru	120.9(8)	C(6)-C(7)-H(7A)	109.3
C(20)-N(1)-Ru	130.6(9)	C(2)-C(7)-H(7B)	109.3
N(1)-C(20)-C(21)	110.0(13)	C(6)-C(7)-H(7B)	109.3
N(1)-C(20)-H(20A)	109.7	H(7A)-C(7)-H(7B)	108.0
C(21)-C(20)-H(20A)	109.7	C(13)-C(8)-C(9)	107.6(8)
N(1)-C(20)-H(20B)	109.7	C(13)-C(8)-P(1)	116.2(6)
C(21)-C(20)-H(20B)	109.7	C(9)-C(8)-P(1)	117.0(6)
H(20A)-C(20)-H(20B)	108.2	C(13)-C(8)-H(8)	104.9
C(20)-C(21)-C(22)	101.6(13)	C(9)-C(8)-H(8)	104.9
C(20)-C(21)-H(21A)	111.4	P(1)-C(8)-H(8)	104.9
C(22)-C(21)-H(21A)	111.4	C(10)-C(9)-C(8)	109.6(7)
C(20)-C(21)-H(21B)	111.4	C(10)-C(9)-H(9A)	109.7
C(22)-C(21)-H(21B)	111.4	C(8)-C(9)-H(9A)	109.7
H(21A)-C(21)-H(21B)	109.3	C(10)-C(9)-H(9B)	109.7
C(23)-C(22)-C(21)	103.8(11)	C(8)-C(9)-H(9B)	109.7
C(23)-C(22)-H(22A)	111.0	H(9A)-C(9)-H(9B)	108.2
C(21)-C(22)-H(22A)	111.0	C(9)-C(10)-C(11)	111.5(8)
C(23)-C(22)-H(22B)	111.0	C(9)-C(10)-H(10A)	109.3
C(21)-C(22)-H(22B)	111.0	C(11)-C(10)-H(10A)	109.3
H(22A)-C(22)-H(22B)	109.0	C(9)-C(10)-H(10B)	109.3
N(1)-C(23)-C(22)	110.0(10)	C(11)-C(10)-H(10B)	109.3
N(1)-C(23)-H(23A)	109.7	H(10A)-C(10)-H(10B)	108.0
C(22)-C(23)-H(23A)	109.7	C(12)-C(11)-C(10)	110.6(8)
N(1)-C(23)-H(23B)	109.7	C(12)-C(11)-H(11A)	109.5
C(22)-C(23)-H(23B)	109.7	C(10)-C(11)-H(11A)	109.5
H(23A)-C(23)-H(23B)	108.2	C(12)-C(11)-H(11B)	109.5
C(7)-C(2)-C(3)	111.1(7)	C(10)-C(11)-H(11B)	109.5
C(7)-C(2)-P(1)	112.9(6)	H(11A)-C(11)-H(11B)	108.1
C(3)-C(2)-P(1)	110.2(6)	C(11)-C(12)-C(13)	109.3(9)
C(7)-C(2)-H(2)	107.5	C(11)-C(12)-H(12A)	109.8
C(3)-C(2)-H(2)	107.5	C(13)-C(12)-H(12A)	109.8
P(1)-C(2)-H(2)	107.5	C(11)-C(12)-H(12B)	109.8
C(4)-C(3)-C(2)	111.9(8)	C(13)-C(12)-H(12B)	109.8
C(4)-C(3)-H(3A)	109.2	H(12A)-C(12)-H(12B)	108.3
C(2)-C(3)-H(3A)	109.2	C(12)-C(13)-C(8)	110.9(8)
C(4)-C(3)-H(3B)	109.2	C(12)-C(13)-H(13A)	109.5
C(2)-C(3)-H(3B)	109.2	C(8)-C(13)-H(13A)	109.5
H(3A)-C(3)-H(3B)	107.9	C(12)-C(13)-H(13B)	109.5
C(5)-C(4)-C(3)	111.3(8)	C(8)-C(13)-H(13B)	109.5
C(5)-C(4)-H(4A)	109.4	H(13A)-C(13)-H(13B)	108.0
C(3)-C(4)-H(4A)	109.4	C(15)-C(14)-C(19)	108.2(8)
C(5)-C(4)-H(4B)	109.4	C(15)-C(14)-P(1)	120.1(7)
C(3)-C(4)-H(4B)	109.4	C(19)-C(14)-P(1)	111.7(6)
H(4A)-C(4)-H(4B)	108.0	C(15)-C(14)-H(14)	105.2
C(4)-C(5)-C(6)	112.0(8)	C(19)-C(14)-H(14)	105.2
C(4)-C(5)-H(5A)	109.2	P(1)-C(14)-H(14)	105.2
C(6)-C(5)-H(5A)	109.2	C(16)-C(15)-C(14)	113.0(9)

C(16)-C(15)-H(15A)	109.0	C(19)-C(18)-C(17)	111.8(8)
C(14)-C(15)-H(15A)	109.0	C(19)-C(18)-Na(1)#3	95.9(7)
C(16)-C(15)-H(15B)	109.0	C(17)-C(18)-Na(1)#3	144.5(7)
C(14)-C(15)-H(15B)	109.0	C(19)-C(18)-H(18A)	109.3
H(15A)-C(15)-H(15B)	107.8	C(17)-C(18)-H(18A)	109.3
C(15)-C(16)-C(17)	110.2(9)	Na(1)#3-C(18)-H(18A)	37.7
C(15)-C(16)-H(16A)	109.6	C(19)-C(18)-H(18B)	109.3
C(17)-C(16)-H(16A)	109.6	C(17)-C(18)-H(18B)	109.3
C(15)-C(16)-H(16B)	109.6	Na(1)#3-C(18)-H(18B)	80.2
C(17)-C(16)-H(16B)	109.6	H(18A)-C(18)-H(18B)	107.9
H(16A)-C(16)-H(16B)	108.1	C(18)-C(19)-C(14)	111.3(8)
C(16)-C(17)-C(18)	111.7(9)	C(18)-C(19)-H(19A)	109.4
C(16)-C(17)-H(17A)	109.3	C(14)-C(19)-H(19A)	109.4
C(18)-C(17)-H(17A)	109.3	C(18)-C(19)-H(19B)	109.4
C(16)-C(17)-H(17B)	109.3	C(14)-C(19)-H(19B)	109.4
C(18)-C(17)-H(17B)	109.3	H(19A)-C(19)-H(19B)	108.0
H(17A)-C(17)-H(17B)	107.9		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y,-z+1/2 #2 -x+2,y+1,-z+1/2 #3 -x+2,y-1,-z+1/2

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru	47(1)	9(1)	8(1)	0	2(1)	0
P(1)	19(1)	10(1)	12(1)	-1(1)	2(1)	0(1)
Cl(1)	39(3)	41(3)	23(2)	-4(2)	1(2)	12(2)
Na(1)	113(12)	40(6)	95(10)	-21(7)	31(9)	-2(7)
C(1)	39(3)	41(3)	23(2)	-4(2)	1(2)	12(2)
O(1)	39(3)	41(3)	23(2)	-4(2)	1(2)	12(2)
N(1)	46(9)	13(7)	4(6)	1(5)	4(7)	-6(6)
C(20)	27(6)	26(6)	24(6)	3(5)	4(5)	6(5)
C(21)	31(6)	25(6)	21(6)	-2(5)	10(5)	3(5)
C(22)	19(6)	12(5)	20(5)	1(5)	4(5)	2(4)
C(23)	16(7)	14(5)	13(5)	3(5)	2(5)	3(4)
C(2)	23(5)	18(4)	14(4)	-1(3)	4(3)	3(4)
C(3)	19(4)	17(4)	29(5)	1(4)	9(4)	-2(3)
C(4)	33(5)	19(4)	27(5)	0(4)	15(4)	6(4)
C(5)	36(6)	11(4)	28(5)	-1(3)	6(4)	5(4)
C(6)	36(6)	13(4)	30(5)	-4(4)	-6(4)	4(4)
C(7)	14(4)	20(4)	30(5)	-7(4)	-1(4)	0(3)
C(8)	21(4)	15(4)	24(4)	-1(4)	4(4)	1(4)
C(9)	31(5)	15(4)	22(4)	2(3)	8(4)	4(4)
C(10)	27(5)	19(4)	23(5)	8(4)	4(4)	2(4)
C(11)	18(5)	22(5)	40(6)	3(4)	0(4)	1(4)
C(12)	25(5)	30(5)	36(6)	-8(4)	-2(4)	18(4)
C(13)	19(5)	26(5)	35(5)	-16(4)	1(4)	14(4)
C(14)	24(5)	14(4)	32(5)	-1(4)	11(4)	-1(4)
C(15)	49(7)	21(5)	30(5)	2(4)	21(5)	0(5)
C(16)	49(7)	20(5)	54(7)	-8(5)	36(6)	-5(5)
C(17)	39(6)	19(5)	67(8)	-7(5)	42(6)	-11(4)
C(18)	27(5)	23(5)	46(6)	-1(4)	5(5)	-17(4)
C(19)	12(4)	14(4)	28(5)	-4(3)	4(3)	-6(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **5**.

	x	y	z	U(eq)
H	10270(70)	1720(40)	2600(60)	27
H(20A)	8654	5913	2744	31
H(20B)	8452	5503	2101	31
H(21A)	8518	8005	2406	30
H(21B)	8735	7567	1826	30
H(22A)	9999	8370	2214	20
H(22B)	9856	8213	2836	20
H(23A)	10519	6327	2226	18
H(23B)	10588	6345	2884	18
H(2)	10333	3849	4342	22
H(3A)	9468	5446	3437	25
H(3B)	9046	4539	3829	25
H(4A)	9072	6833	4096	30
H(4B)	9560	5920	4594	30
H(5A)	10347	7809	4528	30
H(5B)	10292	7536	3882	30
H(6A)	11178	5923	4777	34
H(6B)	11583	6826	4374	34
H(7A)	11078	5403	3618	27
H(7B)	11560	4498	4120	27
H(8)	11636	2541	3699	24
H(9A)	11306	2314	4588	27
H(9B)	11020	805	4431	27
H(10A)	12400	815	4937	28
H(10B)	12648	1806	4492	28
H(11A)	13028	-394	4312	33
H(11B)	12108	-906	4268	33
H(12A)	12325	-598	3363	38
H(12B)	12600	923	3505	38
H(13A)	10985	-92	3484	33
H(13B)	11206	841	3010	33
H(14)	8851	2311	3426	27
H(15A)	9718	1324	4476	38
H(15B)	9259	2736	4391	38
H(16A)	7989	1669	4097	45
H(16B)	8435	1111	4696	45
H(17A)	7885	-673	4081	44
H(17B)	8857	-821	4300	44
H(18A)	8532	-1222	3342	39
H(18B)	8053	173	3229	39
H(19A)	9346	420	3019	22
H(19B)	9791	-109	3623	22

Table 6. Torsion angles [°] for 5.

C(1)#1-Ru-P(1)-C(8)	-17.9(8)	P(1)-C(2)-C(3)-C(4)	179.2(6)
C(1)-Ru-P(1)-C(8)	143.0(8)	C(2)-C(3)-C(4)-C(5)	55.3(10)
N(1)#1-Ru-P(1)-C(8)	-101.6(4)	C(3)-C(4)-C(5)-C(6)	-54.9(11)
N(1)-Ru-P(1)-C(8)	-133.9(4)	C(4)-C(5)-C(6)-C(7)	54.2(11)
Cl(1)#1-Ru-P(1)-C(8)	-40.0(4)	C(3)-C(2)-C(7)-C(6)	54.1(10)
Cl(1)-Ru-P(1)-C(8)	164.3(4)	P(1)-C(2)-C(7)-C(6)	178.4(6)
P(1)#1-Ru-P(1)-C(8)	62.3(3)	C(5)-C(6)-C(7)-C(2)	-53.8(11)
C(1)#1-Ru-P(1)-C(14)	-141.2(8)	C(14)-P(1)-C(8)-C(13)	75.2(8)
C(1)-Ru-P(1)-C(14)	19.7(8)	C(2)-P(1)-C(8)-C(13)	-178.7(7)
N(1)#1-Ru-P(1)-C(14)	135.1(4)	Ru-P(1)-C(8)-C(13)	-49.0(8)
N(1)-Ru-P(1)-C(14)	102.8(4)	C(14)-P(1)-C(8)-C(9)	-53.7(8)
Cl(1)#1-Ru-P(1)-C(14)	-163.3(4)	C(2)-P(1)-C(8)-C(9)	52.4(7)
Cl(1)-Ru-P(1)-C(14)	41.0(4)	Ru-P(1)-C(8)-C(9)	-177.9(6)
P(1)#1-Ru-P(1)-C(14)	-61.0(3)	C(13)-C(8)-C(9)-C(10)	59.0(10)
C(1)#1-Ru-P(1)-C(2)	101.9(8)	P(1)-C(8)-C(9)-C(10)	-168.1(6)
C(1)-Ru-P(1)-C(2)	-97.2(8)	C(8)-C(9)-C(10)-C(11)	-58.4(10)
N(1)#1-Ru-P(1)-C(2)	18.2(4)	C(9)-C(10)-C(11)-C(12)	57.2(11)
N(1)-Ru-P(1)-C(2)	-14.1(4)	C(10)-C(11)-C(12)-C(13)	-57.1(11)
Cl(1)#1-Ru-P(1)-C(2)	79.8(4)	C(11)-C(12)-C(13)-C(8)	60.4(12)
Cl(1)-Ru-P(1)-C(2)	-75.9(4)	C(9)-C(8)-C(13)-C(12)	-61.1(11)
P(1)#1-Ru-P(1)-C(2)	-177.9(3)	P(1)-C(8)-C(13)-C(12)	165.6(8)
C(1)#1-Ru-C(1)-O(1)	-151(29)	C(8)-P(1)-C(14)-C(15)	71.9(8)
N(1)#1-Ru-C(1)-O(1)	31(29)	C(2)-P(1)-C(14)-C(15)	-35.1(8)
N(1)-Ru-C(1)-O(1)	27(29)	Ru-P(1)-C(14)-C(15)	-163.2(7)
Cl(1)#1-Ru-C(1)-O(1)	71(34)	C(8)-P(1)-C(14)-C(19)	-56.2(7)
Cl(1)-Ru-C(1)-O(1)	22(28)	C(2)-P(1)-C(14)-C(19)	-163.2(6)
P(1)#1-Ru-C(1)-O(1)	-72(29)	Ru-P(1)-C(14)-C(19)	68.6(7)
P(1)-Ru-C(1)-O(1)	128(29)	C(19)-C(14)-C(15)-C(16)	-57.0(11)
C(1)#1-Ru-N(1)-C(23)	-6.6(15)	P(1)-C(14)-C(15)-C(16)	173.3(7)
C(1)-Ru-N(1)-C(23)	174.0(14)	C(14)-C(15)-C(16)-C(17)	57.4(13)
N(1)#1-Ru-N(1)-C(23)	0.2(10)	C(15)-C(16)-C(17)-C(18)	-55.0(14)
Cl(1)#1-Ru-N(1)-C(23)	-3.5(12)	C(16)-C(17)-C(18)-C(19)	55.3(13)
Cl(1)-Ru-N(1)-C(23)	176.0(14)	C(16)-C(17)-C(18)-Na(1)#3	-166.1(11)
P(1)#1-Ru-N(1)-C(23)	-97.0(12)	C(17)-C(18)-C(19)-C(14)	-55.8(11)
P(1)-Ru-N(1)-C(23)	88.6(12)	Na(1)#3-C(18)-C(19)-C(14)	146.8(7)
C(1)#1-Ru-N(1)-C(20)	174.2(16)	C(15)-C(14)-C(19)-C(18)	55.3(11)
C(1)-Ru-N(1)-C(20)	-5.2(16)	P(1)-C(14)-C(19)-C(18)	-170.4(7)
N(1)#1-Ru-N(1)-C(20)	-179(2)		
Cl(1)#1-Ru-N(1)-C(20)	177.3(15)		
Cl(1)-Ru-N(1)-C(20)	-3.2(14)		
P(1)#1-Ru-N(1)-C(20)	83.9(15)		
P(1)-Ru-N(1)-C(20)	-90.5(15)		
C(23)-N(1)-C(20)-C(21)	17(2)		
Ru-N(1)-C(20)-C(21)	-164.0(11)		
N(1)-C(20)-C(21)-C(22)	-24.5(19)		
C(20)-C(21)-C(22)-C(23)	21.8(18)		
C(20)-N(1)-C(23)-C(22)	-1.5(19)		
Ru-N(1)-C(23)-C(22)	179.2(11)		
C(21)-C(22)-C(23)-N(1)	-13.8(19)		
C(8)-P(1)-C(2)-C(7)	56.9(7)		
C(14)-P(1)-C(2)-C(7)	169.8(7)		
Ru-P(1)-C(2)-C(7)	-68.0(7)		
C(8)-P(1)-C(2)-C(3)	-178.3(6)		
C(14)-P(1)-C(2)-C(3)	-65.4(7)		
Ru-P(1)-C(2)-C(3)	56.9(7)		
C(7)-C(2)-C(3)-C(4)	-55.0(10)		

Symmetry transformations used to generate
equivalent atoms: #1 -x+2,y,-z+1/2 #2 -x+2,y+1,-
z+1/2 #3 -x+2,y-1,-z+1/2