Expanding the Scope of C–H Amination Through Catalyst Design

Supplementary Material

(14 pages)

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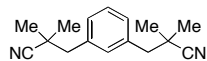
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General. All reagents were obtained commercially unless otherwise noted. Reactions were performed using oven-dried glassware under an atmosphere of dry nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated under reduced pressure (ca. 15 mm Hg) by rotary evaporation. Freshly distilled solvents were employed unless otherwise noted. Dichloromethane and tetrahydrofuran were dried by passage under 12 psi N_2 through activated alumina columns. 1,2-Dichloroethane was used as received.
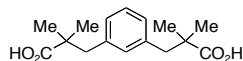
Preparation and oxidative cyclization of sulfamate ester substrates followed a previously published protocol.[1] The synthesis of 2,2,2-trichloroethylsulfamate was performed according to the literature report.[2] Chromatographic purification of products was accomplished using forced-flow chromatography on EM Science Geduran silica gel 60 (35–75 mm). Compounds purified by chromatography on silica gel were typically applied to the adsorbent bed in dichloromethane with a minimum amount of added methanol as needed for solubility. Thin layer chromatography was performed on EM Science silica gel 60 F_{254} plates (250 mm). Visualization of the developed chromatogram was accomplished by fluorescence quenching and by staining with ethanolic anisaldehyde, aqueous potassium permanganate, or aqueous ceric ammonium molybdate (CAM) solution.

Nuclear magnetic resonance (NMR) spectra were acquired on a Varian Mercury spectrometer operating at 400 and 100 MHz for ^{1}H and ^{13}C, respectively, or on a Varian Inova spectrometer operating at 500 and 125 MHz for ^{1}H and ^{13}C, respectively, and are referenced internally according to residual solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; br s, broad singlet; d, doublet; br d, broad doublet; t, triplet; q, quartet; quint, quintet; sept, septet; m, multiplet), integration, coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Infrared spectra were recorded on a Thermo Nicolet IR300 spectrometer and are reported in terms of frequency of absorption. Sample preparation was done either as a thin film on a NaCl salt plate or as a KBr pellet. High-resolution mass spectra were obtained from the Vincent Coates Foundation Mass Spectrometry Laboratory at Stanford University.

Experimental procedures and characterization data for Rh₂(esp)₂

α,α,α',α'-Tetramethyl-1,3-benzenedipropionitrile. *n*-Butyllithium (13.4 mL of a 2.5 M solution in hexanes, 33.5 mmol, 2.5 equiv) was added slowly to a solution of *i*-Pr$_2$NH (4.7 mL, 33.5 mmol, 2.5 equiv) in 16 mL of THF at 0 °C. The mixture was stirred for 20 min following which time isobutyronitrile (3.0 mL, 33.5 mmol, 2.5 equiv) was added dropwise via syringe. The reaction was stirred at 0 °C for 1.5 h. A solution of α,α'-dichloro-*m*-xylene (2.35 g, 13.4 mmol) in 9 mL of THF was then slowly cannulated into the reaction flask. The resulting orange, slightly turbid mixture was warmed to 23 °C and stirred for 10 h. The reaction was quenched with 50 mL of H$_2$O and transferred to a separatory funnel with 150 mL of EtOAc. The organic layer was collected, washed with 30 mL of saturated aqueous NaCl, dried over MgSO$_4$, and concentrated under reduced pressure. Purification of the oily residue by chromatography on silica gel (6:1 hexanes/EtOAc) yielded 2.4 g of the dinitrile product as a white solid (75%); TLC R_f = 0.18 (6:1 hexanes/EtOAc): ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.33–7.30 (m, 1H), 7.23–7.18 (m, 3H), 2.81 (s, 4H), 1.35 (s, 12H) ppm; ^{13}C NMR (CDCl$_3$, 100 MHz) δ 135.8, 132.1, 129.1, 128.4, 124.6, 46.4, 33.5, 26.4 ppm; IR (thin film) ν 2979, 2936, 2876, 2234, 1608, 1469, 1490, 1381, 1369, 1275, 1195, 807, 714 cm^{-1}.
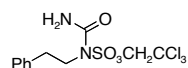

α,α,α',α'-Tetramethyl-1,3-benzenedipropionic acid. α,α,α',α'-Tetramethyl-1,3-benzenedipropionitrile (1.1 g, 4.58 mmol) and KOH (1.43 g, 25.4 mmol, 5.6 equiv) were combined in 6.3 mL of ethylene glycol. The flask was

equipped with a Vigreux column and the mixture was heated at 180 °C for 6 h. After cooling the reaction to 23 °C, the contents were partitioned between 12 mL of $CHCl_3$ and 12 mL of H_2O. The aqueous layer was collected, acidified with 8 mL of 6 M aqueous HCl, and extracted with 1 x 90 mL of EtOAc. The organic layer was washed successively with 2 x 30 mL of H_2O and 2 x 30 mL of saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. Recrystallization of the isolated material from hexanes/EtOAc afforded the desired diacid as a powdery solid (850 mg, 68%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 (t, 1H, J = 8.0 Hz), 7.03–7.00 (m, 3H), 2.85 (s, 4H), 1.17 (s, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.4, 137.3, 131.6, 128.7, 127.6, 45.9, 43.5, 24.4 ppm; IR (thin film) ν 2976, 2930, 2605, 1698, 1474, 1409, 1288, 1218, 1163, 1131, 944, 910, 734 cm^{-1}.

$Rh_2(esp)_2$. A variant of a protocol described by Taber and co-workers was employed.[3] A 15 mL thick-walled tube was charged with $Rh_2(O_2CCF_3)_4$ (297 mg, 0.45 mmol), α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid (26 mg, 92 µmol, 0.2 equiv), and 3.0 mL of 1,2-dichloroethane. The vessel was sealed with a screw–cap and immersed in an oil bath preheated to 125 °C (Note: For proper heating, the reaction flask should be immersed so that the oil level is at the height of the solvent line). At twenty minute intervals, the flask was removed from the heating bath and the contents slowly cooled (5 min) to 23 °C. The vessel was charged with 26 mg (0.2 equiv) of the diacid and sealed, and heating at 125 °C was resumed. This process was repeated an additional three times, following which the reaction was stirred at 125 °C for 5 h. Within this period, the reaction mixture slowly becomes turbid. A second equivalent of dicarboxylic acid was then introduced in a similar fashion (5 portions of 26 mg at 20 minute intervals). Once again, the mixture was stirred at 125 °C for an additional 5 h, during which time the reaction becomes homogenous. The deep green solution was cooled to 23 °C and the contents were applied directly to a column of silica gel (150 x 40 mm of SiO_2). Purification using gradient elution (15:1→10:1 hexanes/EtOAc) furnished $Rh_2(esp)_2$ as a green microcrystalline product (218 mg, 64%). The first product to elute from the silica gel column using 15:1 hexanes/EtOAc is unreacted $Rh_2(tfa)_4$ and the second is $Rh_2(esp)(tfa)_2$. The third-running green band constitutes the desired complex. Solid $Rh_2(esp)_2$ is sparingly soluble in CH_3CN. Crystals suitable for X-ray diffraction were obtained by slow evaporation of 1:1 CH_2Cl_2/acetone or 1:1 CH_2Cl_2/acetonitrile solutions of $Rh_2(esp)_2$. TLC R_f = 0.43 (20:1 CH_2Cl_2/EtOAc); ^{1}H NMR (CD_3CN, 400 MHz) δ 7.06 (t, 2H, J = 7.6 Hz), 6.88 (s, 2H), 6.83 (dd, 4H, J = 7.4, 1.6 Hz), 2.58 (s, 8H), 0.89 (s, 24H) ppm; IR (thin film) ν 3432, 1643, 1565, 1471, 1407, 1373 cm^{-1}; HRMS (ES$^+$) calcd for $C_{32}H_{40}O_8Rh_2$ 758.08 found 781.0731 (MNa$^+$).
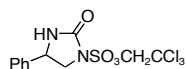
Experimental procedure and characterization data for urea and sulfamide reactions (Figure 4)

To a solution of substrate (0.3 mmol) in 2.0 mL of toluene were added sequentially MgO (28 mg, 0.69 mmol, 2.3 equiv), PhI(OAc)$_2$ (106 mg, 0.33 mmol, 1.1 equiv) and $Rh_2(esp)_2$ (2.3 mg, 3 µmol, 0.01 equiv). The resulting green solution was stirred and heated at 40 °C until TLC indicated no further progress in the reaction (~10 h). The reaction was cooled to 23 °C, diluted with 4 mL of CH_2Cl_2, and filtered through a pad of Celite (30 x 20 mm). The filter cake was rinsed with 2 x 5 mL of CH_2Cl_2 and the combined filtrates were evaporated under reduced pressure. Purification of the isolated material by chromatography on silica gel (conditions given below) afforded the desired product.

Purified by chromatography on silica gel (gradient elution: 10:1→6:1 hexanes/EtOAc) and recrystallized from hexanes/EtOAc; white solid (60%): TLC R_f = 0.4 (3:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.33 (m, 2H), 7.28-7.24 (1H, m), 7.22-7.19 (m, 2H), 7.02 (br s, 1H), 5.49 (br s, 1H), 4.63 (s, 2H), 4.48 (t, 2H, J = 6.8 Hz),

3.00 (t, 2H, J = 7.2 Hz) ppm; ^{13}C NMR (CDCl$_3$, 100 MHz) δ 160.4, 137.0, 129.1, 129.0, 127.2, 93.9, 78.7, 69.7, 35.0 ppm; IR (thin film) ν 3455, 3351, 1628, 1544, 1476, 1447, 1332, 1177, 1087, 1017, 853 cm^{-1}; HRMS (ES$^-$) calcd for C$_{11}$H$_{13}$Cl$_3$N$_2$O$_4$S 373.9662 found 372.9569 (M–H$^+$).

Purified by chromatography on silica gel (gradient elution: 5:1→2:1 hexanes/EtOAc); white solid (79%): TLC R$_f$ = 0.25 (3:1 hexanes/EtOAc); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.66 (br s, 1H), 7.47-7.41 (m, 3H), 7.33-7.31 (m, 2H), 5.21 (dd, 1H, J = 9.2, 7.2 Hz), 4.94 (t, 1H, J = 9.2 Hz), 4.73 (d, 1H, J = 10.8 Hz), 4.70 (d, 1H, J = 10.8 Hz), 4.42 (dd, 1H, J = 8.8, 6.8 Hz) ppm; ^{13}C NMR (CDCl$_3$, 100 MHz) δ 163.0, 137.0, 130.0, 129.7, 126.3, 93.8, 78.7, 74.7, 58.9 ppm; IR (thin film) ν 3384, 1628, 1480, 1460, 1440, 1342, 1177, 1101, 1017, 879 cm^{-1}; HRMS (ES$^-$) calcd for C$_{11}$H$_{11}$Cl$_3$N$_2$O$_4$S 371.9505 found 370.9411 (M–H$^+$).
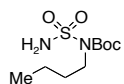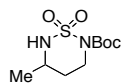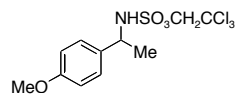

Purified by chromatography on silica gel (gradient elution: 10:1→5:1 hexanes/EtOAc) and recrystallized from hexanes/EtOAc; white solid (67%): TLC R$_f$ = 0.21 (3:1 hexanes/EtOAc); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.29 (br s, 2H), 3.67 (t, 2H, J = 7.2 Hz), 1.64-1.60 (m, 2H), 1.53 (s, 9H), 1.38-1.28 (m, 2H), 0.93 (t, 3H, J = 7.6 Hz) ppm; ^{13}C NMR (CDCl$_3$, 100 MHz) δ 152.5, 84.3, 47.5, 31.8, 28.2, 19.9, 13.8 ppm; IR (thin film) ν 3363, 3277, 2967, 2936, 2872, 1692, 1376, 1344, 1300, 1184, 1143 cm^{-1}; HRMS (ES$^-$) calcd for C$_9$H$_{20}$N$_2$O$_4$S 252.1144 found 251.1062 (M–H$^+$).

Purified by chromatography on silica gel (gradient elution: 6:1→3:1 hexanes/EtOAc); white solid (83%): TLC R$_f$ = 0.15 (3:1 hexanes/EtOAc); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 4.02 (dt, 1H, J = 13.6, 4.4 Hz), 3.57-3.47 (m, 1H), 3.40 (ddd, 1H, J = 12.0, 11.2, 3.2 Hz), 2.54 (s, 1H), 1.76 (dq, 1H, J = 14.0, 3.6 Hz), 1.48-1.31 (m, 1H), 1.36 (s, 9H), 1.11 (d, 3H, J = 6.4 Hz) ppm; ^{13}C NMR (CDCl$_3$, 100 MHz) δ 151.3, 83.3, 51.2, 45.7, 31.6, 27.5, 20.0 ppm; IR (thin film) ν 3254, 2980, 1721, 1427, 1301, 1257, 1152, 798 cm^{-1}; HRMS (ES$^-$) calcd for C$_9$H$_{18}$N$_2$O$_4$S 250.0987 found 249.0897 (M–H$^+$).

Experimental procedure and characterization data for intermolecular C–H amination reactions (Figure 5)

A flask containing 2,2,2-trichloroethylsulfamate (137 mg, 0.60 mmol) in 1.2 mL of C$_6$H$_6$ was charged with catalyst (12 μmol of either Rh$_2$(O$_2$C^{t}Bu)$_4$ or Rh$_2$(esp)$_2$) and substrate (1.0, 2.0, or 5.0 equiv). To this bright green mixture was added seven portions of PhI(OAc)$_2$ (290 mg, 0.90 mmol, 1.5 equiv) every ten minutes over the course of 1 h (7 portions of ~41 mg). During the addition of PhI(OAc)$_2$, a change in the reaction color to brown or red was generally observed. Following the transfer of oxidant, the contents were stirred at 23 °C until TLC indicated the complete consumption of starting material or no further progress in the reaction (1–8 h). All volatiles were then removed under reduced pressure and the isolated material was purified by chromatography on silica gel (conditions given below) to afford the desired product.

Purified by column chromatography on silica gel (9:1 hexanes/EtOAc); pale yellow oil: TLC R_f = 0.35 (4:1 hexanes/EtOAc); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.30-7.26 (m, 2H), 6.91-6.86 (m, 2H), 5.31 (br d, 1H, J = 5.2 Hz), 4.67 (quint, 1H, J = 6.9 Hz), 4.42 (d, 1H, J = 10.8 Hz), 4.38 (d, 1H, J = 10.8 Hz), 3.79 (s, 3H), 1.59 (d, 3H, J = 6.9 Hz) ppm; ^{13}C NMR (CDCl$_3$, 100 MHz) δ 159.3, 133.5, 127.5, 114.2, 93.3, 78.0, 55.3, 54.3, 22.7 ppm; IR (thin film) ν 3299, 2978, 2360, 1613, 1586, 1515, 1306, 1283, 1249, 1178, 1124, 1014, 977, 852, 833 cm^{-1}.
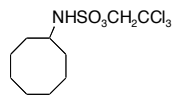

Purified by column chromatography on silica gel (gradient elution: 12:1→4:1 hexanes/EtOAc); white solid: TLC R_f = 0.49 (4:1 hexanes/EtOAc); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 4.62 (s, 2H), 4.54 (br d, 1H, J = 8.1 Hz), 3.74-3.65 (m, 1H), 2.04-1.96 (m, 2H), 1.74-1.64 (m, 4H), 1.63-1.48 (m, 8H) ppm; ^{13}C NMR (CDCl$_3$, 100 MHz) δ 93.5, 78.0, 55.6, 32.4, 27.1, 25.2, 23.1 ppm; IR (thin film) ν 3306, 2925, 2857, 1447, 1360, 1181, 1090, 1059, 1009, 960, 855 cm^{-1}; HRMS (ES$^+$) calcd for $C_{10}H_{18}Cl_3NO_3S$ 359.9971 found 359.9971 (M$^+$).

(1)   Espino, C. G.; Wehn, P. M.; Chow, J.; Du Bois, J. *J. Am. Chem. Soc.*, **2001**, *123*, 6935-6936.

(2)   Guthikonda, K.; Du Bois, J. *J. Am. Chem. Soc.*, **2002**, *124*, 13672-13673.

(3)   Taber, D. F.; Meagley, R. P.; Louey, J. P.; Rheingold, A. L. *Inorg. Chim. Acta*, **1995**, *239*, 25-28.

Crystallographic Data For $Rh_2(ESP)_2 \cdot (acetone)_2$

Experimental

Data Collection

A rod-shaped crystal of $C_{38}H_{52}O_{10}Rh_2$ having approximate dimensions of 0.16 x 0.09 x 0.09 mm was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a Siemens SMART-APEX[1] CCD area detector with monochromatic radiation of wavelength 0.71073 Å.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the measured positions of 2000 centered reflections with $I > 10\sigma(I)$ in the range $2.34° < \theta < 25.13°$, corresponded to a primitive triclinic cell with dimensions:

$$a = 9.731(4) \text{ Å} \qquad \alpha = 66.441(6)°$$
$$b = 9.878(4) \text{ Å} \qquad \beta = 84.297(7)°$$
$$c = 11.256(5) \text{ Å} \qquad \gamma = 73.066(7)°$$
$$V = 948.7(6) \text{ Å}^3$$

For $Z = 1$ and *F.W.* = 874.62, the calculated density is 1.531 g/cm^3.

Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P-1

The data were collected at a temperature of 159 K. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 10 seconds per frame.

Data Reduction

Data were integrated by the program SAINT[2] with box parameters of 1.6 x 1.6 x 1.0° to a maximum θ value of 26.41°. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient, μ, for 0.71073 Å radiation is 0.925 mm^{-1}. Data were analyzed for agreement and possible absorption using SADABS[3]. A semi-empirical absorption correction based on 2.04 reflections with $I > 5\sigma(I)$ was applied that resulted in normalized transmission factors ranging from 0.84 to 0.92. Of the 6182 reflections that were collected, 3767 were unique ($R_{int} = 0.0183$); equivalent reflections were merged. No decay correction was deemed necessary.

Structure Solution and Refinement

The structure was solved by direct methods (SIR-92)[4] and expanded using Fourier techniques[5]. All non-H atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located using the HFIX command (idealized positions via a riding refinement). A single torsional parameter about the H-C bond was refined in the case of methyl groups. The final cycle of full-matrix least-squares refinement[6] was based on 3767 reflections (all data) and 232 variable parameters and converged (largest parameter shift was 0.002 times its esd) with conventional unweighted and weighted agreement factors of:

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0268 \text{ for 3031 data with } F_o > 4\sigma(F_o)$$

$$wR_2 = [(\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^2)]^{1/2} = 0.0567$$

The standard deviation of an observation of unit weight (S)[7] was 0.947. Sheldrick weights[6] were used; where applicable, weights were refined to convergence. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.57 and -0.30 e$^-$/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[8]. Anomalous dispersion effects were included in Fcalc[9]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[10]. The values for the mass attenuation coefficients were those of Creagh and Hubbel[11]. All calculations were performed using the Crystal Structure[12] crystallographic software package.

References

(1) SMART: Area-Detector Software Package, Siemens Industrial Automation, Inc.: Madison, WI (1995).

(2) SAINT: SAX Area-Dectector Integration Program, V5.04; Siemens Industrial Automation, Inc.: Madison, WI, (1995)

(3) SADABS: Siemens Area Detector ABSorption correction program, George Sheldrick, (1996). Advance copy, private communication.

(4) SIR92: a program for automatic solution of crystal structures by direct methods. Altomare, A., Cascarano, G., Giacovazzo G., Guagliardi A., Burla M.C., Polidori, G. & Camalli, M. J. Appl. Cryst. (27), 435 (1994).

(5) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(6) Least-Squares:
$$\text{Function minimized: } \Sigma w \, (|F_o|^2 - |F_c|^2)^2$$
$$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2] \text{ where } P = (F_o^2 + 2F_c^2)/3$$

Sheldrick weights: G. M. Sheldrick (1997)

(7) Standard deviation of an observation of unit weight:

$$S = [\Sigma w \, (|F_o|^2 - |F_c|^2)^2/(N_o - N_v)]^{1/2}$$
$$\text{where: } N_o = \text{number of observations}$$
$$N_v = \text{number of variables}$$

(8) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(9) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(10) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(11) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(12) CrystalStructure 3.51: Crystal Structure Analysis Package, Rigaku and MSC (2000-3).

(13) CRYSTALS Issue 10: Watkin, D.J.; Prout, C.K.; Carruthers, J.R.; Betteridge, P.W. Chemical Crystallography Laboratory, Oxford, UK.

Experimental Details

A. Crystal Data

Empirical Formula	$C_{38}H_{52}O_{10}Rh_2$
Formula Weight	874.62
Crystal Color, Habit	unknown, rod
Crystal Dimensions	0.16 x 0.09 x 0.09 mm
Crystal System	triclinic
Lattice Type	primitive
Lattice Parameters	$a = 9.731(4)$ Å
	$b = 9.878(4)$ Å
	$c = 11.256(5)$ Å
	$\alpha = 66.441(6)°$
	$\beta = 84.297(7)°$
	$\gamma = 73.066(7)°$
	$V = 948.7(6)$ Å^3
Space Group	P-1
Z value	1
d_{calc}	1.531 g/cm^3
F_{000}	450
μ(0.71073 Å radiation)	0.93 cm^{-1}

B. Intensity Measurements

Diffractometer	Siemens SMART-APEX CCD
Radiation	$\lambda = 0.71073$ Å
	graphite monochromated
Exposure Time	10 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
θ_{max}	26.41°
Data Collection Temperature	159 K
No. of Reflections Measured	Total: 6182
	Unique: 3767 ($R_{int} = 0.0183$)
Corrections	Lorentz-polarization
	Absorption:
	$T_{max} = 0.92$
	$T_{min} = 0.84$

C. Structure Solution and Refinement

Structure Solution	Direct (SIR-92)
Refinement	Full-matrix least-squares (SHELXL-97)
Function Minimized	$\Sigma w(|F_o|^2 - |F_c|^2)^2$
Least Squares Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($F_o > 4\sigma(F_o)$)	3031
No. Variables	232
Reflection/Parameter Ratio	16.24
Residuals: R_1; wR_2	0.0268; 0.0567
Goodness of Fit Indicator (S)	0.947
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	0.57 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.30e$^-$/Å^3

Table 1a. Atomic coordinates, U_{iso}/U_{eq}, and occupancy

atom	x	y	z	U_{eq}	occ
Rh1	0.0302(1)	0.1029(1)	1.0111(1)	0.017(1)	1
O1	0.2035(2)	0.0663(2)	0.8986(2)	0.021(1)	1
O2	-0.0977(2)	0.2492(2)	0.8513(2)	0.022(1)	1
O3	-0.1451(2)	0.1270(2)	1.1238(2)	0.022(1)	1
O4	0.1523(2)	-0.0528(2)	1.1693(2)	0.021(1)	1
O5	0.0934(2)	0.2865(2)	1.0540(2)	0.027(1)	1
C1	0.2241(3)	-0.0390(3)	0.8558(2)	0.021(1)	1
C2	0.3586(3)	-0.0605(3)	0.7753(3)	0.026(1)	1
C3	0.4888(3)	-0.0955(3)	0.8600(3)	0.033(1)	1
C4	0.3737(3)	-0.1921(3)	0.7316(3)	0.037(1)	1
C5	0.3497(3)	0.0929(3)	0.6558(3)	0.029(1)	1
C6	0.2152(3)	0.1557(3)	0.5725(3)	0.029(1)	1
C7	0.2095(3)	0.1212(4)	0.4649(3)	0.037(1)	1
C8	0.0824(4)	0.1737(4)	0.3957(3)	0.046(1)	1
C9	-0.0403(3)	0.2654(4)	0.4297(3)	0.038(1)	1
C10	-0.0359(3)	0.3043(3)	0.5331(3)	0.030(1)	1
C11	0.0931(3)	0.2495(3)	0.6031(3)	0.028(1)	1
C12	-0.1666(3)	0.4024(3)	0.5751(3)	0.032(1)	1
C13	-0.2577(3)	0.3081(3)	0.6779(3)	0.026(1)	1
C14	-0.3238(3)	0.2244(3)	0.6219(3)	0.034(1)	1
C15	-0.3770(3)	0.4183(3)	0.7221(3)	0.040(1)	1
C16	-0.1614(3)	0.1934(3)	0.7960(2)	0.020(1)	1
C17	0.1655(3)	0.3732(3)	0.9987(3)	0.030(1)	1
C18	0.2072(4)	0.4040(4)	0.8613(3)	0.052(1)	1
C19	0.2157(3)	0.4545(4)	1.0648(4)	0.048(1)	1
H3A	0.4791	-0.0118	0.8861	0.050	1
H3B	0.5750	-0.1084	0.8113	0.050	1
H3C	0.4939	-0.1881	0.9354	0.050	1
H4A	0.3808	-0.2859	0.8063	0.056	1
H4B	0.4586	-0.2028	0.6811	0.056	1
H4C	0.2910	-0.1701	0.6800	0.056	1
H5A	0.3563	0.1697	0.6864	0.035	1
H5B	0.4323	0.0769	0.6021	0.035	1
H7	0.2914	0.0628	0.4398	0.045	1
H8	0.0783	0.1478	0.3255	0.055	1
H9	-0.1253	0.3002	0.3821	0.045	1
H11	0.0972	0.2767	0.6725	0.033	1
H12A	-0.2270	0.4725	0.4994	0.038	1
H12B	-0.1349	0.4635	0.6102	0.038	1
H14A	-0.2489	0.1559	0.5943	0.051	1
H14B	-0.3849	0.2977	0.5490	0.051	1
H14C	-0.3794	0.1666	0.6869	0.051	1
H15A	-0.4313	0.3606	0.7888	0.059	1
H15B	-0.4395	0.4902	0.6498	0.059	1
H15C	-0.3348	0.4728	0.7555	0.059	1
H18A	0.2684	0.3114	0.8552	0.078	1
H18B	0.2576	0.4817	0.8318	0.078	1
H18C	0.1225	0.4389	0.8083	0.078	1
H19A	0.1824	0.4250	1.1523	0.072	1
H19B	0.1783	0.5634	1.0192	0.072	1

H19C	0.3188	0.4274	1.0655	0.072	1

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor

Table 2a. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh1	0.017(1)	0.016(1)	0.020(1)	-0.008(1)	0.000(1)	-0.006(1)
O1	0.022(1)	0.021(1)	0.025(1)	-0.012(1)	0.004(1)	-0.007(1)
O2	0.021(1)	0.020(1)	0.024(1)	-0.007(1)	-0.004(1)	-0.006(1)
O3	0.020(1)	0.024(1)	0.027(1)	-0.014(1)	0.004(1)	-0.009(1)
O4	0.024(1)	0.020(1)	0.021(1)	-0.008(1)	-0.003(1)	-0.008(1)
O5	0.026(1)	0.025(1)	0.037(1)	-0.017(1)	0.002(1)	-0.010(1)
C1	0.018(1)	0.025(1)	0.017(1)	-0.006(1)	-0.001(1)	-0.004(1)
C2	0.021(2)	0.030(1)	0.029(2)	-0.014(1)	0.007(1)	-0.008(1)
C3	0.022(2)	0.038(2)	0.037(2)	-0.015(1)	0.004(1)	-0.005(1)
C4	0.036(2)	0.039(2)	0.046(2)	-0.027(2)	0.016(2)	-0.013(1)
C5	0.028(2)	0.037(2)	0.029(2)	-0.016(1)	0.009(1)	-0.017(1)
C6	0.032(2)	0.034(2)	0.022(2)	-0.007(1)	0.005(1)	-0.021(1)
C7	0.035(2)	0.054(2)	0.032(2)	-0.022(2)	0.007(2)	-0.019(2)
C8	0.057(2)	0.070(2)	0.021(2)	-0.020(2)	0.005(2)	-0.031(2)
C9	0.040(2)	0.052(2)	0.021(2)	-0.005(2)	-0.008(2)	-0.022(2)
C10	0.033(2)	0.029(1)	0.023(2)	0.003(1)	0.000(1)	-0.019(1)
C11	0.033(2)	0.028(1)	0.022(2)	-0.004(1)	-0.001(1)	-0.017(1)
C12	0.033(2)	0.025(1)	0.029(2)	0.002(1)	-0.012(1)	-0.011(1)
C13	0.023(2)	0.026(1)	0.027(2)	-0.005(1)	-0.005(1)	-0.008(1)
C14	0.032(2)	0.038(2)	0.030(2)	-0.004(1)	-0.009(1)	-0.017(1)
C15	0.030(2)	0.035(2)	0.044(2)	-0.011(2)	-0.011(2)	0.002(1)
C16	0.014(1)	0.023(1)	0.020(2)	-0.007(1)	0.002(1)	-0.004(1)
C17	0.021(2)	0.020(1)	0.048(2)	-0.015(1)	-0.006(1)	0.001(1)
C18	0.068(3)	0.047(2)	0.043(2)	-0.006(2)	0.004(2)	-0.037(2)
C19	0.032(2)	0.043(2)	0.087(3)	-0.043(2)	-0.001(2)	-0.011(2)

The general temperature factor expression: $\exp(-2p^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*$

Table 3a. Bond Lengths (Å)

atom	atom	distance	atom	atom	distance
Rh1	O4	2.0286(18)	C8	C9	1.396(4)
Rh1	O3	2.0374(18)	C8	H8	0.9300
Rh1	O1	2.0403(18)	C9	C10	1.371(4)
Rh1	O2	2.0484(18)	C9	C10	1.371(4)
Rh1	O5	2.3042(19)	C9	H9	0.9300
Rh1	Rh1¹	2.3817(9)	C10	C11	1.396(4)
O1	C1	1.271(3)	C10	C12	1.520(4)
O2	C16	1.274(3)	C11	H11	0.9300
O3	C1¹	1.263(3)	C12	C13	1.552(4)
O4	C16¹	1.261(3)	C12	H12A	0.9700
O5	C17	1.204(3)	C12	H12B	0.9700
C1	O3¹	1.263(3)	C13	C14	1.517(4)
C1	C2	1.528(3)	C13	C16	1.534(3)
C2	C4	1.529(4)	C13	C15	1.537(4)

C2	C3	1.535(4)		C14	H14A	0.9600
C2	C5	1.559(4)		C14	H14B	0.9600
C3	H3A	0.9600		C14	H14C	0.9600
C3	H3B	0.9600		C15	H15A	0.9600
C3	H3C	0.9600		C15	H15B	0.9600
C4	H4A	0.9600		C15	H15C	0.9600
C4	H4B	0.9600		C16	O4[1]	1.261(3)
C4	H4C	0.9600		C17	C19	1.489(4)
C5	C6	1.512(4)		C17	C18	1.490(4)
C5	H5A	0.9700		C18	H18A	0.9600
C5	H5B	0.9700		C18	H18B	0.9600
C6	C11	1.386(4)		C18	H18C	0.9600
C6	C7	1.392(4)		C19	H19A	0.9600
C7	C8	1.379(4)		C19	H19B	0.9600
C7	H7	0.9300		C19	H19C	0.9600

Symmetry transformations used to generate equivalent atoms: [1] -x,-y,-z+2

Table 4a. Bond Angles (º)

atom	atom	atom	angle	atom	atom	atom	angle
O4	Rh1	O3	90.70(7)	C7	C8	H8	119.6
O4	Rh1	O1	88.69(7)	C9	C8	H8	119.6
O3	Rh1	O1	176.37(7)	C10	C9	C8	120.2(3)
O4	Rh1	O2	176.38(6)	C10	C9	H9	119.9
O3	Rh1	O2	88.74(7)	C8	C9	H9	119.9
O1	Rh1	O2	91.64(8)	C9	C10	C11	118.5(3)
O4	Rh1	O5	86.17(7)	C9	C10	C12	122.4(3)
O3	Rh1	O5	88.80(7)	C11	C10	C12	119.1(3)
O1	Rh1	O5	94.73(7)	C6	C11	C10	122.1(3)
O2	Rh1	O5	97.39(7)	C6	C11	H11	119.0
O4	Rh1	Rh1[1]	88.64(5)	C10	C11	H11	119.0
O3	Rh1	Rh1[1]	89.00(5)	C10	C12	C13	113.8(2)
O1	Rh1	Rh1[1]	87.41(5)	C10	C12	H12A	108.8
O2	Rh1	Rh1[1]	87.78(5)	C13	C12	H12A	108.8
O5	Rh1	Rh1[1]	174.34(5)	C10	C12	H12B	108.8
C1	O1	Rh1	119.65(16)	C13	C12	H12B	108.8
C16	O2	Rh1	118.84(15)	H12A	C12	H12B	107.7
C1[1]	O3	Rh1	118.28(16)	C14	C13	C16	110.5(2)
C16[1]	O4	Rh1	119.21(16)	C14	C13	C15	109.8(2)
C17	O5	Rh1	133.7(2)	C16	C13	C15	108.1(2)
O3[1]	C1	O1	125.7(2)	C14	C13	C12	110.7(2)
O3[1]	C1	C2	118.4(2)	C16	C13	C12	108.9(2)
O1	C1	C2	115.9(2)	C15	C13	C12	108.8(2)
C1	C2	C4	111.2(2)	C13	C14	H14A	109.5
C1	C2	C3	107.7(2)	C13	C14	H14B	109.5
C4	C2	C3	110.0(2)	H14A	C14	H14B	109.5
C1	C2	C5	108.7(2)	C13	C14	H14C	109.5
C4	C2	C5	110.6(2)	H14A	C14	H14C	109.5
C3	C2	C5	108.6(2)	H14B	C14	H14C	109.5
C2	C3	H3A	109.5	C13	C15	H15A	109.5
C2	C3	H3B	109.5	C13	C15	H15B	109.5
H3A	C3	H3B	109.5	H15A	C15	H15B	109.5

atom	atom	atom	angle		atom	atom	atom	angle
C2	C3	H3C	109.5		C13	C15	H15C	109.5
H3A	C3	H3C	109.5		H15A	C15	H15C	109.5
H3B	C3	H3C	109.5		H15B	C15	H15C	109.5
C2	C4	H4A	109.5		O4¹	C16	O2	125.5(2)
C2	C4	H4B	109.5		O4¹	C16	C13	117.7(2)
H4A	C4	H4B	109.5		O2	C16	C13	116.8(2)
C2	C4	H4C	109.5		O5	C17	C19	121.2(3)
H4A	C4	H4C	109.5		O5	C17	C18	121.4(3)
H4B	C4	H4C	109.5		C19	C17	C18	117.4(3)
C6	C5	C2	115.2(2)		C17	C18	H18A	109.5
C6	C5	H5A	108.5		C17	C18	H18B	109.5
C2	C5	H5A	108.5		H18A	C18	H18B	109.5
C6	C5	H5B	108.5		C17	C18	H18C	109.5
C2	C5	H5B	108.5		H18A	C18	H18C	109.5
H5A	C5	H5B	107.5		H18B	C18	H18C	109.5
C11	C6	C7	118.4(3)		C17	C19	H19A	109.5
C11	C6	C5	119.9(3)		C17	C19	H19B	109.5
C7	C6	C5	121.7(3)		H19A	C19	H19B	109.5
C8	C7	C6	119.9(3)		C17	C19	H19C	109.5
C8	C7	H7	120.0		H19A	C19	H19C	109.5
C6	C7	H7	120.0		H19B	C19	H19C	109.5
C7	C8	C9	120.8(3)					

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

Table 5a. Torsion Angles (º)

atom	atom	atom	atom	angle		atom	atom	atom	atom	angle
O4	Rh1	O1	C1	89.08(18)		O3	Rh1	O1	C1	8.6(13)
O2	Rh1	O1	C1	-87.31(18)		O5	Rh1	O1	C1	175.13(18)
Rh1¹	Rh1	O1	C1	0.39(17)		O4	Rh1	O2	C16	-8.1(12)
O3	Rh1	O2	C16	-89.28(17)		O1	Rh1	O2	C16	87.11(17)
O5	Rh1	O2	C16	-177.91(17)		Rh1¹	Rh1	O2	C16	-0.23(17)
O4	Rh1	O3	C1¹	-89.46(18)		O1	Rh1	O3	C1¹	-9.0(13)
O2	Rh1	O3	C1¹	86.96(18)		O5	Rh1	O3	C1¹	-175.62(18)
Rh1¹	Rh1	O3	C1¹	-0.84(17)		O3	Rh1	O4	C16¹	89.93(18)
O1	Rh1	O4	C16¹	-86.49(18)		O2	Rh1	O4	C16¹	8.8(12)
O5	Rh1	O4	C16¹	178.67(18)		Rh1¹	Rh1	O4	C16¹	0.94(17)
O4	Rh1	O5	C17	112.7(2)		O3	Rh1	O5	C17	-156.5(2)
O1	Rh1	O5	C17	24.4(3)		O2	Rh1	O5	C17	-67.9(3)
Rh1¹	Rh1	O5	C17	136.4(4)		Rh1	O1	C1	O3¹	0.2(3)
Rh1	O1	C1	C2	-178.53(16)		O3¹	C1	C2	C4	0.0(3)
O1	C1	C2	C4	178.8(2)		O3¹	C1	C2	C3	-120.6(3)
O1	C1	C2	C3	58.2(3)		O3¹	C1	C2	C5	122.0(2)
O1	C1	C2	C5	-59.2(3)		C1	C2	C5	C6	-54.8(3)
C4	C2	C5	C6	67.6(3)		C3	C2	C5	C6	-171.6(2)
C2	C5	C6	C11	86.7(3)		C2	C5	C6	C7	-92.9(3)
C11	C6	C7	C8	-3.2(4)		C5	C6	C7	C8	176.4(3)
C6	C7	C8	C9	1.9(5)		C7	C8	C9	C10	-0.1(5)
C8	C9	C10	C11	-0.4(4)		C8	C9	C10	C12	-179.4(2)
C7	C6	C11	C10	2.8(4)		C5	C6	C11	C10	-176.8(2)
C9	C10	C11	C6	-1.0(4)		C12	C10	C11	C6	178.0(2)
C9	C10	C12	C13	91.0(3)		C11	C10	C12	C13	-88.0(3)

C10	C12	C13	C14	-64.9(3)	C10	C12	C13	C16	56.8(3)
C10	C12	C13	C15	174.4(2)	Rh1	O2	C16	O4[1]	-0.5(3)
Rh1	O2	C16	C13	179.11(16)	C14	C13	C16	O4[1]	-1.3(3)
C15	C13	C16	O4[1]	118.9(2)	C12	C13	C16	O4[1]	-123.0(2)
C14	C13	C16	O2	179.1(2)	C15	C13	C16	O2	-60.7(3)
C12	C13	C16	O2	57.3(3)	Rh1	O5	C17	C19	-165.48(19)
Rh1	O5	C17	C18	14.8(4)					

Symmetry transformations used to generate equivalent atoms: [1] -x,-y,-z+2