Efficient Aziridination of Olefins Catalyzed by Mixed Valent Dirhodium(II,III) Caprolactamate

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Supporting Information

General. All reagents were commercially obtained unless otherwise noted. Yields reported are for isolated yields. All products were characterized and in agreement with those previously reported.¹ NBS was recrystallized from water according to the guidelines of Armarego and Chai.² *p*-TsNH₂ and K₂CO₃ (anhydrous, granular) were used as received. Olefins (except entries 10 and 11, Table 1) were filtered over a plug of alumina and distilled prior to use. *Trans*-2-phenyl-1-vinylcyclopropane **9** was prepared according the procedure of Fu, *et al.*³ Sulfamate indan-2-yl ester **7** was prepared according to the procedure of Espino, *et al.*⁴ 2-Vinylbenzenesulfonamide (entry 10, Table 1) and 2-allylbenzenesulfonamide (entry 11, Table 1) were prepared according the procedure of Dauban and Dodd.^{1d} The preparation of dirhodium(II) caprolactamate [Rh₂(cap)₄·2CH₃CN] has been previously described.⁵ ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained on a Bruker DRX-400 NMR as solutions in CDCl₃. Chemical shifts are reported in parts per million (ppm, δ) downfield from Me₄Si (TMS); coupling constants are reported in Hertz (Hz). UV-Visible spectra were obtained on a Varian Cary 50 spectrophotometer using a xenon flash lamp. Preparative chromatographic purification was performed using SiliCycle (60Å, 40-63 mesh) silica gel according to the method of Still.⁶ Thin layer chromatography (TLC) was performed on Merck 0.25 mm silica gel 60 F₂₅₄ plates with visualization by fluorescence quenching or aqueous KMnO₄ stain. Anhydrous CH₂Cl₂ was purified prior to use by nitrogen forced-flow over activated alumina as described.⁷

¹ For characterization data see: (a) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742. (b) Jeong, J. U.; Tao, B.; Sagasser, I.; Henniges, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1998**, *120*, 6844. (c) Cui, Y.; He, C. *J. Am. Chem. Soc.* **2003**, *125*, 16202. (d) Dauban, P.; Dodd, R. H. *Org. Lett.* **2000**, *2*, 2327.

² Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*; 5th ed., Elsevier Science: New York, 2003.

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⁶ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

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NMR Experiments.

Control Experiment

29 minutes after addition of 0.5 mL (0.152 mmol) of a 3.03×10^{-1} M solution of *p*-toluenesulfonamide in *d*-DCM to 0.5 mL (0.149 mmol) of a 2.98×10^{-1} M solution of *N*-bromosuccinimide.

N-bromo-*p*-toluenesulfonamide was observed as the product in this equilibrium mixture. ¹H NMR (400 MHz) δ 7.81-7.83 (d, *J* = 8.0 Hz, 2H), 7.40-7.38 (d, *J* = 8.0 Hz, 2H), 5.95 (s, 1H), 2.46 (s, 3H)

@ 29 mins. - CH₃(TsNH₂):CH₃(TsNHBBr) = 2.7:1.0

@ 20 hrs. - CH₃(TsNH₂):CH₃(TsNHBBr) = 2.9:1.0

Addition of 100 μL of D₂O exchanged protons in the δ 5.95 (s, 1H, -SO₂BrN-H) and 5.08 (s, 2H, -SO₂NH₂) indicated by loss of signal.

Equilibrium Experiment

A series of 100 μL aliquots of a succinimide solution (1.52×10^{-1} M in *d*-dichloromethane) was added to an NMR tube with *N*-bromosuccinimide (1.5×10^{-1} mmol) and *p*-toluenesulfonamide (1.5×10^{-1} mmol) in 1 mL of *d*-dichloromethane. The ratio of $-\text{CH}_3$ substituents was measured and is reported below:

Initial - $\text{CH}_3(\text{TsNH}_2):\text{CH}_3(\text{TsNHBr}) = 2.0:1.0$

100 μL succinimide solution - $\text{CH}_3(\text{TsNH}_2):\text{CH}_3(\text{TsNHBr}) = 3.0:1.0$

200 μL succinimide solution - $\text{CH}_3(\text{TsNH}_2):\text{CH}_3(\text{TsNHBr}) = 4.3:1.0$

300 μL succinimide solution - $\text{CH}_3(\text{TsNH}_2):\text{CH}_3(\text{TsNHBr}) = 6.0:1.0$

400 μL succinimide solution - $\text{CH}_3(\text{TsNH}_2):\text{CH}_3(\text{TsNHBr}) = 6.0:1.0$

900 μL succinimide solution - $\text{CH}_3(\text{TsNH}_2):\text{CH}_3(\text{TsNHBr}) = 12.0:1.0$

Characterization of Basified Salt

A solution of *N*-bromosuccinimide (2.75×10^{-1} mmol) and *p*-toluenesulfonamide (2.75×10^{-1} mmol) in 1 mL of *d*-chloroform was placed in an NMR tube. A control spectrum indicated the previously observed equilibrium had been established. Anhydrous potassium carbonate (76 mg) was added. A yellow precipitate formed above the potassium carbonate. The following is the relative ratios of from ^1H NMR (400 MHz) spectra obtained:

$\text{CH}_3(\text{TsNH}_2):\text{CH}_3(\text{TsNHBr}) = 1.0:0.0$ – TsNHBr was not observed.

$\text{CH}_2(\text{NBS}):\text{CH}_2(\text{succinimide}) = 1.0:1.5$

$\text{NBS}:\text{TsNH}_2 = 1.1:1.0$

$\text{TsNH}_2:\text{Succinimide} = 1.0:1.4$

Isolation of Salt

A solution of *N*-bromosuccinimide (2.75×10^{-1} mmol) and *p*-toluenesulfonamide (2.75×10^{-1} mmol) in 1 mL of dichloromethane was placed in a vial. Anhydrous potassium carbonate (76 mg) was added and a yellow precipitate formed. The precipitate was filtered and dried in vacuo. The yellow powder (10 mg) was placed in an NMR tube and dissolved with *d*-dimethylsulfoxide. The following is the relative ratios from the ^1H NMR (400 MHz) spectra obtained:

$\text{CH}_3(\text{TsNH}_2):\text{CH}_3(\text{TsNHBr}) = 3.0:1.0$ – Signals of TsNBr^- were shifted upfield from TsNH_2 as expected for the anion.

Potassium *N*-bromo-*p*-toluenesulfonamide was only observed product in an equilibrium mixture. ^1H NMR in DMSO (400 MHz) δ 7.58-7.56 (d, $J = 8.0$ Hz, 2H), 7.27-7.25 (d, $J = 8.0$ Hz, 2H), 2.31 (s, 3H)

(2-(4-Methylphenyl)-2-(*N*-bromo-*p*-toluenesulfonamino)-1-bromo-ethane, **12**:

12 (10 mg, 2.2×10^{-2} mmol) was placed in an NMR tube and diluted with 1 mL of *d*-dichloromethane. Succinimide (3 mg, 3.0×10^{-2} mmol) was added giving *N*-bromosuccinimide and aminobromide **3** as observed by ^1H NMR. Relative ratios are given below.

$\text{CH}_2(\text{NBS}) : \text{CH}_2(\text{succinimide}) = 1.0:7.1$

$\text{CH}_2(\text{NBS}) : \text{CH}_3(\text{N-bromo-aminobromide}) = 1.0:5.4$

$\text{CH}_3(\text{aminobromide}) : \text{CH}_3(\text{N-bromo-aminobromide}) = 1.0:5.3$

$\text{CH}_2(\text{succinimide}) : \text{CH}_3(\text{N-bromo-aminobromide}) = 1.3:1.0$

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To a solution of $\text{Rh}_2(\text{cap})_4$ (0.014 mmol, 100 mol%) in 5 mL CH_2Cl_2 was added *N*-chlorosuccinimide (0.020 mmol, 140 mol%) to which the color of the solution turned from light blue to red. After 1 hr, 1 mL of MeOH was added. The solution was passed through a short plug of silica gel and evaporated yielding a red solid (6:1 $\text{CH}_2\text{Cl}_2/\text{MeOH}$, TLC $R_f = 0.40$). Crystals were obtained by slow evaporation from MeOH/hexanes (1:50). $\text{C}_{27}\text{H}_{51}\text{Cl}_1\text{N}_4\text{O}_7\text{Rh}_2$, $M = 784.99$, monoclinic, space group $P2_1$, $a = 8.3834(5)$ Å, $b = 18.8291(11)$ Å, $c = 10.2686(6)$ Å, $\beta = 98.088(1)$, $U = 1604.8(2)$ Å³, $Z = 2$, $T = 173$ K, MoK α (0.71073 Å), 25387 reflection measured, 7344 unique ($R_{\text{int}} = 0.0318$), which were all used in calculations. The final $wR2$ was 0.0623 (all data).

Purification by chromatography on silica gel (4:1 hexanes/EtOAc) gave a clear oil: TLC $R_f = 0.22$ (5:1 hexanes/EtOAc); ^1H NMR (400 MHz) δ 7.58 (d, $J = 8.0$ Hz, 2H), 7.20-7.15 (m, 5H), 7.08-7.04 (m, 2H), 5.66 (dt, $J = 15.2, 7.6$ Hz, 1H), 5.42 (dt, $J = 14.8, 7.2$ Hz, 1H), 5.10 (d, $J = 7.2$ Hz, 1H), 4.35 (q, $J = 7.2$ Hz, 1H), 3.78 (d, $J = 7.6$, 2H), 2.53-2.43 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz) δ 143.2, 140.0, 137.4, 130.5, 130.2, 129.4, 128.5, 127.5, 127.1, 126.4, 57.3, 39.9, 32.2, 21.5; HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{21}\text{BrNO}_2\text{S}$ 394.0476, found 394.0463 ($\text{M}+\text{H}$)⁺.

X-Ray Data.

A reddish-orange plate with approximate orthogonal dimensions 0.306 x 0.124 x 0.018 mm³ was placed and optically centered on the Bruker SMART CCD system at -100°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω -scans, 10 seconds per frame, and 25 frames per series that were well distributed in reciprocal space. Data frames were collected [MoK α] with 0.3° wide ω -scans, 40 seconds per frame and 606 frames per series.

Five complete series were collected at varying ϕ angles ($\phi=0^\circ, 72^\circ, 144^\circ, 216^\circ, 288^\circ$). The crystal to detector distance was 4.893 cm, thus providing a nearly complete sphere of data to $2\theta_{\max}=55.13^\circ$. A total of 25387 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS^{1,2} with 7378 unique.

Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with a Pentium 1.80GHz processor and 512MB of extended memory. The SHELXTL³ program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the unique chiral monoclinic space group P2₁ (no. 4). The structure was determined by direct methods with the successful location of all the non-hydrogen atoms using the program XS⁴. The structure was refined with XL⁵. The 25387 data collected were merged during least-squares refinement to 7344 unique data [R(int)=0.0318]. Multiple least-squares difference-Fourier cycles were required to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were allowed to refine freely (xyzU) but for those attached to the methanol oxygen atoms (U only). The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with R(F)=5.91%, wR(F²)=11.59%, GOF=1.048 for all 12386 unique reflections [R(F)=4.20%, wR(F²)=10.62% for those 9858 data with $F_o > 4\sigma(F_o)$]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete. The absolute structure parameter, Flack(x)⁶, was refined and found to be 0.26(2) indicating racemic twinning that was also refined.

The function minimized during the full-matrix least-squares refinement was $\sum w(F_o^2 - F_c^2)^2$ where $w = 1/[\sigma^2(F_o^2) + (0.0382 \cdot P)^2 + 0.0 \cdot P]$ and $P = (\max(F_o^2, 0) + 2 \cdot F_c^2)/3$. An empirical correction for extinction was also attempted but found to be negative and therefore not applied.

References:

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5. Sheldrick, G.M., (1993). Shelxl93 Program for the Refinement of Crystal Structures. University of Göttingen, Germany.
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Methanol moles not shown in stereoview diagram.

Table 1. Crystal data and structure refinement for [C₂₅H₄₃N₄O₅ClRh₂][CH₃OH]₂.

Identification code	1071ff	
Empirical formula	C ₂₇ H ₅₁ Cl N ₄ O ₇ Rh ₂	
Formula weight	784.99	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.3834(5) Å	α = 90°.
	b = 18.8291(11) Å	β = 98.0880(10)°.
	c = 10.2686(6) Å	γ = 90°.
Volume	1604.79(16) Å ³	
Z	2	
Density (calculated)	1.625 Mg/m ³	
Absorption coefficient	1.160 mm ⁻¹	
F(000)	808	
Crystal size	0.31 x 0.12 x 0.02 mm ³	
Theta range for data collection	2.16 to 27.50°.	
Index ranges	-10 ≤ h ≤ 10, -24 ≤ k ≤ 24, -13 ≤ l ≤ 13	
Reflections collected	25387	
Independent reflections	7344 [R(int) = 0.0318]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Empirical, SADABS (multi-scan)	
Max. and min. transmission	0.9794 and 0.7179	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7344 / 1 / 571	
Goodness-of-fit on F ²	1.029	
Final R indices [I > 2σ(I)]	R1 = 0.0267, wR2 = 0.0597 [6732 Data]	
R indices (all data)	R1 = 0.0334, wR2 = 0.0623	
Absolute structure parameter	0.26(2)	
Largest diff. peak and hole	0.912 and -0.721 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_{25}\text{H}_{43}\text{N}_4\text{O}_5\text{ClRh}_2][\text{CH}_3\text{OH}]_2$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Rh(1)	7771(1)	1436(1)	3732(1)	20(1)
Rh(2)	8801(1)	313(1)	3098(1)	19(1)
Cl(1)	6354(1)	2524(1)	4603(1)	34(1)
C(1)	8873(4)	1421(2)	1169(3)	22(1)
N(1)	8238(3)	1826(2)	1996(3)	22(1)
O(1)	9275(3)	770(1)	1411(2)	24(1)
C(2)	9120(5)	1679(2)	-191(4)	29(1)
C(3)	7522(5)	1769(2)	-1097(4)	35(1)
C(4)	6670(5)	2461(2)	-877(4)	37(1)
C(5)	6263(5)	2566(2)	504(4)	37(1)
C(6)	7709(5)	2553(2)	1594(4)	31(1)
C(7)	5377(4)	543(2)	2254(3)	21(1)
N(7)	6556(3)	82(2)	2256(3)	21(1)
O(7)	5571(3)	1149(1)	2833(2)	24(1)
C(8)	3703(4)	403(2)	1543(4)	28(1)
C(9)	3637(5)	389(3)	51(4)	35(1)
C(10)	4232(5)	-296(3)	-498(4)	37(1)
C(11)	5958(5)	-506(3)	60(4)	33(1)
C(12)	6236(5)	-596(2)	1554(4)	25(1)
C(13)	7700(4)	322(2)	5650(3)	22(1)
N(13)	8340(3)	-82(2)	4810(3)	22(1)
O(13)	7288(3)	974(1)	5396(2)	24(1)
C(14)	7497(4)	64(2)	7003(3)	25(1)
C(15)	9148(5)	12(2)	7860(4)	29(1)
C(16)	10014(5)	-681(2)	7654(4)	33(1)
C(17)	10385(5)	-799(2)	6265(4)	31(1)
C(18)	8883(5)	-801(2)	5224(4)	26(1)
C(19)	11220(4)	1208(2)	4524(3)	23(1)
N(19)	10039(3)	1659(2)	4565(3)	22(1)
O(19)	11017(3)	598(1)	3948(2)	25(1)
C(20)	12927(4)	1364(2)	5153(4)	30(1)

C(21)	13109(5)	1391(3)	6669(4)	40(1)
C(22)	12539(6)	2092(3)	7195(5)	45(1)
C(23)	10801(5)	2278(3)	6722(4)	40(1)
C(24)	10400(5)	2348(2)	5237(4)	30(1)
C(25)	10265(5)	-843(3)	1143(4)	34(1)
O(25)	10052(3)	-725(1)	2475(2)	24(1)
C(31)	2606(6)	2597(3)	2061(6)	49(1)
O(31)	3470(4)	3166(2)	2666(4)	62(1)
C(41)	4051(5)	-687(3)	4596(5)	41(1)
O(41)	2926(3)	-1113(2)	3758(3)	40(1)

Table 3. Bond lengths [Å] and angles [°] for [C₂₅H₄₃N₄O₅ClRh₂][CH₃OH]₂.

Rh(1)-O(13)	2.008(2)	C(8)-H(8A)	0.96(5)
Rh(1)-O(7)	2.017(2)	C(8)-H(8B)	0.98(4)
Rh(1)-N(19)	2.017(3)	C(9)-C(10)	1.519(7)
Rh(1)-N(1)	2.017(3)	C(9)-H(9A)	0.92(5)
Rh(1)-Rh(2)	2.4078(3)	C(9)-H(9B)	0.93(4)
Rh(1)-Cl(1)	2.5887(9)	C(10)-C(11)	1.531(6)
Rh(2)-N(13)	1.996(3)	C(10)-H(10A)	1.11(4)
Rh(2)-N(7)	2.006(3)	C(10)-H(10B)	0.96(5)
Rh(2)-O(19)	2.011(2)	C(11)-C(12)	1.529(6)
Rh(2)-O(1)	2.023(2)	C(11)-H(11A)	0.98(4)
Rh(2)-O(25)	2.349(2)	C(11)-H(11B)	0.97(4)
C(1)-O(1)	1.286(5)	C(12)-H(12A)	0.94(3)
C(1)-N(1)	1.309(5)	C(12)-H(12B)	0.94(4)
C(1)-C(2)	1.520(5)	C(13)-O(13)	1.292(5)
N(1)-C(6)	1.480(5)	C(13)-N(13)	1.319(4)
C(2)-C(3)	1.529(6)	C(13)-C(14)	1.504(5)
C(2)-H(2A)	0.97(4)	N(13)-C(18)	1.473(5)
C(2)-H(2B)	0.89(5)	C(14)-C(15)	1.535(5)
C(3)-C(4)	1.518(7)	C(14)-H(14A)	1.00(4)
C(3)-H(3A)	1.00(4)	C(14)-H(14B)	0.81(4)
C(3)-H(3B)	0.99(4)	C(15)-C(16)	1.522(6)
C(4)-C(5)	1.517(6)	C(15)-H(15A)	1.10(4)
C(4)-H(4A)	0.94(4)	C(15)-H(15B)	0.84(5)
C(4)-H(4B)	0.91(6)	C(16)-C(17)	1.518(6)
C(5)-C(6)	1.530(6)	C(16)-H(16A)	0.90(5)
C(5)-H(5A)	0.96(4)	C(16)-H(16B)	1.03(6)
C(5)-H(5B)	1.13(5)	C(17)-C(18)	1.533(5)
C(6)-H(6A)	0.91(4)	C(17)-H(17A)	0.98(4)
C(6)-H(6B)	1.00(4)	C(17)-H(17B)	0.99(4)
C(7)-O(7)	1.285(4)	C(18)-H(18A)	0.98(4)
C(7)-N(7)	1.316(4)	C(18)-H(18B)	0.92(4)
C(7)-C(8)	1.511(5)	C(19)-O(19)	1.293(4)
N(7)-C(12)	1.472(4)	C(19)-N(19)	1.310(4)
C(8)-C(9)	1.525(5)	C(19)-C(20)	1.514(5)

N(19)-C(24)	1.481(5)	O(13)-Rh(1)-Rh(2)	88.43(7)
C(20)-C(21)	1.543(5)	O(7)-Rh(1)-Rh(2)	88.87(7)
C(20)-H(20A)	1.00(5)	N(19)-Rh(1)-Rh(2)	86.85(8)
C(20)-H(20B)	0.92(4)	N(1)-Rh(1)-Rh(2)	87.64(8)
C(21)-C(22)	1.528(7)	O(13)-Rh(1)-Cl(1)	83.80(7)
C(21)-H(21A)	1.10(5)	O(7)-Rh(1)-Cl(1)	86.34(7)
C(21)-H(21B)	1.02(4)	N(19)-Rh(1)-Cl(1)	98.01(8)
C(22)-C(23)	1.511(6)	N(1)-Rh(1)-Cl(1)	99.94(9)
C(22)-H(22A)	0.95(5)	Rh(2)-Rh(1)-Cl(1)	170.90(2)
C(22)-H(22B)	0.94(5)	N(13)-Rh(2)-N(7)	90.73(11)
C(23)-C(24)	1.520(6)	N(13)-Rh(2)-O(19)	89.90(11)
C(23)-H(23A)	0.91(5)	N(7)-Rh(2)-O(19)	177.06(12)
C(23)-H(23B)	0.87(4)	N(13)-Rh(2)-O(1)	176.67(12)
C(24)-H(24A)	0.97(5)	N(7)-Rh(2)-O(1)	90.50(11)
C(24)-H(24B)	1.02(4)	O(19)-Rh(2)-O(1)	88.72(10)
C(25)-O(25)	1.421(4)	N(13)-Rh(2)-O(25)	94.54(10)
C(25)-H(25A)	0.95(6)	N(7)-Rh(2)-O(25)	97.45(10)
C(25)-H(25B)	0.91(5)	O(19)-Rh(2)-O(25)	85.36(9)
C(25)-H(25C)	0.93(4)	O(1)-Rh(2)-O(25)	88.37(9)
C(31)-O(31)	1.391(7)	N(13)-Rh(2)-Rh(1)	88.13(8)
C(31)-H(31A)	0.84(7)	N(7)-Rh(2)-Rh(1)	87.53(8)
C(31)-H(31B)	1.04(5)	O(19)-Rh(2)-Rh(1)	89.62(7)
C(31)-H(31C)	0.89(5)	O(1)-Rh(2)-Rh(1)	88.83(7)
O(31)-H(31)	0.8400	O(25)-Rh(2)-Rh(1)	174.30(6)
C(41)-O(41)	1.429(5)	O(1)-C(1)-N(1)	123.3(3)
C(41)-H(41A)	0.93(8)	O(1)-C(1)-C(2)	114.6(3)
C(41)-H(41B)	1.02(10)	N(1)-C(1)-C(2)	122.1(3)
C(41)-H(41C)	0.98(6)	C(1)-N(1)-C(6)	119.4(3)
O(41)-H(41)	0.8400	C(1)-N(1)-Rh(1)	120.6(2)
		C(6)-N(1)-Rh(1)	119.8(2)
O(13)-Rh(1)-O(7)	89.59(10)	C(1)-O(1)-Rh(2)	119.6(2)
O(13)-Rh(1)-N(19)	91.18(11)	C(1)-C(2)-C(3)	111.9(3)
O(7)-Rh(1)-N(19)	175.63(11)	C(1)-C(2)-H(2A)	103(2)
O(13)-Rh(1)-N(1)	175.61(12)	C(3)-C(2)-H(2A)	111(2)
O(7)-Rh(1)-N(1)	88.36(11)	C(1)-C(2)-H(2B)	106(3)
N(19)-Rh(1)-N(1)	90.59(11)	C(3)-C(2)-H(2B)	113(3)

H(2A)-C(2)-H(2B)	113(4)	C(9)-C(8)-H(8B)	110(2)
C(4)-C(3)-C(2)	113.3(4)	H(8A)-C(8)-H(8B)	106(3)
C(4)-C(3)-H(3A)	109(2)	C(10)-C(9)-C(8)	114.9(4)
C(2)-C(3)-H(3A)	104(2)	C(10)-C(9)-H(9A)	114(3)
C(4)-C(3)-H(3B)	109(2)	C(8)-C(9)-H(9A)	108(3)
C(2)-C(3)-H(3B)	115(2)	C(10)-C(9)-H(9B)	101(2)
H(3A)-C(3)-H(3B)	107(3)	C(8)-C(9)-H(9B)	120(2)
C(5)-C(4)-C(3)	115.0(4)	H(9A)-C(9)-H(9B)	98(4)
C(5)-C(4)-H(4A)	107(2)	C(9)-C(10)-C(11)	115.0(3)
C(3)-C(4)-H(4A)	110(2)	C(9)-C(10)-H(10A)	110(2)
C(5)-C(4)-H(4B)	102(3)	C(11)-C(10)-H(10A)	110(2)
C(3)-C(4)-H(4B)	120(4)	C(9)-C(10)-H(10B)	106(3)
H(4A)-C(4)-H(4B)	102(4)	C(11)-C(10)-H(10B)	107(3)
C(4)-C(5)-C(6)	115.0(4)	H(10A)-C(10)-H(10B)	109(4)
C(4)-C(5)-H(5A)	114(2)	C(12)-C(11)-C(10)	114.0(3)
C(6)-C(5)-H(5A)	106(2)	C(12)-C(11)-H(11A)	106(3)
C(4)-C(5)-H(5B)	105(3)	C(10)-C(11)-H(11A)	114(2)
C(6)-C(5)-H(5B)	100(3)	C(12)-C(11)-H(11B)	107(3)
H(5A)-C(5)-H(5B)	117(3)	C(10)-C(11)-H(11B)	113(3)
N(1)-C(6)-C(5)	113.2(3)	H(11A)-C(11)-H(11B)	103(3)
N(1)-C(6)-H(6A)	114(3)	N(7)-C(12)-C(11)	112.7(3)
C(5)-C(6)-H(6A)	109(3)	N(7)-C(12)-H(12A)	110(2)
N(1)-C(6)-H(6B)	108(2)	C(11)-C(12)-H(12A)	109(2)
C(5)-C(6)-H(6B)	108(2)	N(7)-C(12)-H(12B)	105(2)
H(6A)-C(6)-H(6B)	105(3)	C(11)-C(12)-H(12B)	115(2)
O(7)-C(7)-N(7)	122.6(3)	H(12A)-C(12)-H(12B)	105(3)
O(7)-C(7)-C(8)	115.3(3)	O(13)-C(13)-N(13)	122.5(3)
N(7)-C(7)-C(8)	122.1(3)	O(13)-C(13)-C(14)	115.6(3)
C(7)-N(7)-C(12)	119.2(3)	N(13)-C(13)-C(14)	121.8(3)
C(7)-N(7)-Rh(2)	121.1(2)	C(13)-N(13)-C(18)	118.6(3)
C(12)-N(7)-Rh(2)	119.7(2)	C(13)-N(13)-Rh(2)	120.6(2)
C(7)-O(7)-Rh(1)	119.9(2)	C(18)-N(13)-Rh(2)	120.4(2)
C(7)-C(8)-C(9)	112.9(3)	C(13)-O(13)-Rh(1)	120.2(2)
C(7)-C(8)-H(8A)	108(3)	C(13)-C(14)-C(15)	109.9(3)
C(9)-C(8)-H(8A)	107(3)	C(13)-C(14)-H(14A)	113(2)
C(7)-C(8)-H(8B)	111(2)	C(15)-C(14)-H(14A)	112(2)

C(13)-C(14)-H(14B)	109(3)	C(21)-C(20)-H(20A)	109(3)
C(15)-C(14)-H(14B)	107(3)	C(19)-C(20)-H(20B)	105(2)
H(14A)-C(14)-H(14B)	106(3)	C(21)-C(20)-H(20B)	108(2)
C(16)-C(15)-C(14)	112.6(3)	H(20A)-C(20)-H(20B)	113(3)
C(16)-C(15)-H(15A)	110.6(17)	C(22)-C(21)-C(20)	113.2(4)
C(14)-C(15)-H(15A)	106.2(18)	C(22)-C(21)-H(21A)	114(3)
C(16)-C(15)-H(15B)	110(4)	C(20)-C(21)-H(21A)	104(3)
C(14)-C(15)-H(15B)	107(4)	C(22)-C(21)-H(21B)	112(2)
H(15A)-C(15)-H(15B)	110(4)	C(20)-C(21)-H(21B)	106(2)
C(17)-C(16)-C(15)	114.9(3)	H(21A)-C(21)-H(21B)	107(3)
C(17)-C(16)-H(16A)	115(3)	C(23)-C(22)-C(21)	115.0(4)
C(15)-C(16)-H(16A)	108(3)	C(23)-C(22)-H(22A)	109(3)
C(17)-C(16)-H(16B)	101(3)	C(21)-C(22)-H(22A)	111(3)
C(15)-C(16)-H(16B)	116(3)	C(23)-C(22)-H(22B)	109(3)
H(16A)-C(16)-H(16B)	101(4)	C(21)-C(22)-H(22B)	110(3)
C(16)-C(17)-C(18)	113.5(3)	H(22A)-C(22)-H(22B)	102(4)
C(16)-C(17)-H(17A)	108(2)	C(22)-C(23)-C(24)	114.2(4)
C(18)-C(17)-H(17A)	108(2)	C(22)-C(23)-H(23A)	110(3)
C(16)-C(17)-H(17B)	109(3)	C(24)-C(23)-H(23A)	110(3)
C(18)-C(17)-H(17B)	108(3)	C(22)-C(23)-H(23B)	107(3)
H(17A)-C(17)-H(17B)	109(3)	C(24)-C(23)-H(23B)	117(3)
N(13)-C(18)-C(17)	112.9(3)	H(23A)-C(23)-H(23B)	96(4)
N(13)-C(18)-H(18A)	103(2)	N(19)-C(24)-C(23)	113.1(4)
C(17)-C(18)-H(18A)	118(2)	N(19)-C(24)-H(24A)	110(3)
N(13)-C(18)-H(18B)	109(3)	C(23)-C(24)-H(24A)	111(3)
C(17)-C(18)-H(18B)	109(3)	N(19)-C(24)-H(24B)	109(2)
H(18A)-C(18)-H(18B)	105(4)	C(23)-C(24)-H(24B)	107(2)
O(19)-C(19)-N(19)	122.7(3)	H(24A)-C(24)-H(24B)	105(4)
O(19)-C(19)-C(20)	115.0(3)	O(25)-C(25)-H(25A)	106(3)
N(19)-C(19)-C(20)	122.2(3)	O(25)-C(25)-H(25B)	113(3)
C(19)-N(19)-C(24)	118.5(3)	H(25A)-C(25)-H(25B)	101(4)
C(19)-N(19)-Rh(1)	121.5(2)	O(25)-C(25)-H(25C)	107(3)
C(24)-N(19)-Rh(1)	120.0(2)	H(25A)-C(25)-H(25C)	109(4)
C(19)-O(19)-Rh(2)	119.3(2)	H(25B)-C(25)-H(25C)	120(4)
C(19)-C(20)-C(21)	113.0(3)	C(25)-O(25)-Rh(2)	120.9(2)
C(19)-C(20)-H(20A)	108(3)	O(31)-C(31)-H(31A)	121(4)

O(31)-C(31)-H(31B)	109(3)
H(31A)-C(31)-H(31B)	93(5)
O(31)-C(31)-H(31C)	114(3)
H(31A)-C(31)-H(31C)	108(5)
H(31B)-C(31)-H(31C)	109(4)
C(31)-O(31)-H(31)	109.5
O(41)-C(41)-H(41A)	106(4)
O(41)-C(41)-H(41B)	102(6)
H(41A)-C(41)-H(41B)	121(7)
O(41)-C(41)-H(41C)	112(3)
H(41A)-C(41)-H(41C)	113(5)
H(41B)-C(41)-H(41C)	103(6)
C(41)-O(41)-H(41)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_{25}\text{H}_{43}\text{N}_4\text{O}_5\text{ClRh}_2][\text{CH}_3\text{OH}]_2$. 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}
Rh(1)	18(1)	21(1)	19(1)	-1(1)	-2(1)	0(1)
Rh(2)	18(1)	21(1)	17(1)	0(1)	-1(1)	1(1)
Cl(1)	30(1)	28(1)	42(1)	-9(1)	-2(1)	4(1)
C(1)	20(1)	25(2)	22(2)	3(2)	0(1)	-3(2)
N(1)	23(1)	21(2)	21(2)	1(1)	-2(1)	-1(1)
O(1)	26(1)	26(1)	21(1)	3(1)	4(1)	1(1)
C(2)	31(2)	30(2)	26(2)	4(2)	6(2)	-1(2)
C(3)	34(2)	44(2)	25(2)	3(2)	-2(2)	-11(2)
C(4)	35(2)	37(2)	33(2)	9(2)	-9(2)	-7(2)
C(5)	34(2)	34(2)	41(2)	9(2)	-2(2)	6(2)
C(6)	40(2)	24(2)	30(2)	3(2)	2(2)	-3(2)
C(7)	21(2)	24(2)	19(2)	2(1)	1(1)	-3(1)
N(7)	20(1)	23(2)	20(1)	-1(1)	-1(1)	-2(1)
O(7)	21(1)	25(1)	26(1)	-3(1)	0(1)	1(1)
C(8)	18(2)	32(2)	33(2)	-5(2)	0(1)	-3(2)
C(9)	25(2)	47(3)	29(2)	0(2)	-5(1)	-3(2)
C(10)	29(2)	51(3)	27(2)	-7(2)	-4(2)	-3(2)
C(11)	24(2)	49(3)	27(2)	-13(2)	1(2)	-4(2)
C(12)	21(2)	21(2)	31(2)	-5(2)	0(2)	-3(2)
C(13)	16(1)	27(2)	21(2)	-1(2)	-1(1)	0(2)
N(13)	24(1)	23(2)	18(1)	0(1)	-2(1)	0(1)
O(13)	25(1)	26(1)	21(1)	-1(1)	3(1)	2(1)
C(14)	25(2)	32(2)	19(2)	0(1)	2(1)	-1(2)
C(15)	37(2)	35(2)	14(2)	-1(2)	-1(2)	0(2)
C(16)	31(2)	42(2)	21(2)	4(2)	-9(2)	2(2)
C(17)	27(2)	35(2)	31(2)	5(2)	0(2)	5(2)
C(18)	32(2)	24(2)	22(2)	1(2)	1(2)	5(2)
C(19)	19(2)	28(2)	22(2)	1(1)	2(1)	-3(1)
N(19)	20(1)	23(2)	21(2)	-3(1)	-1(1)	-4(1)
O(19)	20(1)	26(1)	26(1)	-3(1)	-3(1)	1(1)
C(20)	19(2)	34(2)	33(2)	-6(2)	-1(1)	1(2)

C(21)	32(2)	45(2)	38(2)	2(2)	-15(2)	3(2)
C(22)	38(2)	65(3)	29(2)	-15(2)	-8(2)	-5(2)
C(23)	38(2)	47(3)	35(2)	-17(2)	6(2)	-5(2)
C(24)	23(2)	28(2)	35(2)	-6(2)	-5(2)	-2(2)
C(25)	34(2)	40(2)	28(2)	-4(2)	5(2)	7(2)
O(25)	28(1)	24(1)	19(1)	-1(1)	-1(1)	4(1)
C(31)	37(2)	52(3)	58(3)	-1(3)	6(2)	3(2)
O(31)	50(2)	54(2)	74(3)	-8(2)	-17(2)	19(2)
C(41)	32(2)	42(3)	47(3)	9(2)	-1(2)	-2(2)
O(41)	38(2)	37(2)	41(2)	11(1)	-12(1)	3(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for $[\text{C}_{25}\text{H}_{43}\text{N}_4\text{O}_5\text{ClRh}_2][\text{CH}_3\text{OH}]_2$.

	x	y	z	U(eq)
H(2A)	9750(40)	1300(20)	-500(30)	20(9)
H(2B)	9670(60)	2080(30)	-60(50)	45(13)
H(3A)	7830(50)	1770(20)	-2010(40)	27(10)
H(3B)	6750(40)	1380(20)	-1060(30)	19(8)
H(4A)	7300(50)	2850(20)	-1060(40)	19(9)
H(4B)	5710(70)	2560(30)	-1380(50)	68(17)
H(5A)	5520(50)	2230(20)	760(40)	22(10)
H(5B)	5900(60)	3140(30)	540(50)	58(15)
H(6A)	8510(50)	2830(20)	1350(40)	25(11)
H(6B)	7380(50)	2800(20)	2380(40)	27(10)
H(8A)	3010(50)	780(20)	1750(40)	32(12)
H(8B)	3250(40)	-38(19)	1850(30)	11(8)
H(9A)	2620(60)	520(20)	-320(40)	39(12)
H(9B)	4210(50)	720(20)	-360(40)	25(10)
H(10A)	4110(50)	-270(20)	-1590(40)	38(12)
H(10B)	3540(60)	-660(30)	-250(40)	40(12)
H(11A)	6310(50)	-950(20)	-310(40)	29(11)
H(11B)	6750(50)	-160(20)	-150(40)	35(12)
H(12A)	5320(40)	-820(20)	1810(30)	11(8)
H(12B)	7100(40)	-890(20)	1880(40)	16(9)
H(14A)	6880(40)	-390(20)	6990(30)	11(8)
H(14B)	6970(50)	350(20)	7340(40)	20(9)
H(15A)	9850(40)	469(19)	7590(30)	14(9)
H(15B)	8980(60)	40(30)	8650(50)	56(16)
H(16A)	10870(60)	-720(20)	8290(50)	39(12)
H(16B)	9410(60)	-1140(30)	7810(50)	58(15)
H(17A)	10930(40)	-1260(20)	6240(30)	14(8)
H(17B)	11120(50)	-420(20)	6040(40)	31(12)
H(18A)	8960(50)	-1040(20)	4390(40)	25(10)
H(18B)	8060(50)	-1030(20)	5560(40)	32(11)

H(20A)	13260(60)	1830(30)	4820(50)	48(14)
H(20B)	13520(50)	990(20)	4920(40)	20(10)
H(21A)	12440(60)	920(30)	6930(50)	47(13)
H(21B)	14290(50)	1290(20)	6990(40)	27(10)
H(22A)	12710(60)	2100(30)	8130(50)	47(13)
H(22B)	13200(50)	2460(30)	6990(40)	31(11)
H(23A)	10520(60)	2680(30)	7120(50)	43(13)
H(23B)	10210(50)	1990(20)	7110(40)	29(11)
H(24A)	9520(50)	2680(20)	5000(40)	35(12)
H(24B)	11370(50)	2580(20)	4900(40)	34(11)
H(25A)	9340(70)	-1100(30)	760(50)	65(16)
H(25B)	11060(60)	-1160(30)	1060(50)	58(15)
H(25C)	10270(50)	-400(20)	740(40)	32(11)
H(31A)	3050(80)	2210(40)	1940(60)	70(20)
H(31B)	2340(60)	2690(30)	1060(50)	56(15)
H(31C)	1690(60)	2500(30)	2380(50)	46(13)
H(31)	4289	3014	3152	90(20)
H(41A)	3890(80)	-220(40)	4290(70)	90(20)
H(41B)	5110(120)	-950(60)	4540(90)	170(40)
H(41C)	3920(70)	-740(30)	5520(60)	71(17)
H(41)	2943	-1530	4049	59(16)

Table 6. Hydrogen bonds for [C₂₅H₄₃N₄O₅ClRh₂][CH₃OH]₂ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(31)-H(31)...Cl(1)	0.84	2.31	3.149(4)	173.8
O(41)-H(41)...Cl(1)#1	0.84	2.28	3.083(3)	159.4

Symmetry transformations used to generate equivalent atoms:

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