Chiral Phosphine–Olefin Ligands in the Rhodium-Catalyzed Asymmetric 1,4-Addition Reactions

Wei-Liang Duan, Hiroshi Iwamura, Ryo Shintani,* and Tamio Hayashi*

Department of Chemistry, Graduate School of Science, Kyoto University,
Sakyo, Kyoto 606-8502, Japan

and

Mitsubishi Pharma Corporation, Kamisu, Ibaraki 314-0255, Japan

Supporting Information

I. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon.

1,4-Dioxane was distilled over benzophenone ketyl under nitrogen. A mixture of 1,4-dioxane and H₂O was degassed by bubbling nitrogen gas prior to use. Methyl vinyl ketone and 2-cyclohexen-1-one were distilled over CaCl₂ under vacuum. Phenylboroxine was prepared following the literature procedure.¹

II. Experimental Procedure for Kinetic Studies Using Reaction Calorimetry

Reactions were performed in an Omnical SuperCRC reaction calorimeter. The instrument contains a differential scanning calorimeter (DSC), which compares the heat released or consumed in a sample vessel to a reference vessel. The reaction vessels were 16 mL borosilicate screw-thread vials fit with opentop black phenolic screw caps and white PTFE septa charged with Teflon stir bars. Sample volumes did not exceed 3.5 mL. In a typical calorimetry experiment, a reaction vessel containing a

¹ (a) Chen, F.-X.; Kina, A.; Hayashi, T. *Org. Lett.* **2006**, *8*, 341. (b) Hayashi, T.; Takahashi, M.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **2002**, *124*, 5052.

solution of rhodium complex **6** (4.2 mg, 9.0 μmol) in 1,4-dioxane (2.0 mL) and H_2O (0.20 mL) was placed in the calorimeter and stirred for over 30 min, allowing the contents of the vessel to reach thermal equilibrium. The vessel containing the same amount of 1,4-dioxane (2.0 mL) and H_2O (0.20 mL) was prepared as a reference vessel. A syringe containing a solution of phenylboroxine **13** (23.4 mg, 0.225 mmol PhBO) and methyl vinyl ketone **14** (56.2 μL , 0.675 mmol) in 1,4-dioxane (1.0 mL) and H_2O (0.10 mL) was placed in the sample injection port of the calorimeter for the reaction vessel and a syringe containing the same chemical was placed in the sample injection port of the calorimeter for the reference vessel. These two syringes were allowed to thermally equilibrate. The reaction was initiated by injecting the solution of phenylboroxine and methyl vinyl ketone into the reaction and the reference vessels at the same time. The temperature of the DSC was held constant at 30 $^{\circ}\text{C}$ using Titec CL-150F (water circulator), ensuring that the reaction would proceed under isothermal conditions. A raw data curve was produced by measuring the heat flow from the sample vessel every 3 seconds during the reaction. Due to the delay between the instantaneous moment heat is evolved from the reaction vessel and the time the thermophile sensor detects the heat flow, the raw data curve must be calibrated. To accomplish this calibration, a constant amount of current was passed through a resistor in the sample chamber of the calorimeter thereby producing a known quantity of heat. This process results in a response curve, which is then transformed into a square wave allowing for the response time of the instrument to be calculated using the WinCRC software. Application of the response time to the raw data results in a “tau corrected data curve.” The tau corrected data curve is a plot of heat flow (mJ/s) versus time. The reaction rate, which is directly proportional to the heat flow (eq S1), fraction conversion (eq S2) and instantaneous concentrations of reactants/products can all be calculated from this tau corrected data curve.

$$q = \Delta H_{\text{rxn}} \cdot V \cdot v \quad (\text{S1})$$

q is the reaction heat flow, ΔH_{rxn} is the heat of reaction, V is the reaction volume, and v is the reaction rate. The heat of reaction from integration of the observed heat flow versus time curves gave an average value of $178 \pm 3 \text{ kJ/mol}$.

$$\text{conversion} = \frac{\int_0^t q(t) dt}{\int_0^{if} q(t) dt} \quad (\text{S2})$$

The numerator represents the area under the heat flow to any time point t and

the denominator represents the total area under the heat flow curve.

III. Kinetic Model for α,β -Unsaturated Ketones with Rh/(7S)-1a Catalyst

Because $k_2[14]$ is much larger than $k_1[13]$, the reaction rate is given by:

$$v = k_1[13][16] \quad (S3)$$

The concentration of each catalyst species is related by a material balance on the total amount of rhodium concentration:

$$[\text{Rh}]_{\text{total}} = 3[6] + [16] \quad (S4)$$

The equilibrium constant K_{trimer} is defined as association constant rather than as dissociation constant:

$$K_{\text{trimer}} = \frac{[6]}{[16]^3} \quad (S5)$$

$$[6] = K_{\text{trimer}}[16]^3 \quad (S6)$$

substituting for [6] in the eq S4:

$$[\text{Rh}]_{\text{total}} = 3K_{\text{trimer}}[16]^3 + [16] \quad (S7)$$

$$[16] = \frac{[\text{Rh}]_{\text{total}}^{1/3}}{(6K_{\text{trimer}})^{1/3}} \left\{ (1 + A)^{1/3} + (1 - A)^{1/3} \right\} \quad (S8)$$

$$A = \left(1 + \frac{4}{81K_{\text{trimer}}[\text{Rh}]_{\text{total}}^2} \right)^{1/2}$$

under our experimental conditions, $A \approx 1$:

$$[16] = \frac{[\text{Rh}]_{\text{total}}^{1/3}}{(3K_{\text{trimer}})^{1/3}} \quad (S9)$$

substituting for [16] in the eq S3:

$$v = \frac{k_1[13][\text{Rh}]_{\text{total}}^{1/3}}{(3K_{\text{trimer}})^{1/3}} \quad (S10)$$

IV. Kinetic Studies for the Reaction of Phenylboronic Acid (**13**) to Methyl Vinyl Ketone (**14**) in the Presence of Complex **6** at 30 °C

The kinetic behavior was analyzed by using the method of ["excess"] relationship and graphical rate equation developed by Blackmond.² The term ["excess"], which is defined as the concentration difference between the two reaction components, allows us to relate the concentrations of two reaction substrates at any point during the kinetic measurement. The detailed treatments of the data and the rate law of the reactions are similar to those reported in our previous kinetic studies.³

(1) Same ["excess"]

Figure S1. Reaction conditions: 1,4-dioxane = 3.0 mL, H₂O = 0.30 mL, [6]₀ = 2.7 mM Rh at 30 °C.

a, —: [13]₀ = 67 mM, [14]₀ = 201 mM (["excess"] = 134 mM).

b, ---: [13]₀ = 80 mM, [14]₀ = 214 mM (["excess"] = 134 mM).

² (a) Blackmond, D. G. *Angew. Chem., Int. Ed.* **2005**, 44, 4302. (b) Mathew, J. S.; Klusmann, M.; Iwamura, H.; Valera, F.; Futran, A.; Emanuelsson, E. A. C.; Blackmond, D. G. *J. Org. Chem.* **2006**, 71, 4711. (c) Rosner, T.; Le Bars, J.; Pfaltz, A.; Blackmond, D. G. *J. Am. Chem. Soc.* **2001**, 123, 1848. (d) Singh, U. K.; Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Soc. Chem.* **2002**, 124, 14104. (e) Mathew, S. P.; Gunathilagan, S.; Roberts, S. M.; Blackmond, D. G. *Org. Lett.* **2005**, 7, 4847.

³ Kina, A.; Iwamura, H.; Hayashi, T. *J. Am. Chem. Soc.* **2006**, 128, 3904.

The two curves overlay exactly one another except during the induction period, which shows that neither catalyst deactivation nor product inhibition takes place during the reaction.

(2) Different ["excess"]

Figure S2. Reaction conditions: 1,4-dioxane = 3.0 mL, H₂O = 0.30 mL, [6]₀ = 2.7 mM Rh at 30 °C.

a, - - : [13]₀ = 67 mM, [14]₀ = 201 mM, (["excess"] = 134 mM).

c, - - : [13]₀ = 67 mM, [14]₀ = 101 mM, (["excess"] = 34 mM).

d, - - : [13]₀ = 85 mM, [14]₀ = 201 mM, (["excess"] = 116 mM).

Plotting the graphical rate equation of rate versus [13] for these reactions carried out at two different ["excess"] values (a and b) gives first-order relationship for rate versus [13]. The curves a and c overlay, which indicates that the reaction follows zero-order kinetics in [14].

(3) Order in $[\text{Rh}]_{\text{total}}$

Figure S3. Reaction conditions: 1,4-dioxane = 3.0 mL, H_2O = 0.30 mL at 30 °C.

a, --: $[\text{13}]_0 = 67 \text{ mM}$, $[\text{14}]_0 = 201 \text{ mM}$, $[\text{6}]_0 = 2.7 \text{ mM Rh}$.

e, --: $[\text{13}]_0 = 67 \text{ mM}$, $[\text{14}]_0 = 201 \text{ mM}$, $[\text{6}]_0 = 3.8 \text{ mM Rh}$.

The relationship is much clearer in the right graph, which is plotted rate divided by $[\text{Rh}]_{\text{total}}^{0.4}$ versus $[\text{13}]$. Therefore, the reaction follows 0.4-order kinetics in $[\text{Rh}]_{\text{total}}$ at these rhodium concentrations.

(4) Fitting rate expression to the experimental data

Figure S4. Fitting eq S10 to the experimental data.

Kinetic modeling of the data to fit the proposed rate expression (eq S10) was carried out using the Excel Solver program with $K_{\text{trimer}} = 9 \times 10^5 \text{ M}^{-2}$, which was obtained from the nonlinear effect experiments (vide infra). Only data collected between 50–80% conversion were used in modeling because of the presence of the induction period. Solid lines represent the calculated rates given in eq S10. These data gave good fits with $k_1 = 5 \text{ M}^{-1}\text{s}^{-1}$.

V. Nonlinear Effect Analysis

(1) Experimental details and the results

The reactions were carried out with 2-cyclohexen-1-one (**S1**) instead of methyl vinyl ketone (**14**), and a 1,4-dioxane solution of $\text{Rh}_3\text{O}_2\text{H}((7S)\text{-1a})_3$ ((SSS)-**6**) and $\text{Rh}_3\text{O}_2\text{H}((7R)\text{-1a})_3$ ((RRR)-**6**) in a given ratio was used as a catalyst solution. The reaction was initiated by injecting the solution of 2-cyclohexen-1-one and phenylboroxine to the solution of catalyst **6**. The enantiomeric purity of the product, (*R*)-3-phenylcyclohexanone (**S2**), was determined by the HPLC analysis with a chiral column (Daicel Chiralcel OD-H, hexane/2-propanol = 98/2, 0.50 mL/min flow).

Reaction conditions: $[\text{13}]_0 = 67 \text{ mM}$, $[\text{S1}]_0 = 201 \text{ mM}$, 1,4-dioxane = 3.0 mL, $\text{H}_2\text{O} = 0.30 \text{ mL}$, $[\text{6}]_0 = 2.7 \text{ mM Rh}$ at 30°C .

- 1: $\text{ee}_{\text{cat}} = 20\% \text{ ee}$; $\text{ee}_{\text{prod}} = 9\% \text{ ee}$, $v_{\text{ee}}/v_{100\% \text{ ee}} = 1.44$.
- 2: $\text{ee}_{\text{cat}} = 40\% \text{ ee}$; $\text{ee}_{\text{prod}} = 21\% \text{ ee}$, $v_{\text{ee}}/v_{100\% \text{ ee}} = 1.42$.
- 3: $\text{ee}_{\text{cat}} = 60\% \text{ ee}$; $\text{ee}_{\text{prod}} = 32\% \text{ ee}$, $v_{\text{ee}}/v_{100\% \text{ ee}} = 1.34$.
- 4: $\text{ee}_{\text{cat}} = 80\% \text{ ee}$; $\text{ee}_{\text{prod}} = 52\% \text{ ee}$, $v_{\text{ee}}/v_{100\% \text{ ee}} = 1.24$.
- 5: $\text{ee}_{\text{cat}} = 100\% \text{ ee}$; $\text{ee}_{\text{prod}} = 93\% \text{ ee}$, $v_{\text{ee}}/v_{100\% \text{ ee}} = 1.00$.

(2) Mathematical treatment

The enantioselectivity of the reaction and the reaction rate were treated mathematically according to the references.⁴ We assume that the monomeric rhodium species *S*-16 and *R*-16 give identical reaction rate and the opposite enantioselectivities as active species. The enantiomeric purity of the product ee_{prod} and the rate v_{ee} of the reaction with non-enantiopure catalyst may be calculated by the concentrations of monomers, [*S*-16] and [*R*-16], where $ee_{100\%ee}$ (93% *ee*) and $v_{100\%ee}$ are the enantioselectivity and the rate of the reaction with the enantiopure catalyst *SSS*-6, respectively:

$$ee_{\text{prod}} = ee_{100\%} \frac{[S-16] - [R-16]}{[S-16] + [R-16]} \quad (\text{S11})$$

$$\frac{v_{ee}}{v_{100\%ee}} = \frac{[S-16] + [R-16]}{[S-16]_{100\%ee}} \quad (\text{S12})$$

³¹P NMR of the non-enantiopure **6** complex showed only one doublet at δ 73.4 ppm ($J_{\text{PRh}} = 210$ Hz), which is the same as that of enantiopure complex **6**, indicating that the homochiral trimers are overwhelmingly more stable than the heterochiral trimers. The formation of heterochiral trimers is considered to be negligible:

$$K_{\text{hetero}} = 0 \quad (\text{S13})$$

Then, the total *R* or *S* catalyst concentrations are given by:

$$\begin{aligned} [S]_{\text{total}} &= 3[SSS-6] + [S-16] \\ [R]_{\text{total}} &= 3[RRR-6] + [R-16] \end{aligned} \quad (\text{S14})$$

The overall catalyst *ee* based on total ligand concentrations is given by:

$$ee_{\text{cat}} = \frac{[S]_{\text{total}} - [R]_{\text{total}}}{[S]_{\text{total}} + [R]_{\text{total}}} \quad (\text{S15})$$

The monomer and trimer concentrations are related through K_{trimer} :

⁴ (a) Kitamura, M.; Okada, S.; Suga, S.; Noyori, R. *J. Am. Chem. Soc.* **1989**, *111*, 4028. (b) Kitamura, M.; Suga, S.; Oka, H.; Noyori, R. *J. Am. Chem. Soc.* **1998**, *120*, 9800. (c) Blackmond, D. G. *Acc. Chem. Res.* **2000**, *33*, 402.

$$K_{\text{trimer}} = \frac{[\text{SSS-6}]}{[\text{S-16}]^3} = \frac{[\text{RRR-6}]}{[\text{R-16}]^3} \quad (\text{S16})$$

The concentrations of monomeric active species **S-16** and **R-16** can be derived from eqs S14 and S16:

$$[\text{S-16}] = \left[\frac{[\text{S}]_{\text{total}}}{6K_{\text{trimer}}} + \left\{ \left(\frac{[\text{S}]_{\text{total}}}{6K_{\text{trimer}}} \right)^2 + \left(\frac{1}{9K_{\text{trimer}}} \right)^3 \right\}^{1/2} \right]^{1/3} + \left[\frac{[\text{S}]_{\text{total}}}{6K_{\text{trimer}}} - \left\{ \left(\frac{[\text{S}]_{\text{total}}}{6K_{\text{trimer}}} \right)^2 + \left(\frac{1}{9K_{\text{trimer}}} \right)^3 \right\}^{1/2} \right]^{1/3} \quad (\text{S17})$$

$$[\text{R-16}] = \left[\frac{[\text{R}]_{\text{total}}}{6K_{\text{trimer}}} + \left\{ \left(\frac{[\text{R}]_{\text{total}}}{6K_{\text{trimer}}} \right)^2 + \left(\frac{1}{9K_{\text{trimer}}} \right)^3 \right\}^{1/2} \right]^{1/3} + \left[\frac{[\text{R}]_{\text{total}}}{6K_{\text{trimer}}} - \left\{ \left(\frac{[\text{R}]_{\text{total}}}{6K_{\text{trimer}}} \right)^2 + \left(\frac{1}{9K_{\text{trimer}}} \right)^3 \right\}^{1/2} \right]^{1/3}$$

(3) Simulation by changing K_{trimer}

Figure S5 illustrates the simulation of the nonlinear relationship between ee_{prod} and ee_{cat} and the relationship between normalized rate and ee_{cat} by changing K_{trimer} . Based on this simulation, the trimerization constant is estimated to be $K_{\text{trimer}} = 9 \times 10^5 \text{ M}^{-2}$, which allows us to calculate k_1 to be $5 \text{ M}^{-1}\text{s}^{-1}$ using eq S10 and Figure S4 (vide supra).

Figure S5. Simulation of the nonlinear relationship between ee_{prod} and ee_{cat} (left) and the relationship between $v_{\text{ee}}/v_{100\%ee}$ and ee_{cat} (right). Reaction conditions: $[\mathbf{13}]_0 = 67 \text{ mM}$, $[\mathbf{S1}]_0 = 201 \text{ mM}$, 1,4-dioxane = 3.0 mL, $\text{H}_2\text{O} = 0.30 \text{ mL}$, $[\mathbf{6}]_0 = 2.7 \text{ mM}$ Rh at 30 °C.

VI. X-ray Crystal Structure of Complex 6

Data Collection

An orange CH₂Cl₂/hexane solution of **6** was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature.

An orange prism crystal of C₇₈H₇₆Cl₆O₂P₃Rh₃ having approximate dimensions of 0.50 x 0.40 x 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku CCD area detector with graphite monochromated Mo-K α radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions:

$$a = 15.182(1) \text{ \AA}$$

$$b = 19.779(2) \text{ \AA}$$

$$c = 23.308(2) \text{ \AA}$$

$$V = 6999.1(11) \text{ \AA}^3$$

For $Z = 4$ and F.W. = 1659.81, the calculated density is 1.58 g/cm³. The systematic absences of:

$$h00: h \pm 2n$$

$$0k0: k \pm 2n$$

$$00l: l \pm 2n$$

uniquely determine the space group to be:

$$P2_12_12_1 (\#19)$$

The data were collected at a temperature of 23 ± 1 °C to a maximum 2θ value of 56.6°.

Data Reduction

Of the 44105 reflections that were collected, 44036 were unique ($R_{\text{int}} = 0.026$). Data were collected and processed using CrystalClear (Rigaku). Net intensities and sigmas were derived as follows:

$$F^2 = [\Sigma(P_i - mB_{ave})] \cdot Lp^{-1}$$

where P_i is the value in counts of the i^{th} pixel

m is the number of pixels in the integration area

B_{ave} is the background average

Lp is the Lorentz and polarization factor

$$B_{ave} = \Sigma(B_j)/n$$

where n is the number of pixels in the background area

B_j is the value of the j^{th} pixel in counts

$$\sigma^2(F^2_{hkl}) = [(\Sigma P_i) + m((\Sigma(B_{ave} - B_j)^2)/(n-1))] \cdot Lp \cdot errmul + (erradd \cdot F^2)^2$$

where $erradd = 0.00$

$errmul = 1.00$

The linear absorption coefficient, μ , for Mo-K α radiation is 10.4 cm⁻¹. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods⁵ and expanded using Fourier techniques.⁶ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement⁷ on F was based on 41936 observed reflections ($I > 3.00\sigma(I)$) and 906 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.029$$

$$R_w = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2} = 0.036$$

⁵ SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, 27, 435.

⁶ DIRDIF99: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands (1999).

⁷ Least Squares function minimized:

$$\Sigma w (|F_o| - |F_c|)^2 \quad \text{where } w = \text{Least Squares weights.}$$

The standard deviation of an observation of unit weight⁸ was 1.01. A Chebychev polynomial weighting scheme was used.⁹ Plots of $\sum w (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 7.69 and $-4.51 \text{ e}^-/\text{\AA}^3$, respectively. The flack parameter¹⁰ is $-0.01(1)$.

Neutral atom scattering factors were taken from Cromer and Waber.¹¹ Anomalous dispersion effects were included in Fcalc;¹² the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.¹³ The values for the mass attenuation coefficients are those of Creagh and Hubbell.¹⁴ All calculations were performed using the CrystalStructure^{15,16} crystallographic software package.

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 619818). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.

⁸ Standard deviation of an observation of unit weight:

$$[\sum w (|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations, N_v = number of variables

⁹ Carruthers, J. R.; Watkin, D. J. *Acta Cryst.* **1979**, A35, 698.

¹⁰ Flack, H. D. *Acta Cryst.* **1983**, A39, 876.

¹¹ Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

¹² Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, 17, 781.

¹³ Creagh, D. C.; McAuley, W. J. "International Tables for Crystallography", Vol C, (Wilson, A. J. C., ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219–222 (1992).

¹⁴ Creagh, D. C.; Hubbell, J. H. "International Tables for Crystallography", Vol C, (Wilson, A. J. C., ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200–206 (1992).

¹⁵ CrystalStructure 3.6.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSO (2000-2004). 9009 New Trails Dr. The Woodlands TX 77381 USA.

¹⁶ CRYSTALS Issue 10: Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. Chemical Crystallography Laboratory, Oxford, UK. (1996).

Experimental Details

A. Crystal Data

Empirical Formula	$\text{C}_{78}\text{H}_{76}\text{Cl}_6\text{O}_2\text{P}_3\text{Rh}_3$
Formula Weight	1659.81
Crystal Color, Habit	orange, prism
Crystal Dimensions	0.50 X 0.40 X 0.30 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	$a = 15.182(1) \text{ \AA}$ $b = 19.779(2) \text{ \AA}$ $c = 23.308(2) \text{ \AA}$ $V = 6999.1(11) \text{ \AA}^3$
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.575 g/cm^3
F_{000}	3368.00
$\mu(\text{MoK}\alpha)$	10.43 cm^{-1}

B. Intensity Measurements

Detector	Rigaku CCD
Radiation	MoK α ($\lambda = 0.71069$ Å) graphite monochromated
Detector Aperture	70 mm x 70 mm
$2\theta_{\text{max}}$	56.6°
No. of Reflections Measured	Total: 44105 Unique: 44036 ($R_{\text{int}} = 0.026$)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	$\sum w (F_o - F_c)^2$
Least Squares Weights	Chebyshev polynomial with 3 parameters 0.3977, 0.5291, 0.1773
2 $\theta_{\max}$ cutoff	56.6°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00 σ (I))	41936
No. Variables	906
Reflection/Parameter Ratio	46.29
Residuals: R (I>3.00 σ (I))	0.029
Residuals: Rw (I>3.00 σ (I))	0.036
Goodness of Fit Indicator	1.010
Flack Parameter	−0.01(1)
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	7.69 e [−] /Å ³
Minimum peak in Final Diff. Map	−4.51 e [−] /Å ³