

## Mechanisms of Allene Stereoinversion by Imidozirconium Complexes

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### Supporting Information

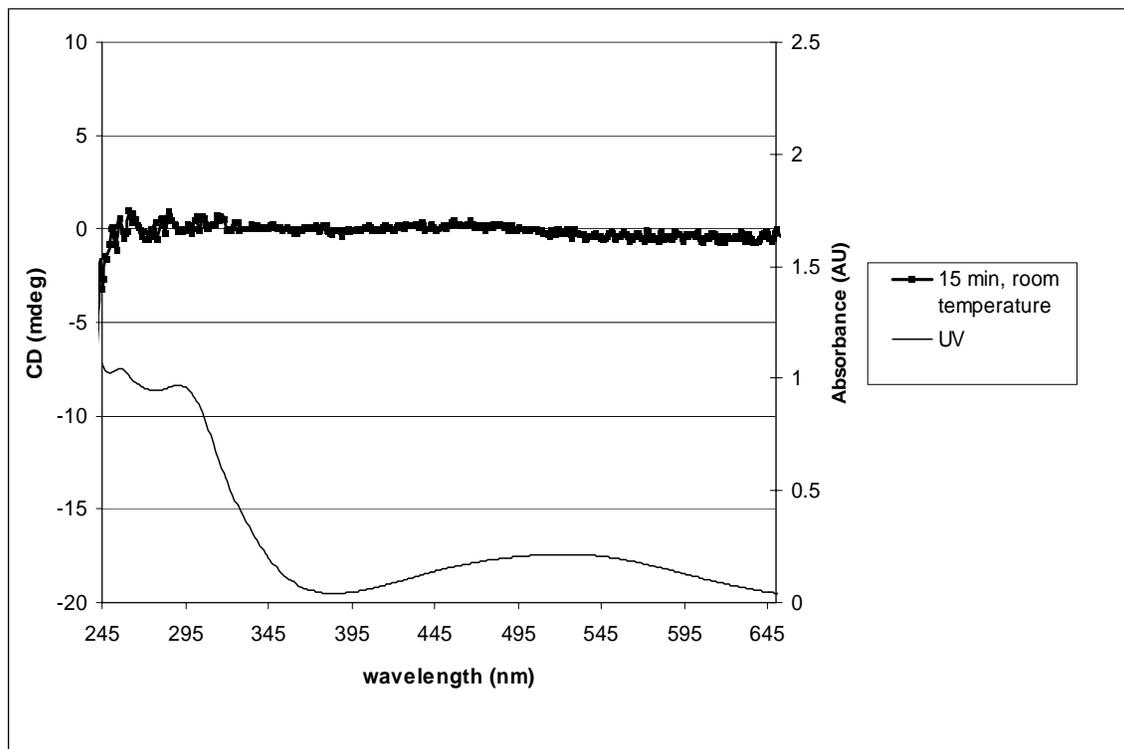
**General Procedures.** Unless otherwise noted, reactions and manipulations were performed at ambient temperature in an inert atmosphere (N<sub>2</sub>) glovebox, or using standard Schlenk and high vacuum line techniques. Glassware was dried overnight at 150 °C or flame dried under vacuum immediately prior to use. All NMR spectra were obtained at ambient temperature using Bruker AMX-300, AMX-400, or DRX-500 spectrometers. <sup>1</sup>H NMR chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS and are referenced relative to residual protiated solvent. <sup>13</sup>C NMR chemical shifts (δ) are reported in ppm relative to the carbon resonance of the deuterated solvent. In cases where assignment of <sup>13</sup>C resonances was ambiguous, standard DEPT 45, 90 and/or 135 pulse sequences or <sup>13</sup>C-<sup>1</sup>H HMQC experiments were used. Infrared (IR) spectra were recorded as a Nujol mull or a thin film between NaCl plates. Elemental analyses were performed at the University of California, Berkeley Microanalytical facility on a Perkin Elmer 2400 Series II CHNO/S Analyzer. Optical rotations were measured on a Perkin Elmer Model 241 polarimeter at room temperature.

**Materials.** Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Pentane, hexanes, benzene, and toluene (Fisher) were passed through a column of activated alumina (type A2, size 12 x 32, Purifry Co.) under nitrogen pressure and sparged with N<sub>2</sub> prior to use. Diethyl ether and tetrahydrofuran (Fisher) were distilled from sodium/benzophenone ketyl under N<sub>2</sub> prior

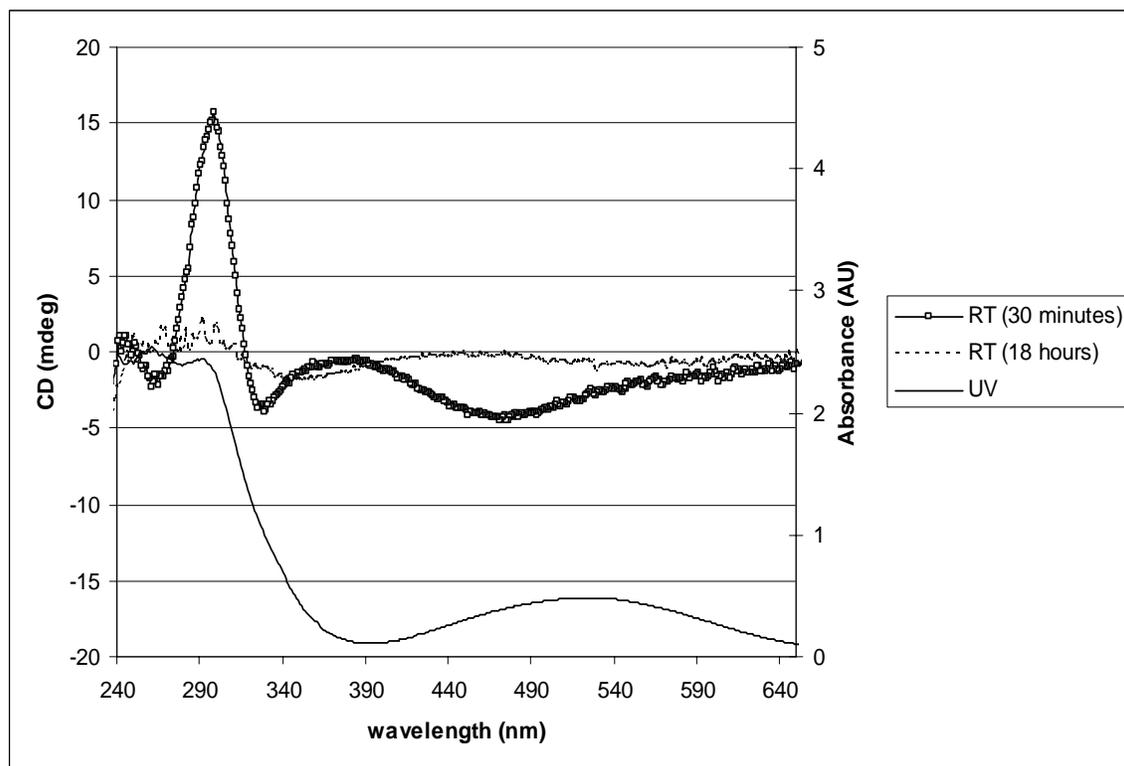
to use. Deuterated solvents (Cambridge Isotope Laboratories) were purified by vacuum-transfer from the appropriate drying agent (Na/Ph<sub>2</sub>CO or CaH<sub>2</sub>) prior to use. Imido complexes **1** and **3** were prepared according to literature procedures.<sup>1,2</sup> (*rac*)-1,2-dicyclopropylallene was a generous gift of Dr. Armin DeMeijere.

**General Procedures for Circular Dichroism Experiments.** All circular dichroism spectra were recorded at room temperature on a Jasco J-810 spectropolarimeter. In experiments to determine the change in optical activity with time and/or temperature, benzene or hexanes solutions of metallacycles were stored and/or heated in glass ampoules to which a Kontes vacuum stopcock had been sealed. For metallacycle **6**: an analytical solution of the metallacycle in hexanes was prepared in the glovebox. The solution was transferred to a 1 cm quartz glass cuvette, to which a Kontes vacuum stopcock had been sealed. For metallacycles **7** and **8**: The imido complex **3** (2 mg) was stirred in hexanes (20 mL) for 30 min to allow it to dissolve, and then an excess (5-10 equiv) of the appropriate enantioenriched allene (**5b** or **5c**) was added. The solution took on a pale purple color within 5 min at room temperature. The metallacycle solutions were filtered and transferred to an airtight cuvette, as described above. Initial spectra were taken within 30 min of mixing the reagents.

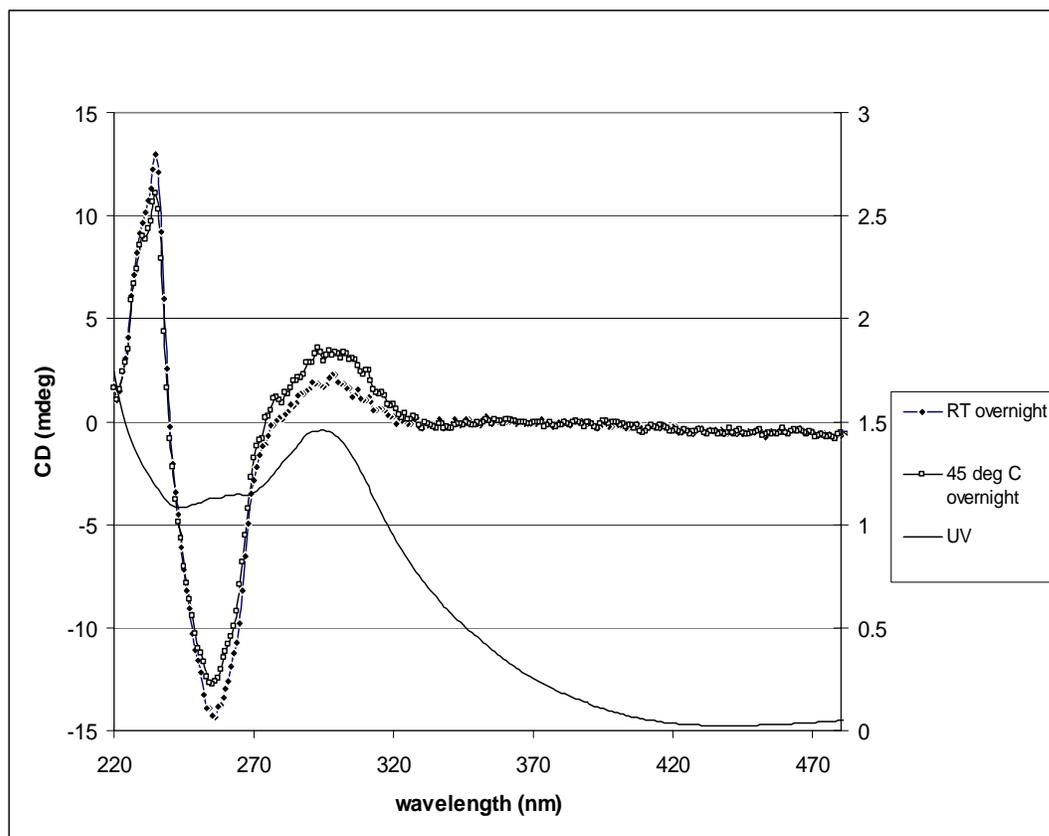
**CD and UV-Vis spectra of 7 at room temperature:**



**CD and UV-Vis spectra of 8 at room temperature:**



**CD and UV-Vis spectra of 6 at room temperature and 45 °C:**



**1-triisopropylsilylhex-1-yn-3-one.** To a suspension of  $\text{AlCl}_3$  (3.47 g, 26 mmol) in  $\text{CH}_2\text{Cl}_2$  (100 mL) at 0 °C was added a solution of 1-triisopropylsilyl-3-trimethylsilylacetylene (5.0 g, 20 mmol) and butyryl chloride (2.1 mL, 20 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL). After warming to room temperature, the mixture was stirred 2 h, then quenched by the addition of 1N HCl. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (2x). The combined organic layers were dried ( $\text{MgSO}_4$ ), concentrated, and distilled (110 °C @ 1 torr) to yield a pale yellow liquid (3.33 g, 66%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  2.53 (t, 2 H,  $J = 7.5$  Hz,  $\text{COCH}_2$ ), 1.71 (sext, 2 H,  $J = 7.5$  Hz,  $\text{CH}_3\text{CH}_2$ ), 1.1-1.0 (m, 21 H, TIPS), 0.94 (t, 3H,  $J = 7.5$  Hz,  $\text{CH}_3$ ) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  187.9, 104.2, 95.2, 47.4, 18.4, 17.6, 13.5, 10.9 ppm; IR (film) 2944 (s), 2867 (s), 2146 (w), 1679 (s), 1463 (m), 1232 (w), 1181 (m), 1137 (m), 1064 (m), 1016 (w), 997 (w), 883 (m), 832 (w), 679

(m), 582 (w)  $\text{cm}^{-1}$ ; GC-MS (CI)  $m/z$  252 ( $\text{M}^+$ ), 209 ( $\text{M}-\text{C}_3\text{H}_7$ ), 181 ( $\text{M}-\text{C}_3\text{H}_7\text{CO}$ ), Anal. Calcd for  $\text{C}_{15}\text{H}_{28}\text{OSi}$ : C, 71.35; H, 11.17. Found: C, 71.14; H, 11.30.

**(R)-hex-1-yn-3-ol (4b).** A mixture of 1-triisopropylsilylhex-1-yn-3-one (2.64 g, 10.4 mmol) and (*R*)-Alpine Borane (4.05 g, 15.7 mmol) were stirred at room temperature 8 h. Valeraldehyde (1.2 mL) was added and stirred overnight. The reaction mixture was pumped down for 2 h, then  $\text{Et}_2\text{O}$  (40 mL) and ethanolamine (0.96 mL) were added. After stirring for 1.5 h, the precipitate was removed by filtration and the filtrate was concentrated. Chromatography (20%  $\text{Et}_2\text{O}$ /pentane) yielded the protected alcohol as a pale yellow liquid (1.98 g, 74%). This material (1.37 g, 5.4 mmol) was dissolved in THF (10 mL), cooled to  $0\text{ }^\circ\text{C}$ , and a solution of TBAF $\cdot\text{H}_2\text{O}$  (1.55 g, 5.9 mmol) in THF (10 mL) was added. The mixture was warmed to room temperature and stirred 2 h. The reaction was quenched by addition of saturated  $\text{NH}_4\text{Cl}$ , and extracted with  $\text{Et}_2\text{O}$  (3x). The combined organic layers were washed with brine, dried ( $\text{MgSO}_4$ ), concentrated on a rotary evaporator, and chromatographed (30%  $\text{Et}_2\text{O}$ /pentane) to yield the product as a colorless liquid (530 mg, quant.).  $^1\text{H}$  NMR matches literature values<sup>3</sup>: ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  4.37 (m, 1H,  $\text{CH}(\text{OH})$ ), 2.45 (d,  $J = 2\text{ Hz}$ , 1H,  $\equiv\text{CH}$ ), 1.70 (m, 2H,  $\text{CH}_2$ ), 1.50 (m, 2H,  $\text{CH}_2$ ), 0.94 (t,  $J = 7\text{ Hz}$ , 3H,  $\text{CH}_3$ ) ppm. HPLC (of benzoate) (Chiracel OD; 1% isopropyl alcohol in hexanes; 1 mL/min): 95% ee;  $t_r$  (*R*) = 5.0 min,  $t_r$  (*S*) = 5.5 min.

Enantioenriched (*R*)-4-methylpent-1-yn-3-ol and (*R*)-1-ethynylcyclohexan-1-ol were obtained by asymmetric addition of trimethylsilylacetylene to the appropriate aldehydes, according to the method reported by Carriera, *et al.*,<sup>4,5</sup> followed by desilylation ( $\text{K}_2\text{CO}_3$ ).

**(R)-4-methylpent-1-yn-3-ol (4c):**<sup>6</sup> 66% yield (from isobutyraldehyde and trimethylsilylacetylene) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 4.17 (m, 1H, C(H)OH), 2.44 (d, *J* = 2 Hz, ≡ CH), 1.89 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.01 (d, *J* = 6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.98 (d, *J* = 6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. HPLC (of benzoate) (Chiracel OD; 1% isopropanol in hexanes; 1 mL/min): 94% ee; *t<sub>r</sub>* (*R*) = 7.0 min, *t<sub>r</sub>* (*S*) = 8.2 min.

**(R)-1-ethynylcyclohexan-1-ol (4d):**<sup>7</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 4.15 (m, 1H, CH(OH)), 2.46 (d, *J* = 2 Hz, 1H, ≡ CH), 1.04-1.87 (m, 11H, C<sub>6</sub>H<sub>11</sub>) ppm. HPLC (of benzoate) (Chiracel OD; 100% hexanes; 1 mL/min): > 95% ee; *t<sub>r</sub>* (*R*) = 7.1 min, *t<sub>r</sub>* (*S*) = 8.0 min.

**General procedure for synthesis of allenes: (S)-4,5-Nonadiene (5b).** To a suspension of CuBr (747 mg, 5.1 mmol), and LiBr (446 mg, 5.1 mmol) in THF (20 mL) at -78 °C was added *n*-PrMgBr (2.6 mL, 2 M in Et<sub>2</sub>O, 5.1 mmol) and the resulting mixture was stirred 15 min. In a separate flask, to a solution of (*R*)-hex-1-yn-3-ol (504 mg, 5.1 mmol) in THF (30 mL) at 78 °C was added BuLi (3.4 mL, 1.6 M in hexanes, 5.1 mmol); after 5 min stirring, MsCl (0.4 mL, 5.1 mmol) was added. This solution was added to the first solution via cannula and stirred 15 min at 78 °C. The mixture was poured into a separatory funnel containing NaCN (1 g) in 2% NH<sub>4</sub>Cl (100 mL) and separated. The aqueous layer was washed with Et<sub>2</sub>O (2x), then the combined organic layers were washed with brine, dried (MgSO<sub>4</sub>), and concentrated on a rotary evaporator. This material was dissolved in pentane, flushed through a short column of alumina, and concentrated under vacuum to give the product as a pale yellow liquid (125 mg, 20% yield). <sup>1</sup>H NMR matches literature values<sup>8</sup>: (CDCl<sub>3</sub>, 300 MHz) δ 5.05 (m, 2H, =CH), 1.95 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.40 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.91 (t, *J* = 7.5 Hz, 3H, CH<sub>3</sub>)

ppm. >90% ee by NMR shift reagent (allene:Ag(fod):(+)–Yb(hfc)<sub>3</sub> = 1.0:0.9:0.9).  $[\alpha]_D = +80^\circ$  (EtOH, *c* = 0.69).

**(R)-1,3-diphenylpropadiene (5a).** Procedure as for **5b**. 30% yield. After elution through a plug of alumina, (*R*)-1,3-diphenylallene was further purified by crystallization from dry, degassed hexanes at  $-30^\circ\text{C}$ . <sup>1</sup>H NMR matches literature values<sup>9</sup> (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.19-7.37 (m, 10H, ArH), 6.59 (s, 2H, =CH) ppm. HPLC: > 98% ee (Chiracel OD; 3% isopropyl alcohol in hexanes; 1 mL/min) *t<sub>r</sub>* (*R*) = 4.5 min, *t<sub>r</sub>* (*S*) = 5.9 min.  $[\alpha]_D = -1016^\circ$  (EtOH, *c* = 0.43).

**(S)-2,6-dimethyl-3,4-heptadiene (5c).** Procedure as for **5b**. 57% yield. <sup>1</sup>H NMR matches literature values<sup>8</sup>: (CDCl<sub>3</sub>, 300 MHz)  $\delta$  5.15 (t, *J* = 4 Hz, 2H, =CH) 2.25 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.98 (d, *J* = 6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. GC: > 95% ee (B-DM (30 m); 65 °C; 0.8 mL/min) *t<sub>r</sub>* (*R*) = 5.6 min, *t<sub>r</sub>* (*S*) = 5.9 min.  $[\alpha]_D = +91^\circ$  (EtOH, *c* = 0.45).

**(S)-1,3-dicyclohexylallene (5d):** Procedure as for **5b**. 66% yield. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)  $\delta$  5.22 (m, 2H, =CH), 1.95 (m, 2H, =CCH), 1.80 (m, 4H, CH<sub>2</sub>), 1.65 (m, 4H, CH<sub>2</sub>) 1.12 (m, 12H, CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz)  $\delta$  202.9 (C=C=C), 99.3 (=CCH), 38.6 (CH<sub>2</sub>), 34.5 (CH<sub>2</sub>), 34.4 (CH<sub>2</sub>), 27.4 (CH<sub>2</sub>), 27.3 (CH<sub>2</sub>) ppm. FT-IR (neat): 2922 (s), 2851 (s), 2658 (w), 1958 (w,  $\nu_{\text{C}=\text{C}=\text{C}}$ ), 1448 (m), 891 (m) cm<sup>-1</sup>. MS (EI) *m/z* = 204 (M<sup>+</sup>). HRMS (EI): Calcd; *m/z* = 204.1874. Found; 204.1878. <sup>1</sup>H NMR: ee > 95% (allene: Ag(fod):(+)–Yb(hfc)<sub>3</sub> = 1.0: 0.8: 0.8).  $[\alpha]_D = +131^\circ$  (EtOH, *c* = 0.60).

**(R)-2,6-dideutero-2,6-dimethyl-4-heptyn-3-ol (13-d<sub>2</sub>).** A flask containing Zn(OTf)<sub>2</sub> (364 mg, 1 mmol) was heated with a heat gun under vacuum until gas evolution ceased and was then allowed to cool to room temperature. (+)-*N*-methylephedrine (198

mg, 1.1 mmol) was added and the flask evacuated for 5 min. The flask was refilled with N<sub>2</sub>, and toluene (5 mL) and NEt<sub>3</sub> (250 mg, 2.5 mmol) were added. After stirring the mixture for 2 h, 3-methyl-1-butyne (0.767 mL, 5 mmol) was added, followed by isobutyraldehyde (0.460 mL, 5 mmol). The flask was stoppered and the mixture heated to 60 °C for 12 h. After cooling to room temperature, saturated NH<sub>4</sub>Cl was added and the mixture was extracted with Et<sub>2</sub>O (3x). The combined organic phases were washed with brine, dried (MgSO<sub>4</sub>), concentrated and chromatographed (15% Et<sub>2</sub>O/pentane) to give the product as a colorless liquid (491 mg, 71%). <sup>1</sup>H NMR matches literature values for **13-d<sub>0</sub>**, minus the two methine protons, which were observed in the <sup>2</sup>H NMR spectrum. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 4.15 (s, 1H, *CHOH*), 1.69 (s, 1H, *CHOH*), 1.16 (s, 6H, CH(*CH*<sub>3</sub>)<sub>2</sub>), 0.98 (s, 3H, CH(*CH*<sub>3</sub>)<sub>2</sub>), 0.96 (s, 3H, CH(*CH*<sub>3</sub>)<sub>2</sub>) ppm. <sup>2</sup>H NMR (CDCl<sub>3</sub>, 61.6 MHz) δ 2.65 (br s), 1.91 (br s) ppm.

**General Experimental Details for X-ray Structure Determination.** A crystal was mounted onto a glass fiber using Paratone N hydrocarbon oil and was transferred to a Siemens SMART diffractometer/CCD area detector,<sup>10</sup> centered in the beam, and cooled by a nitrogen-flow low-temperature apparatus. Preliminary orientation matrix and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected using ω scans of 0.3° counted for a total of 10.0 seconds per frame. The raw data were integrated by the program SAINT.<sup>11</sup> Data analysis was performed using XPREP.<sup>12</sup> An absorption correction was applied using SADABS.<sup>13</sup> The unit cell parameters and statistical analysis of the intensity distribution were used for space group determination.<sup>14</sup> The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was

applied. Unique or equivalent reflections were merged. The structure was solved by direct methods<sup>15</sup> and expanded using Fourier techniques.<sup>16</sup> Except where noted, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as fixed contributions but not refined. The quantity minimized by the least squares program was  $\sum_w (|F_o| - |F_c|)^2$ , where  $w$  is the weight of a given observation. The weighting scheme was based on counting statistics and included a factor ( $p = 0.030$ ) to downweight the intense reflections. The analytical forms of the scattering factor tables for the neutral atoms were used,<sup>17</sup> and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.<sup>14</sup> All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation.<sup>18</sup>

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