

General Information. All reactions were carried out in an inert-atmosphere glove box or by using standard high vacuum line 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 organic substrates were received from commercial sources and used without further purification. The ¹H, ¹³C and ³¹P NMR spectra were recorded on a GE GN-Omega 300 MHz FT-NMR spectrometer. Mass spectra were recorded from a Hewlett-Packard HP 5970 GC/MS spectrometer. High resolution FAB mass spectra were performed at the Center of Mass Spectrometry, Washington University, St. Louis, MO. Elemental analyses were performed at the Midwest Microlab, Indianapolis, IN.

Preparation of (PCy₃)₂(CO)(CH₃CONH)(*i*-PrOH)RuH (1). In the glove box, complex **2** (200 mg, 0.23 mmol) was mixed with 0.2 M KOH in 2-propanol (2.4 mL, 2 equiv) in a 25 mL Schlenk tube equipped with Teflon stopcock. After adding another 4 mL of 2-propanol, the reaction tube was stirred at room temperature for 5 h. The solvent was removed under vacuum, and the residue was dissolved in 10-15 mL of benzene. The solution was filtered through a frit, and the filtrate was evaporated under vacuum to give **1** as pale yellow solids (180 mg, 96% yield). The isolated product was found to be suitable for catalytic reactions without further purification. Analytically pure single crystals of **1** were obtained after a slow recrystallization in 2-propanol at 0 °C, and these can be stored for weeks in a freezer without losing significant activity.

For **1**: ¹H NMR (CD₂Cl₂, 300 MHz) δ 4.79 (br s, NH), 3.97 (m, CH(CH₃)₂), 2.2-1.2 (m, PCy₃), COCH₃ signal obscured by PCy₃, 1.15 (d, *J* = 5.4 Hz, CH(CH₃)₂), -18.38 (br s, Ru-H); ¹³C{¹H} NMR (CD₂Cl₂, 75 MHz) δ 207.0 (br s, CO), 178.2 (NHCOCH₃), 64.6 (CH(CH₃)₂), 35.8 (t, *J*_{PC} = 9.6 Hz, C_{ipso} of cyclohexyl), 30.7 and 29.8 (C_{meta} of cyclohexyl), 28.7 (m, C_{ortho} of cyclohexyl), 27.4 (C_{para} of cyclohexyl), 26.1 (NHCOCH₃), 25.7 (CH(CH₃)₂); ³¹P{¹H} NMR (CD₂Cl₂, 125 MHz) δ 46.3 (PCy₃); IR (CH₂Cl₂) ν_{CO} = 1886, ν_{C=O (amide)} = 1545 cm⁻¹; Anal Calcd for C₄₂H₇₉NO₃P₂Ru: C, 62.35; H, 9.84; N, 1.73. Found C, 61.51; H, 9.99; N, 1.78.

Preparation of $[(PCy_3)_2(CO)(CH_3CN)_2RuH]^+BF_4^-$ (2). In a 25 mL Schlenk tube equipped with Teflon stopcock, $(PCy_3)_2(CO)(Cl)RuH$ (100 mg, 0.14 mmol) and $NaBF_4$ (16 mg, 1.1 equiv) were dissolved in 5 mL of acetonitrile. The reaction mixture was stirred for 8 h in an oil bath at 80 °C. After cooling to room temperature, the solution was filtered through a celite, and washed with additional 15-20 mL of acetonitrile. The combined filtrate was evaporated under vacuum to give **2** as white solids (110 mg, 95% yield).

For **2**: 1H NMR (CD_2Cl_2 , 300 MHz) δ 2.37 and 2.30 (s, CH_3CN), 2.1-1.2 (m, PCy_3), -14.13 (t, $J_{PH} = 19.5$ Hz, Ru-H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 75 MHz) δ 204.2 (t, $J_{PC} = 13.2$ Hz, CO), 125.5 (CH_3CN), 35.8 (t, $J_{PC} = 10.6$ Hz, C_{ipso} of cyclohexyl), 29.9 (C_{meta} of cyclohexyl), 28.4 (m, C_{ortho} of cyclohexyl), 27.2 (C_{para} of cyclohexyl), 4.0 (CH_3CN); $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 125 MHz) δ 43.3 (PCy_3); Anal Calcd for $C_{41}H_{73}BF_4N_2OP_2Ru$: C, 57.27; H, 8.56; N, 3.26. Found C, 56.56; H, 8.71; N, 3.40.

Preparation of $(PCy_3)_2(CO)(CH_3CO_2)RuH$ (4). The complex **2** (100 mg, 0.12 mmol) and anhydrous KOAc (23 mg, 0.24 mmol) were dissolved in 5 mL of 2-propanol in a 25 mL Schlenk flask. The reaction mixture was stirred at room temperature for 20 h. The solvent was removed under vacuum, and the residue was dissolved in 10 mL of benzene. The resulting benzene solution was filtered through a celite, and washed with additional 10 mL of benzene. The solvent was evaporated under vacuum to give **4** as white solids (85 mg, 95% yield).

For **4**: 1H NMR (C_6D_6 , 300 MHz) δ 2.40-1.25 (m, PCy_3), 1.92 (s, CH_3CO_2), -17.38 (t, $J_{PH} = 19.7$ Hz, Ru-H); $^{13}C\{^1H\}$ NMR (C_6D_6 , 75 MHz) δ 208.2 (t, $J_{PC} = 14.2$ Hz, CO), 182.1 (CH_3CO_2), 35.9 (t, $J_{PC} = 9.5$ Hz, C_{ipso} of cyclohexyl), 31.2 and 30.2 (C_{meta} of cyclohexyl), 28.8 (m, C_{ortho} of cyclohexyl), 27.4 (C_{para} of cyclohexyl), 25.1 (CH_3CO_2); $^{31}P\{^1H\}$ NMR (C_6D_6 , 125 MHz) δ 47.3 (PCy_3); IR (CH_2Cl_2) $\nu_{CO} = 1900$ cm^{-1} ; Anal Calcd for $C_{39}H_{70}O_3P_2Ru$: C, 62.46; H, 9.41. Found C, 62.00; H, 9.36.

Typical Procedure of the Catalytic Transfer Hydrogenation Reaction. In the glove box, complex **1** (4 mg, 0.5 mol %) was charged with acetophenone (1.0 mmol) in a 25 mL Schlenk tube

equipped with Teflon stopcock. After 2-propanol (1.0 mL) was added to the reaction tube, the tube was brought out of the box, and was stirred in an oil bath at 80 °C for 6 h. The tube was opened to air at room temperature, and filtered through a short silica gel column to remove the metal catalyst. The crude product mixture was analyzed by GC. The pure organic product was isolated after a column chromatography on a silica gel (Et₂O/hexane).

General Procedure for the Rate Measurements of Hydrogenation of Acetophenone.

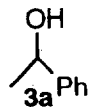
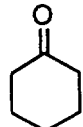
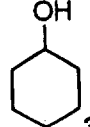
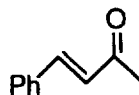
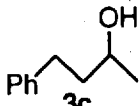
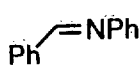
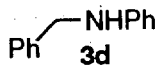
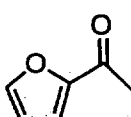
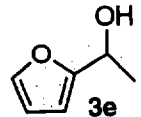
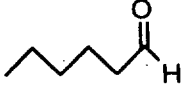
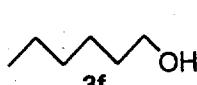
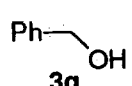
In the glove box, six NMR samples were prepared by adding 5, 10, 15, 20, 30 and 40 µL of acetophenone via a gas-tight syringe into the separate J-Young NMR tubes equipped with Teflon screw cap containing C₆D₆ solution of **1** (3.7 µmol, 300 µL). For phosphine inhibition experiments, 37 mM of predissolved PCy₃ in C₆D₆ (20 µL, 0.2 equiv; 50 µL, 0.5 equiv based on **1**) was added via syringe to each of these tubes. The degassed 2-propanol (50 µL) was added via syringe to each reaction tubes. The reaction tubes were brought out of the box and were simultaneously immersed in an oil bath (80±1 °C) for a determined period of time (15-30 min). The tube was rapidly cooled to room temperature by running a cold water stream. The initial rate for each reactions was conveniently measured from the proton integration of δ 7.73 (Ph_{ortho} of acetophenone) and 7.32 (Ph_{ortho} of 1-phenylethanol), which were well-separated from each other due to the hydrogen bonding interaction between 1-phenylethanol and 2-propanol. For relatively low [**1**] (1.7-5 mM), a simple empirical rate law was obtained for the reaction: $-d[\text{PhCOCH}_3]/dt = k_{\text{obs}}[\text{PhCOCH}_3]$, where $k_{\text{obs}} = 1.3 \times 10^{-4} \text{ s}^{-1}$ at 80±1 °C in C₆D₆.

Deuterium Isotope Effect Measurements. Method A: In a glove box, complex **1** (4 mg, 1.0 mol %) and acetophenone (50 µL, 0.43 mmol) were charged into two separate 25 mL Schlenk tubes, each equipped with a Teflon stopcock. An equal amount of (CH₃)₂CHOH and (CH₃)₂CHOD (1.0 mL) was added via a syringe to each reaction tubes. The reaction tubes were closed, and they were brought out of the box. Both tubes were simultaneously immersed into a preheated oil bath at 80±1 °C, and were stirred for 15 min. The tubes were cooled to room temperature by running a cold water stream, and the crude reaction mixtures were isolated by removing the solvents from a rotary evaporator. Each product

mixtures was analyzed by NMR. For NMR analysis, 30 μL of CD_3OD was added to each crude product mixture dissolved in C_6D_6 . The conversion of each products was determined by comparing the integration of the peaks at δ 7.73 (Ph_{ortho} of acetophenone) and δ 7.32 (Ph_{ortho} of 1-phenylethanol).

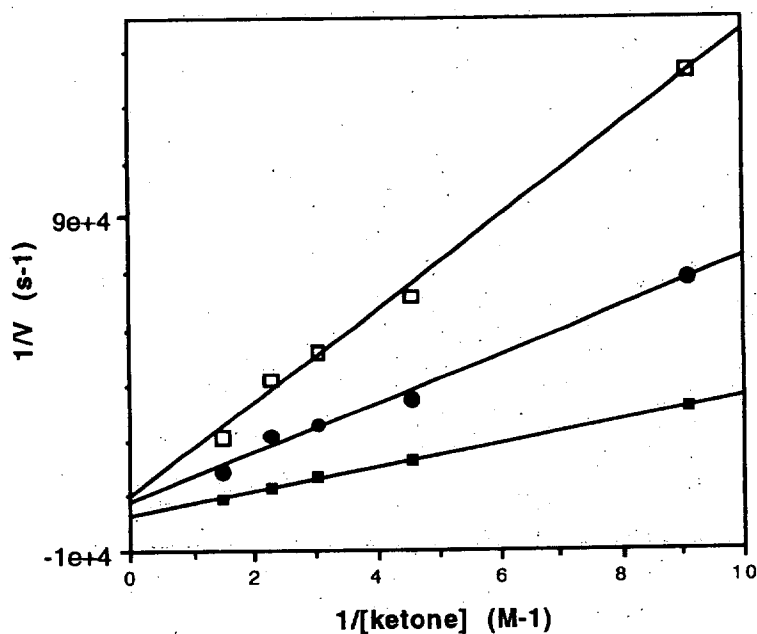
Method B: Complex 1 (4 mg, 1.0 mol %) and acetophenone (50 μL , 0.43 mmol) were charged into a 25 mL Schlenk tube equipped with a Teflon stopcock. The 1:1 mixture of $(\text{CH}_3)_2\text{CHOH}$ and $(\text{CH}_3)_2\text{CDOH}$ (1.0 mL, v/v) was added to the tube via a gas-tight syringe. The reaction tube was stirred in an oil bath at 80 $^\circ\text{C}$ for 1 h. The product mixture was isolated and analyzed as described in Method A. The product ratio was determined by comparing the proton integration at δ 7.32 (Ph_{ortho} 1-phenylethanol) and δ 4.73 (CH of 1-phenylethanol).

Table 1. Transfer Hydrogenation of Carbonyl Compound and Imines Catalyzed by **1**.^a

entry	substrate	product	time (h)	yield (%) ^b
1			6	95
2			6	95
3			12	98
4			12	94
5			12	93
6			24	73 ^c
7			2	92

^a Reaction conditions: 1.0 mmol of the substrate; 0.5 mol % of **1**; 1.0 mL of 2-propanol; 80 °C. ^b Isolated yields. ^c The crude product mixture contained 15% aldol product as determined by GC.

Figure 1. Plot of $1/V_{\text{initial}}$ vs $1/[\text{PhCOCH}_3]$ at 80 °C with 1 mol% of **1**.^a



^aThe reaction was monitored by ^1H NMR under the conditions described in the general procedure: (■) without added PCy_3 , (●) 0.2 equiv of PCy_3 , (□) 0.5 equiv of PCy_3 .

The X-Ray Crystallographic Structure Determination of 1. A colorless air-sensitive crystal with approximate dimensions $0.4 \times 0.2 \times 0.2 \text{ mm}^3$ was selected under oil under ambient conditions and attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(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_α ($\lambda = 0.71073 \text{ \AA}$) 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 37 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 694 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 $0.80 \text{ \AA}$. A total of 25280 data were harvested by collecting three sets of frames with 0.3° scans in ω with an exposure time 30 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.

The systematic absences in the diffraction data were consistent for the space groups $P1$ and $P\bar{1}$. The centrosymmetric space group $P\bar{1}$ 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 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 C(5) atom was disordered over two positions in a 67/33 ratio. The H atom on the minor contributor (carbon with the occupancy factor of 0.33) was ignored. This isopropyl alcohol moiety was refined with an idealized geometry. There was also a severely disordered solvent molecule present in the asymmetric unit. This solvent was modeled as a molecule of isopropyl alcohol. Bond length restraints were applied but the

resulting isotropic displacement coefficients suggested the molecule were mobile. In addition, the refinement was computationally unstable. Option SQUEEZE of program PLATON was used to correct the diffraction data for diffuse scattering effects and to identify the solvate molecule. The PLATON calculated the upper limit of volume that can be occupied by the solvent to be $349.0 \text{ \AA}^3$, or 14.3% of the unit cell volume. The program calculated 47 electrons in the unit cell for the diffused species. This corresponds to one and a half molecule of isopropyl alcohol in the asymmetric unit. The final least-squares refinement of 425 parameters against 8536 data resulted in residuals R (based on F^2 for $I=2\sigma$) and wR (based on F^2 for all data) of 0.0518 and 0.1249, respectively. All hydrogen atoms were treated as idealized contributions. 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 **1**.

Empirical formula	C ₄₂ H ₇₉ N O ₃ P ₂ Ru	
Formula weight	809.07	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 11.1028(13) Å	α = 81.120(3)°
	b = 14.3372(18) Å	β = 89.590(4)°
	c = 15.946(2) Å	γ = 76.281(4)°
Volume	2435.2(5) Å ³	
Z	2	
Density (calculated)	1.103 Mg/m ³	
Absorption coefficient	0.420 mm ⁻¹	
F(000)	872	
Crystal size	0.40 x 0.20 x 0.20 mm ³	
Theta range for data collection	1.81 to 25.00°	
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 17, 0 ≤ l ≤ 18	
Reflections collected	25280	
Independent reflections	8536 [R(int) = 0.0538]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	Empirical with SADABS	
Max. and min. transmission	0.9208 and 0.8501	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8536 / 7 / 425	
Goodness-of-fit on F ²	1.014	
Final R indices [I > 2σ(I)]	R1 = 0.0510, wR2 = 0.1226	
R indices (all data)	R1 = 0.0697, wR2 = 0.1275	
Largest diff. peak and hole	1.436 and -0.726 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Ru	1794(1)	7610(1)	7150(1)	32(1)
P(1)	812(1)	7836(1)	8462(1)	33(1)
P(2)	2944(1)	7873(1)	5909(1)	36(1)
O(1)	-517(3)	8781(3)	6208(2)	69(1)
O(2)	3555(3)	5306(2)	8061(2)	55(1)
N	3490(3)	6909(2)	7867(2)	33(1)
C(1)	379(4)	8297(3)	6566(3)	46(1)
C(2)	4003(3)	6004(3)	8183(3)	38(1)
C(3)	5154(4)	5762(3)	8754(3)	60(1)
O(3)	1625(3)	6040(2)	7081(2)	55(1)
C(4)	-105(5)	5864(5)	6307(4)	103(2)
C(5A)	711(4)	5486(3)	7107(4)	76(3)
C(6)	1367(6)	4416(3)	7158(5)	129(3)
C(5B)	1237(6)	5399(4)	6595(4)	68(5)
C(7)	1121(3)	8919(3)	8851(2)	35(1)
C(8)	570(4)	9881(3)	8280(3)	42(1)
C(9)	831(5)	10737(3)	8665(3)	56(1)
C(10)	2211(5)	10617(3)	8830(3)	61(1)
C(11)	2755(4)	9670(3)	9392(3)	50(1)
C(12)	2510(4)	8815(3)	9011(3)	42(1)
C(13)	-910(3)	8150(3)	8369(2)	37(1)
C(14)	-1450(4)	7399(3)	8027(3)	48(1)
C(15)	-2808(4)	7803(4)	7762(3)	53(1)
C(16)	-3559(4)	8175(4)	8498(3)	59(1)
C(17)	-3022(4)	8916(4)	8859(3)	58(1)
C(18)	-1654(4)	8485(3)	9125(3)	47(1)
C(19)	1371(4)	6887(3)	9406(2)	38(1)
C(20)	1056(4)	7146(3)	10293(3)	51(1)
C(21)	1753(4)	6334(3)	10982(3)	54(1)
C(22)	1495(4)	5369(3)	10901(3)	52(1)
C(23)	1785(4)	5120(3)	10024(3)	48(1)
C(24)	1090(4)	5926(3)	9333(3)	47(1)
C(25)	3312(4)	9088(3)	5780(3)	39(1)
C(26)	4126(4)	9193(3)	6511(3)	47(1)
C(27)	4440(4)	10186(3)	6393(3)	58(1)
C(28)	3266(5)	11000(3)	6261(3)	63(1)
C(29)	2475(5)	10904(3)	5520(3)	57(1)
C(30)	2139(4)	9929(3)	5650(3)	49(1)
C(31)	2136(6)	7941(5)	4883(4)	97(1)
C(32)	1821(6)	6986(5)	4793(4)	97(1)
C(33)	902(6)	7108(5)	4047(3)	97(1)
C(34)	1425(6)	7540(5)	3248(4)	97(1)
C(35)	1766(6)	8458(5)	3306(4)	97(1)
C(36)	2649(6)	8358(5)	4067(3)	97(1)
C(37)	4527(3)	7050(3)	5927(3)	37(1)
C(38)	4519(4)	5981(3)	5990(3)	45(1)
C(39)	5823(4)	5341(3)	6196(3)	57(1)
C(40)	6733(4)	5608(3)	5540(3)	53(1)
C(41)	6725(4)	6677(3)	5455(3)	55(1)
C(42)	5424(4)	7306(3)	5262(3)	51(1)

Table 3. Bond lengths [Å] and angles [°] for **1**.

Ru-C(1)	1.819(4)
Ru-N	2.154(3)
Ru-O(3)	2.321(3)
Ru-P(2)	2.3782(11)
Ru-P(1)	2.3831(11)
P(1)-C(13)	1.859(4)
P(1)-C(7)	1.862(4)
P(1)-C(19)	1.866(4)
P(2)-C(31)	1.849(5)
P(2)-C(25)	1.863(4)
P(2)-C(37)	1.867(4)
O(1)-C(1)	1.165(5)
O(2)-C(2)	1.258(5)
N-C(2)	1.308(5)
C(2)-C(3)	1.514(5)
O(3)-C(5A)	1.427(2)
C(4)-C(5A)	1.522(2)
C(5A)-C(6)	1.524(2)
C(7)-C(8)	1.525(5)
C(7)-C(12)	1.533(5)
C(8)-C(9)	1.541(6)
C(9)-C(10)	1.521(7)
C(10)-C(11)	1.501(6)
C(11)-C(12)	1.529(6)
C(13)-C(14)	1.519(5)
C(13)-C(18)	1.531(5)
C(14)-C(15)	1.519(6)
C(15)-C(16)	1.524(6)
C(16)-C(17)	1.520(6)
C(17)-C(18)	1.533(6)
C(19)-C(24)	1.504(5)
C(19)-C(20)	1.534(5)
C(20)-C(21)	1.533(6)
C(21)-C(22)	1.503(6)
C(22)-C(23)	1.510(6)
C(23)-C(24)	1.531(6)
C(25)-C(26)	1.527(6)
C(25)-C(30)	1.541(5)
C(26)-C(27)	1.528(6)
C(27)-C(28)	1.519(6)
C(28)-C(29)	1.520(7)
C(29)-C(30)	1.515(6)
C(31)-C(36)	1.513(9)
C(31)-C(32)	1.519(9)
C(32)-C(33)	1.535(7)
C(33)-C(34)	1.503(8)
C(34)-C(35)	1.468(8)
C(35)-C(36)	1.533(7)
C(37)-C(42)	1.513(5)
C(37)-C(38)	1.522(5)
C(38)-C(39)	1.526(5)
C(39)-C(40)	1.520(6)
C(40)-C(41)	1.516(6)
C(41)-C(42)	1.516(5)
C(1)-Ru-N	175.23(17)

C(1)-Ru-O(3)	99.77(16)
N-Ru-O(3)	84.96(11)
C(1)-Ru-P(2)	89.68(13)
N-Ru-P(2)	90.14(8)
O(3)-Ru-P(2)	99.20(8)
C(1)-Ru-P(1)	90.47(12)
N-Ru-P(1)	88.14(8)
O(3)-Ru-P(1)	99.65(8)
P(2)-Ru-P(1)	160.84(4)
C(13)-P(1)-C(7)	102.01(17)
C(13)-P(1)-C(19)	110.70(19)
C(7)-P(1)-C(19)	100.16(17)
C(13)-P(1)-Ru	113.48(13)
C(7)-P(1)-Ru	110.91(13)
C(19)-P(1)-Ru	117.62(12)
C(31)-P(2)-C(25)	101.2(3)
C(31)-P(2)-C(37)	109.8(2)
C(25)-P(2)-C(37)	101.42(18)
C(31)-P(2)-Ru	116.3(2)
C(25)-P(2)-Ru	111.15(13)
C(37)-P(2)-Ru	115.06(13)
C(2)-N-Ru	133.5(3)
O(1)-C(1)-Ru	176.4(4)
O(2)-C(2)-N	122.8(4)
O(2)-C(2)-C(3)	116.9(4)
N-C(2)-C(3)	120.2(4)
C(5A)-O(3)-Ru	140.4(3)
O(3)-C(5A)-C(4)	107.2(4)
O(3)-C(5A)-C(6)	108.7(4)
C(4)-C(5A)-C(6)	112.1(5)
C(8)-C(7)-C(12)	109.8(3)
C(8)-C(7)-P(1)	114.1(3)
C(12)-C(7)-P(1)	111.9(3)
C(7)-C(8)-C(9)	110.5(3)
C(10)-C(9)-C(8)	111.8(4)
C(11)-C(10)-C(9)	110.8(4)
C(10)-C(11)-C(12)	111.0(4)
C(11)-C(12)-C(7)	111.8(3)
C(14)-C(13)-C(18)	109.6(3)
C(14)-C(13)-P(1)	114.3(3)
C(18)-C(13)-P(1)	118.7(3)
C(15)-C(14)-C(13)	111.4(3)
C(14)-C(15)-C(16)	110.9(4)
C(15)-C(16)-C(17)	111.6(4)
C(16)-C(17)-C(18)	110.4(4)
C(17)-C(18)-C(13)	110.5(3)
C(24)-C(19)-C(20)	110.0(3)
C(24)-C(19)-P(1)	113.2(3)
C(20)-C(19)-P(1)	118.5(3)
C(21)-C(20)-C(19)	110.7(3)
C(22)-C(21)-C(20)	111.9(4)
C(21)-C(22)-C(23)	110.9(4)
C(22)-C(23)-C(24)	111.6(3)
C(19)-C(24)-C(23)	111.4(4)
C(26)-C(25)-C(30)	110.5(3)
C(26)-C(25)-P(2)	112.6(3)
C(30)-C(25)-P(2)	112.5(3)
C(25)-C(26)-C(27)	112.2(4)

C(28)-C(27)-C(26)	110.8(4)
C(27)-C(28)-C(29)	111.2(4)
C(30)-C(29)-C(28)	111.1(4)
C(29)-C(30)-C(25)	111.0(4)
C(36)-C(31)-C(32)	110.4(5)
C(36)-C(31)-P(2)	119.9(5)
C(32)-C(31)-P(2)	111.9(4)
C(31)-C(32)-C(33)	111.5(5)
C(34)-C(33)-C(32)	109.3(6)
C(35)-C(34)-C(33)	114.1(5)
C(34)-C(35)-C(36)	111.8(5)
C(31)-C(36)-C(35)	111.5(6)
C(42)-C(37)-C(38)	109.9(3)
C(42)-C(37)-P(2)	118.4(3)
C(38)-C(37)-P(2)	113.6(3)
C(37)-C(38)-C(39)	110.5(3)
C(40)-C(39)-C(38)	111.2(4)
C(39)-C(40)-C(41)	111.1(4)
C(42)-C(41)-C(40)	110.9(4)
C(37)-C(42)-C(41)	111.8(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. 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	32(1)	32(1)	30(1)	-8(1)	-5(1)	-1(1)
P(1)	34(1)	32(1)	31(1)	-7(1)	-3(1)	-4(1)
P(2)	38(1)	36(1)	31(1)	-9(1)	-3(1)	1(1)
O(1)	45(2)	93(3)	50(2)	0(2)	-15(2)	14(2)
O(2)	51(2)	35(2)	76(2)	3(2)	-16(2)	-13(1)
N	34(2)	33(2)	33(2)	-6(2)	-5(1)	-8(1)
C(1)	41(2)	58(3)	31(2)	-10(2)	1(2)	2(2)
C(2)	34(2)	39(3)	38(2)	1(2)	-4(2)	-6(2)
C(3)	51(3)	54(3)	67(3)	5(3)	-23(2)	-6(2)
O(3)	49(2)	45(2)	73(2)	-12(2)	-10(2)	-14(2)
C(4)	76(4)	130(6)	118(6)	-61(5)	-27(4)	-26(4)
C(5A)	49(5)	69(6)	119(8)	-51(6)	-3(5)	-9(4)
C(6)	140(6)	70(5)	205(9)	-46(5)	-18(6)	-64(5)
C(5B)	48(9)	97(14)	62(11)	-49(10)	-29(8)	-2(9)
C(7)	42(2)	34(2)	29(2)	-8(2)	-2(2)	-7(2)
C(8)	52(2)	36(2)	37(2)	-8(2)	-3(2)	-6(2)
C(9)	86(4)	32(2)	46(3)	-8(2)	-5(3)	-9(2)
C(10)	96(4)	59(3)	44(3)	-21(2)	8(3)	-37(3)
C(11)	57(3)	51(3)	51(3)	-16(2)	-1(2)	-23(2)
C(12)	47(2)	47(3)	35(2)	-13(2)	-1(2)	-11(2)
C(13)	35(2)	37(2)	37(2)	-10(2)	-1(2)	-3(2)
C(14)	40(2)	58(3)	51(3)	-24(2)	-1(2)	-11(2)
C(15)	45(2)	67(3)	54(3)	-26(3)	-4(2)	-15(2)
C(16)	37(2)	80(4)	66(3)	-25(3)	-4(2)	-14(2)
C(17)	37(2)	78(4)	64(3)	-33(3)	7(2)	-10(2)
C(18)	40(2)	60(3)	46(3)	-19(2)	1(2)	-13(2)
C(19)	42(2)	34(2)	35(2)	-3(2)	-3(2)	-6(2)
C(20)	69(3)	44(3)	33(3)	-8(2)	-2(2)	1(2)
C(21)	71(3)	50(3)	40(3)	-3(2)	-5(2)	-16(2)
C(22)	54(3)	48(3)	49(3)	10(2)	-3(2)	-14(2)
C(23)	51(3)	38(2)	54(3)	-1(2)	3(2)	-11(2)
C(24)	55(3)	45(3)	41(3)	-4(2)	2(2)	-17(2)
C(25)	44(2)	35(2)	35(2)	-2(2)	6(2)	-5(2)
C(26)	52(3)	40(3)	47(3)	-7(2)	2(2)	-8(2)
C(27)	75(3)	52(3)	55(3)	-12(2)	8(3)	-27(3)
C(28)	95(4)	35(3)	58(3)	-9(2)	17(3)	-14(3)
C(29)	79(3)	33(3)	49(3)	-1(2)	11(3)	2(2)
C(30)	54(3)	39(3)	42(3)	2(2)	5(2)	4(2)
C(31)	101(2)	119(2)	59(2)	-34(2)	-33(1)	11(2)
C(32)	101(2)	119(2)	59(2)	-34(2)	-33(1)	11(2)
C(33)	101(2)	119(2)	59(2)	-34(2)	-33(1)	11(2)
C(34)	101(2)	119(2)	59(2)	-34(2)	-33(1)	11(2)
C(35)	101(2)	119(2)	59(2)	-34(2)	-33(1)	11(2)
C(36)	101(2)	119(2)	59(2)	-34(2)	-33(1)	11(2)
C(37)	35(2)	37(2)	37(2)	-11(2)	-2(2)	-2(2)
C(38)	40(2)	36(2)	57(3)	-9(2)	0(2)	-2(2)
C(39)	52(3)	41(3)	72(3)	-9(2)	0(2)	2(2)
C(40)	38(2)	47(3)	74(3)	-21(2)	2(2)	-4(2)
C(41)	40(2)	47(3)	76(4)	-14(2)	9(2)	-6(2)
C(42)	46(2)	45(3)	57(3)	-5(2)	10(2)	-4(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for 1.

	x	y	z	U(eq)
H	2250(30)	8776(15)	7280(30)	60(13)
H(0)	3931	7317	7968	40
H(3A)	5408	5057	8937	90
H(3B)	4975	6089	9253	90
H(3C)	5825	5983	8442	90
H(3)	2422	5637	7013	66
H(4A)	-486	6558	6289	155
H(4B)	-756	5507	6309	155
H(4C)	401	5772	5807	155
H(5AA)	197	5579	7619	91
H(6A)	1887	4203	7678	194
H(6B)	1887	4329	6663	194
H(6C)	748	4028	7165	194
H(7A)	719	8955	9412	42
H(8A)	-337	9965	8210	51
H(8B)	934	9872	7712	51
H(9A)	502	11350	8272	67
H(9B)	393	10783	9206	67
H(10A)	2640	10637	8284	74
H(10B)	2339	11161	9105	74
H(11A)	2386	9676	9959	60
H(11B)	3661	9589	9465	60
H(12A)	2852	8203	9403	51
H(12B)	2943	8774	8468	51
H(13A)	-1114	8731	7913	44
H(14A)	-976	7192	7532	58
H(14B)	-1368	6820	8470	58
H(15A)	-3144	7288	7570	64
H(15B)	-2884	8341	7280	64
H(16A)	-3567	7620	8951	71
H(16B)	-4426	8476	8298	71
H(17A)	-3497	9110	9358	69
H(17B)	-3097	9503	8427	69
H(18A)	-1585	7927	9587	57
H(18B)	-1309	8981	9342	57
H(19A)	2296	6758	9391	45
H(20A)	1286	7761	10346	61
H(20B)	152	7244	10371	61
H(21A)	2655	6285	10939	64
H(21B)	1502	6500	11548	64
H(22A)	611	5391	11013	63
H(22B)	2005	4857	11330	63
H(23A)	1552	4505	9973	58
H(23B)	2689	5018	9940	58
H(24A)	1331	5752	8768	56
H(24B)	187	5984	9381	56
H(25A)	3799	9148	5253	47
H(26A)	4905	8678	6553	56
H(26B)	3690	9101	7050	56
H(27A)	4910	10243	6900	70
H(27B)	4970	10247	5895	70
H(28A)	3492	11634	6151	76

H(28B)	2781	10982	6784	76
H(29A)	1707	11431	5460	68
H(29B)	2935	10975	4989	68
H(30A)	1653	9875	5149	58
H(30B)	1616	9881	6153	58
H(31A)	1312	8400	4926	116
H(32A)	1456	6736	5324	116
H(32B)	2591	6502	4703	116
H(33A)	755	6469	3979	116
H(33B)	99	7540	4159	116
H(34A)	2170	7063	3106	116
H(34B)	806	7654	2777	116
H(35A)	1006	8967	3360	116
H(35B)	2169	8665	2777	116
H(36A)	3461	7930	3968	116
H(36B)	2784	9005	4120	116
H(37A)	4918	7096	6477	45
H(38A)	4210	5862	5445	54
H(38B)	3953	5812	6439	54
H(39A)	6101	5418	6765	68
H(39B)	5807	4651	6212	68
H(40A)	6509	5459	4983	63
H(40B)	7578	5211	5709	63
H(41A)	7050	6809	5990	65
H(41B)	7275	6842	4993	65
H(42A)	5438	7998	5236	61
H(42B)	5134	7221	4699	61

Table 6. Torsion angles [°] for 1.

C(1)-Ru-P(1)-C(13)	20.3(2)
N-Ru-P(1)-C(13)	-164.30(17)
O(3)-Ru-P(1)-C(13)	-79.73(16)
P(2)-Ru-P(1)-C(13)	110.63(17)
C(1)-Ru-P(1)-C(7)	-93.87(19)
N-Ru-P(1)-C(7)	81.56(15)
O(3)-Ru-P(1)-C(7)	166.13(14)
P(2)-Ru-P(1)-C(7)	-3.50(18)
C(1)-Ru-P(1)-C(19)	151.7(2)
N-Ru-P(1)-C(19)	-32.84(17)
O(3)-Ru-P(1)-C(19)	51.73(17)
P(2)-Ru-P(1)-C(19)	-117.90(18)
C(1)-Ru-P(2)-C(31)	-32.7(3)
N-Ru-P(2)-C(31)	152.1(3)
O(3)-Ru-P(2)-C(31)	67.1(2)
P(1)-Ru-P(2)-C(31)	-123.2(3)
C(1)-Ru-P(2)-C(25)	82.3(2)
N-Ru-P(2)-C(25)	-92.92(16)
O(3)-Ru-P(2)-C(25)	-177.84(15)
P(1)-Ru-P(2)-C(25)	-8.19(19)
C(1)-Ru-P(2)-C(37)	-163.2(2)
N-Ru-P(2)-C(37)	21.62(17)
O(3)-Ru-P(2)-C(37)	-63.30(16)
P(1)-Ru-P(2)-C(37)	106.34(17)
C(1)-Ru-N-C(2)	164.8(17)
O(3)-Ru-N-C(2)	-8.2(4)
P(2)-Ru-N-C(2)	-107.4(4)
P(1)-Ru-N-C(2)	91.7(4)
N-Ru-C(1)-O(1)	-5(8)
O(3)-Ru-C(1)-O(1)	168(6)
P(2)-Ru-C(1)-O(1)	-93(6)
P(1)-Ru-C(1)-O(1)	68(6)
Ru-N-C(2)-O(2)	4.6(6)
Ru-N-C(2)-C(3)	-172.7(3)
C(1)-Ru-O(3)-C(5A)	-37.4(5)
N-Ru-O(3)-C(5A)	142.0(5)
P(2)-Ru-O(3)-C(5A)	-128.6(5)
P(1)-Ru-O(3)-C(5A)	54.8(5)
Ru-O(3)-C(5A)-C(4)	67.6(6)
Ru-O(3)-C(5A)-C(6)	-171.1(4)
C(13)-P(1)-C(7)-C(8)	-56.5(3)
C(19)-P(1)-C(7)-C(8)	-170.4(3)
Ru-P(1)-C(7)-C(8)	64.7(3)
C(13)-P(1)-C(7)-C(12)	178.0(3)
C(19)-P(1)-C(7)-C(12)	64.1(3)
Ru-P(1)-C(7)-C(12)	-60.9(3)
C(12)-C(7)-C(8)-C(9)	-55.4(4)
P(1)-C(7)-C(8)-C(9)	178.0(3)
C(7)-C(8)-C(9)-C(10)	56.2(5)
C(8)-C(9)-C(10)-C(11)	-56.2(5)
C(9)-C(10)-C(11)-C(12)	56.0(5)
C(10)-C(11)-C(12)-C(7)	-57.0(5)
C(8)-C(7)-C(12)-C(11)	56.4(4)
P(1)-C(7)-C(12)-C(11)	-175.7(3)
C(7)-P(1)-C(13)-C(14)	177.9(3)
C(19)-P(1)-C(13)-C(14)	-76.2(3)

Ru-P(1)-C(13)-C(14)	58.6(3)
C(7)-P(1)-C(13)-C(18)	-50.2(4)
C(19)-P(1)-C(13)-C(18)	55.6(4)
Ru-P(1)-C(13)-C(18)	-169.6(3)
C(18)-C(13)-C(14)-C(15)	58.0(5)
P(1)-C(13)-C(14)-C(15)	-165.9(3)
C(13)-C(14)-C(15)-C(16)	-56.3(5)
C(14)-C(15)-C(16)-C(17)	54.9(6)
C(15)-C(16)-C(17)-C(18)	-55.6(5)
C(16)-C(17)-C(18)-C(13)	57.5(5)
C(14)-C(13)-C(18)-C(17)	-58.5(5)
P(1)-C(13)-C(18)-C(17)	167.7(3)
C(13)-P(1)-C(19)-C(24)	65.4(3)
C(7)-P(1)-C(19)-C(24)	172.5(3)
Ru-P(1)-C(19)-C(24)	-67.3(3)
C(13)-P(1)-C(19)-C(20)	-65.6(4)
C(7)-P(1)-C(19)-C(20)	41.5(4)
Ru-P(1)-C(19)-C(20)	161.7(3)
C(24)-C(19)-C(20)-C(21)	56.1(5)
P(1)-C(19)-C(20)-C(21)	-171.5(3)
C(19)-C(20)-C(21)-C(22)	-55.9(5)
C(20)-C(21)-C(22)-C(23)	55.1(5)
C(21)-C(22)-C(23)-C(24)	-55.0(5)
C(20)-C(19)-C(24)-C(23)	-56.5(4)
P(1)-C(19)-C(24)-C(23)	168.4(3)
C(22)-C(23)-C(24)-C(19)	56.5(5)
C(31)-P(2)-C(25)-C(26)	-173.6(3)
C(37)-P(2)-C(25)-C(26)	-60.5(3)
Ru-P(2)-C(25)-C(26)	62.3(3)
C(31)-P(2)-C(25)-C(30)	60.8(4)
C(37)-P(2)-C(25)-C(30)	173.9(3)
Ru-P(2)-C(25)-C(30)	-63.3(3)
C(30)-C(25)-C(26)-C(27)	-54.2(5)
P(2)-C(25)-C(26)-C(27)	179.1(3)
C(25)-C(26)-C(27)-C(28)	54.7(5)
C(26)-C(27)-C(28)-C(29)	-55.6(5)
C(27)-C(28)-C(29)-C(30)	57.4(5)
C(28)-C(29)-C(30)-C(25)	-56.9(5)
C(26)-C(25)-C(30)-C(29)	55.1(5)
P(2)-C(25)-C(30)-C(29)	-178.2(3)
C(25)-P(2)-C(31)-C(36)	43.7(5)
C(37)-P(2)-C(31)-C(36)	-62.9(5)
Ru-P(2)-C(31)-C(36)	164.2(4)
C(25)-P(2)-C(31)-C(32)	175.3(4)
C(37)-P(2)-C(31)-C(32)	68.7(5)
Ru-P(2)-C(31)-C(32)	-64.2(5)
C(36)-C(31)-C(32)-C(33)	-56.8(7)
P(2)-C(31)-C(32)-C(33)	167.0(4)
C(31)-C(32)-C(33)-C(34)	55.8(7)
C(32)-C(33)-C(34)-C(35)	-55.0(7)
C(33)-C(34)-C(35)-C(36)	54.0(7)
C(32)-C(31)-C(36)-C(35)	54.4(7)
P(2)-C(31)-C(36)-C(35)	-173.4(4)
C(34)-C(35)-C(36)-C(31)	-52.9(7)
C(31)-P(2)-C(37)-C(42)	60.0(4)
C(25)-P(2)-C(37)-C(42)	-46.4(4)
Ru-P(2)-C(37)-C(42)	-166.5(3)
C(31)-P(2)-C(37)-C(38)	-71.1(4)

C(25)-P(2)-C(37)-C(38)	-177.5(3)
Ru-P(2)-C(37)-C(38)	62.4(3)
C(42)-C(37)-C(38)-C(39)	57.3(5)
P(2)-C(37)-C(38)-C(39)	-167.6(3)
C(37)-C(38)-C(39)-C(40)	-56.8(5)
C(38)-C(39)-C(40)-C(41)	55.5(5)
C(39)-C(40)-C(41)-C(42)	-54.7(5)
C(38)-C(37)-C(42)-C(41)	-57.5(5)
P(2)-C(37)-C(42)-C(41)	169.8(3)
C(40)-C(41)-C(42)-C(37)	56.3(5)

Symmetry transformations used to generate equivalent atoms: