Latent Olefin Metathesis Catalysts Featuring Chelating Alkylidenes

*Andrew Hejl, Michael W. Day, and Robert H. Grubbs**

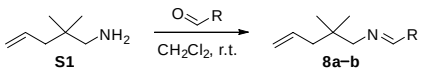
Supporting Information

Methods and Materials

Unless otherwise noted all reagents were purchased from Aldrich. **1** and **2** were donated by Materia, Inc. **3**,[1] **12**,[2] **13**,[3] **S1**[4] were prepared according to literature procedures. Anhydrous CH_2Cl_2 and C_6D_6 were obtained by elution through a solvent column drying system.[5] CD_2Cl_2 was purchased from Cambridge Isotope Laboratories and distilled from CaH_2 into a Schlenk tube and degassed. **10** (Aldrich) was distilled under vacuum prior to use.

Catalyst Synthesis

General procedure for the synthesis of imines CH_2=$CHCH_2CMe_2CH_2N$=CHR (**8a–b**)



The condensation of 2,2-dimethyl-4-pentenylamine (**S1**) with various aldehydes was carried out in CH_2Cl_2 over activated 4Å molecular sieves at r.t. for 12 h. The sieves were removed by filtration and the solution concentrated under vacuum to give the desired imines.

R = CH_2Ph (**8a**)

Amine **S1** (1.00 mL, 0.78 g, 6.9 mmol) and benzaldehyde (0.70 mL, 0.73 g, 6.9 mmol) in CH_2Cl_2 (15 mL) gave **8a** (0.975 g, 4.84 mmol) as a clear liquid containing approximately 8 % excess benzaldehyde. Yield: 70 %. ^{1}H NMR ($CDCl_3$, 299.87 MHz, δ): 8.24 (s, 1 H, C*H*=N), 7.76 (m, 2 H, Ph), 7.42 (m, 3 H, Ph), 5.98–5.82 (m, 1 H, CH_2=C*H*CH_2), 5.09–5.00 (m, 2 H, CH_2=CH), 3.40 (s, 2 H, CMe_2CH_2N), 2.10 (d, *J* = 7.5 Hz, 2 H, =CHC$H_2$$CMe_2$), 0.98 (s, 6 H, C$Me_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.41 MHz, δ): 161.08, 136.69, 135.66, 130.57, 128.72, 128.26, 117.18, 72.27, 45.19, 35.48, 25.80. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1647.5.

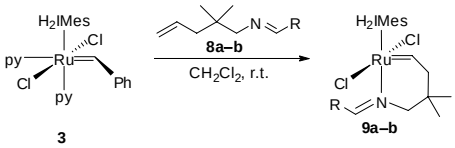
R = CMe_3 (**8b**)

Amine **S1** (0.88 mL, 0.69 g, 6.1 mmol) and trimethylacetaldehyde (0.72 mL, 0.57 g, 6.6 mmol) in CH_2Cl_2 (15 mL) gave **8b** (0.634 g, 3.50 mmol) as a clear liquid. Yield: 58 %. ^{1}H NMR ($CDCl_3$, 300.09 MHz, δ): 7.44 (t, *J* = 1.5 Hz, 1 H, C*H*=N), 5.91–5.76 (m, 1 H, CH_2=C*H*CH_2), 5.04–4.94 (m, 2 H, CH_2=CH), 3.12 (d, *J* = 0.9 Hz, 2 H, CMe_2CH_2N), 1.98 (dt, *J* = 9.0, 1.2 Hz, 2 H, =CHC$H_2$$CMe_2$), 1.06 (s, 9 H, N=CHC$Me_3$), 0.86 (s, 6 H, C$Me_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.41 MHz, δ): 172.26, 135.74, 117.02, 71.78, 45.13, 36.38, 35.01, 27.19, 25.59. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1669.3.

---

[1] Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001,** *20,* 5314–5318.
[2] Wakamatsu, H.; Blechert, S. *Angew. Chem. Int. Ed.* **2002,** *41,* 2403–2405.
[3] Grela, K.; Harutyunyan, S.; Michrowska, A. *Angew. Chem. Int. Ed.* **2002,** *41,* 4038–4040.
[4] Bender, C. F.; Widenhoefer, R. A. *J Am. Chem. Soc.* **2005,** *127,* 1070–1071.
[5] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 518–1520.

General procedure for the synthesis of catalysts **9a–b**



In the glove box, a Schlenk flask was charged with **3** and CH_2Cl_2. The corresponding imine was then added via syringe and the reaction stirred at r.t. for 30 min. The volatiles were removed under vacuum, the residue redissolved in C_6H_6 (2 mL), and precipitated with pentane (20 mL), cooling to -5 ºC. The solid was collected, washed with pentane (3 x 5 mL) and dried under vacuum to give the imine-substituted ruthenium compounds in good yields. Any modifications are described below for each reaction.

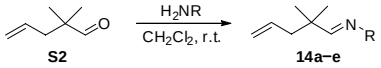
R = CH_2Ph (**9a**)

Ru complex **3** (196 mg, 0.270 mmol), imine **8a** (67.9 mg, 0.337 mmol) and CH_2Cl_2 (5 mL) gave **9a** (151 mg, 0.135 mmol) as a light green solid. Yield: 84 %. ^{1}H NMR (CD_2Cl_2, 299.82 MHz, δ): 18.71 (t, *J* = 5.7 Hz, 1 H, Ru=C*H*CH_2), 8.39 (s, 1 H, C*H*=N), 7.31 (t, *J* = 7.5 Hz, 1 H, Bn), 7.19 (d, *J* = 7.2 Hz, 2 H, Bn), 7.06 (t, *J* = 7.8 Hz, 2 H, Bn), 7.06 (s, 4 H, Mes), 3.95 (s, 2 H, CMe_2CH_2N), 3.88 (s, 4 H, NCH_2CH_2N), 2.78 (d, *J* = 5.4 Hz, 2 H, Ru=CHCH_2CMe_2), 2.44 (s, 12 H, Mes-CH_3), 2.41 (s, 6 H, Mes-CH_3), 0.73 (s, 6 H, CMe_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.42 MHz, δ): 341.41 (Ru=*C*HCH_2), 218.02 (Ru–*C*$(N)_2$), 170.04 (Ru–N=*C*), 138.87, 137.29, 134.62, 130.96, 130.31, 130.11, 128.99, 77.35, 66.70, 51.91, 34.29, 26.35, 21.45, 19.41. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1623.7. HRMS–FAB (m/z): [M]$^+$ calcd for $C_{34}H_{43}Cl_2N_3Ru$, 665.1878; found, 665.1855.

R = CMe_3 (**9b**)

Ru complex **3** (132 mg, 0.182 mmol), imine **8b** (41.6 mg, 0.229 mmol) and CH_2Cl_2 (5 mL) gave **9b** (92.0 mg, 0.142 mmol) as a light green solid. Yield: 78 %. ^{1}H NMR (CD_2Cl_2, 299.82 MHz, δ): 18.54 (t, *J* = 6.0 Hz, 1 H, Ru=C*H*CH_2), 7.45 (t, *J* = 1.5 Hz, 1 H, C*H*=N), 7.00 (br s, 4 H, Mes), 3.90 (br s, 4 H, NCH_2CH_2N), 3.45 (d, *J* = 1.8 Hz, 2 H, CMe_2CH_2N), 2.81 (d, *J* = 6.3 Hz, 2 H, Ru=CHCH_2CMe_2), 2.42 (br s, 12 H, Mes-CH_3), 2.35 (s, 6 H, Mes-CH_3), 0.95 (s, 9 H, N=CHCMe_3), 0.70 (s, 6 H, CMe_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.71 MHz, δ): 343.35 (Ru=*C*HCH_2), 218.91 (Ru–*C*$(N)_2$), 180.80 (Ru–N=*C*), 138.74, 137.48, 130.02, 76.96, 66.43, 51.60, 37.02, 34.61, 26.53, 26.45, 21.36, 19.52 (br). IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1635.6. HRMS–FAB (m/z): [M]$^+$ calcd for $C_{32}H_{47}Cl_2N_3Ru$, 645.2191; found, 645.2204.

General procedure for the synthesis of imines CH_2=$CHCH_2CMe_2CH$=NR (**14a–e**)



The condensation of 2,2-dimethyl-4-pentenal (**S2**) with various primary amines was carried out in CH_2Cl_2 over activated 4Å molecular sieves at r.t. for 12 h. The sieves were removed by filtration and the solution concentrated under vacuum to give the desired imines.

R = Ph, (**14a**)

Aldehyde **S2** (1.00 mL, 0.825 g, 7.35 mmol) and aniline (0.67 mL, 0.674 g, 7.35 mmol) in CH_2Cl_2 (15 mL) gave **14a** (1.094 g, 5.84 mmol) as a clear liquid. Yield: 79 %. ^{1}H NMR ($CDCl_3$, 300.09 MHz, δ): 7.69 (s, 1 H, C*H*=N), 7.35–6.95 (m, 5 H, Ph), 5.92–5.76 (m, 1 H, CH_2=C*H*CH_2), 5.12–5.04 (m, 2 H, CH_2=CH), 2.29 (dt, *J* = 7.5, 1.2 Hz, 2 H, =CHCH_2CMe_2), 1.18 (s, 6 H, CMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.46 MHz, δ): 172.78, 152.84, 134.58, 129.12, 125.36, 120.74, 117.98, 44.87, 39.94, 24.63. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1648.0.

R=^{i}Pr (**14b**)

Aldehyde **S2** (1.00 mL, 0.825 g, 7.35 mmol) and isopropyl amine (1.25 mL, 0.867 g, 14.7 mmol) in CH_2Cl_2 (15 mL) gave **14b** (0.666 g, 4.34 mmol) as a clear liquid. Yield: 59 %. ^{1}H NMR ($CDCl_3$, 300.08 MHz, δ): 7.49 (s, 1 H, C*H*=N), 5.82–5.64 (m, 1 H, CH_2=C*H*CH_2), 5.06–4.92 (m, 2 H, CH_2=CH), 3.24 (sept., *J* = 6.3 Hz, 1 H, NC*H*Me_2), 2.13 (d, *J* = 7. 2 Hz, 2 H, =CHCH_2CMe_2), 1.11 (d, *J* = 6.6 Hz, 6 H, NCHMe_2), 1.02 (s, 6 H, CMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.46 MHz, δ): 168.35, 134.97, 117.41, 61.69, 44.99, 38.62, 24.92, 24.35. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1661.4.

R=Cy (**14c**)

Aldehyde **S2** (1.00 mL, 0.825 g, 7.35 mmol) and cyclohexyl amine (0.88 mL, 0.762 g, 7.69 mmol) in CH_2Cl_2 (15 mL) gave **14c** (0.730 g, 3.77 mmol) as a clear liquid. Yield: 51 %. ^{1}H NMR ($CDCl_3$, 300.08 MHz, δ): 7.50 (s, 1 H, C*H*=N), 5.82–5.66 (m, 1 H, CH_2=C*H*CH_2), 5.04–4.94 (m, 2 H, CH_2=CH), 2.89 (tt, *J* = 10.5, 4.2 Hz, 1 H, NC*H*–Cy), 2.13 (dt, *J* = 7. 5 Hz, 0.9 Hz, 2 H, =CHCH_2CMe_2), 1.82–1.10 (m, 10 H, Cy), 1.01 (s, 6 H, CMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.46 MHz, δ): 168.73, 135.03, 117.37, 70.04, 45.00, 38.69, 34.60, 25.81, 25.10, 24.94. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1662.7.

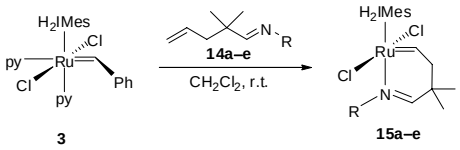
R=^{t}Bu (**14d**)

Aldehyde **S2** (1.00 mL, 0.825 g, 7.35 mmol) and *t*-butyl amine (0.93 mL, 0.647 g, 8.85 mmol) in CH_2Cl_2 (15 mL) gave **14d** (0.555 g, 3.32 mmol) as a clear liquid. Yield: 45 %. ^{1}H NMR ($CDCl_3$, 300.08 MHz, δ): 7.43 (s, 1 H, C*H*=N), 5.82–5.66 (m, 1 H, CH_2=C*H*CH_2), 5.03–4.94 (m, 2 H, CH_2=CH), 2.14 (dt, *J* = 7. 5, 1.2 Hz, 2 H, =CHCH_2CMe_2), 1.13 (s, 9 H, NCMe_3), 1.01 (s, 6 H, CMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.46 MHz, δ): 164.63, 135.31, 117.19, 56.42, 45.09, 38.68, 29.97, 24.92. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1665.9.

R=Me (**14e**)

Aldehyde **S2** (1.00 mL, 0.825 g, 7.35 mmol) and methyl amine (2.0 *M* THF, 6.00 mL, 12.0 mmol) in CH_2Cl_2 (15 mL) gave **14e** (0.631 g, 5.04 mmol) as a clear liquid. Yield: 69 %. ^{1}H NMR ($CDCl_3$, 300.09 MHz, δ): 7.49 (q, *J* = 1.5 Hz, 1 H, C*H*=N), 5.80–5.64 (m, 1 H, CH_2=C*H*CH_2), 5.04–4.94 (m, 2 H, CH_2=CH), 3.23 (d, *J* = 1.5 Hz, 3 H, N*Me*), 2.12 (dt, *J* = 7. 2, 1.2 Hz, 2 H, =CHCH_2CMe_2), 1.01 (s, 6 H, CMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.46 MHz, δ): 172.72, 134.74, 117.59, 48.08, 44.79, 39.13, 24.63. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1670.9.

General procedure for the synthesis of catalysts **15a–e**



In the glove box, a Schlenk flask was charged with **3** and CH_2Cl_2. The corresponding imine was then added via syringe and the reaction stirred at r.t. for 30 min. The volatiles were removed under vacuum, the residue redissolved in C_6H_6 (2 mL), and precipitated with pentane (20 mL), cooling to -5 ºC. The solid was collected, washed with pentane (3 x 5 mL) and dried under vacuum to give the imine-substituted ruthenium compounds in good yields. Any modifications are described below for each reaction.

R=Ph (**15a**)

Ru complex **3** (155 mg, 0.213 mmol), imine **14a** (59.8 mg, 0.319 mmol) and CH_2Cl_2 (5 mL) gave **15a** (116 mg, 0.177 mmol) as a light green solid. Yield: 83 %. ^{1}H NMR (CD_2Cl_2, 299.87 MHz, δ): 18.80 (t, *J* = 5.4 Hz, 1 H, Ru=C*H*CH_2), 7.64 (s, 1 H, C*H*=N), 7.2–6.9 (m, 9 H, Ph and Mes), 4.01 (s, 4 H, NCH_2CH_2N), 3.02 (d, *J* = 5.4 Hz, 2 H, Ru=CHCH_2CMe_2), 2.5–2.3 (m, 18 H, Mes–CH_3), 1.07 (s, 6 H, CMe_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.71 MHz, δ): 345.10 (Ru=*C*HCH_2), 218.03 (Ru–*C*(N)$_2$), 176.96 (Ru–N=*C*), 149.63, 138.81, 129.82, 129.40, 127.12, 122.48, 64.30, 51.82, 42.69, 26.89, 21.46, 19.28. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1634.3. HRMS–FAB (m/z): [M]$^+$ calcd for $C_{33}H_{41}Cl_2N_3Ru$, 651.1722; found, 651.1726. Anal. Calcd for $C_{33}H_{41}Cl_2N_3Ru$: C, 60.82; H, 6.34; N, 6.45. Found: C, 60.72; H, 6.38; N, 6.48.

R=^{i}Pr (**15b**)

Ru complex **3** (239 mg, 0.328 mmol), imine **14b** (75.7 mg, 0.493 mmol) and CH_2Cl_2 (5 mL) gave **15b** (162 mg, 0.262 mmol) as a light green solid. Yield: 80 %. ^{1}H NMR (CD_2Cl_2, 299.82 MHz, δ): 18.58 (t, *J* = 5.4 Hz, 1 H, Ru=C*H*CH_2), 7.41 (d, *J* = 1.5 Hz, 1 H, C*H*=N), 6.99 (s, 4 H, Mes), 4.02 (s, 4 H, NCH_2CH_2N), 3.32 (sept.d, *J* = 6.6, 1.5 Hz, 1H, NC*H*Me_2), 2.96 (d, *J* = 5.4 Hz, 2 H, Ru=CHCH_2CMe_2), 2.42 (br s, 12 H, Mes–CH_3), 2.34 (s, 6 H, Mes–CH_3), 0.92 (s, 6 H, CMe_2), 0.90 (d, *J* = 6.9 Hz, 6 H, NCHMe_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.71 MHz, δ): 345.17 (Ru=*C*HCH_2), 219.54 (Ru–*C*(N)$_2$), 173.68 (Ru–N=*C*), 138.91, 129.74, 64.21, 60.78, 51.60,

42.51, 26.96, 22.47, 21.36, 19.36 (br). IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1642.6. HRMS–FAB (m/z): $[M]^+$ calcd for $C_{30}H_{43}Cl_2N_3Ru$, 617.1878; found, 617.1853.

R=Cy (**15c**)

Ru complex **3** (192 mg, 0.263 mmol), imine **14c** (74.0 mg, 0.382 mmol) and CH_2Cl_2 (5 mL) gave **15c** (146 mg, 0.222 mmol) as a light green solid. Yield: 84 %. ^{1}H NMR (CD_2Cl_2, 299.87 MHz, δ): 18.56 (t, *J* = 5.4 Hz, 1 H, Ru=C*H*CH_2), 7.41 (d, *J* = 0.9 Hz, 1 H, C*H*=N), 7.00 (br s, 4 H, Mes), 4.00 (br s, 4 H, NCH_2CH_2N), 2.96 (d, *J* = 5.7 Hz, 2 H, Ru=CHCH_2CMe_2), 2.7–2.2 (br m, 12 H, Mes–CH_3), 2.34 (s, 6 H, Mes–CH_3), 1.7–0.8 (m, 11 H, Cy), 0.91 (s, 6 H, CMe_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.71 MHz, δ): 345.00 (Ru=*C*HCH_2), 219.49 (Ru–*C*$(N)_2$), 173.76 (Ru–N=*C*), 138.76, 129.76, 69.99, 64.07, 51.63, 42.23, 33.47, 26.90, 26.10, 25.49, 21.39, 20.00 (br), 18.78 (br). IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1641.1. HRMS–FAB (m/z): $[M]^+$ calcd for $C_{33}H_{47}Cl_2N_3Ru$, 657.2191; found, 657.2163.

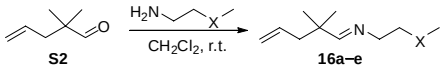
R=^{t}Bu (**15d**)

Ru complex **3** (188 mg, 0.258 mmol), imine **14d** (56.0 mg, 0.335 mmol) and CH_2Cl_2 (5 mL) gave **15d** (90.8 mg, 0.143 mmol) as a light green solid. Yield: 56 %. ^{1}H NMR (CD_2Cl_2, 299.82 MHz, δ): 18.37 (t, *J* = 5.7 Hz, 1 H, Ru=C*H*CH_2), 7.43 (s, 1 H, C*H*=N), 7.04–6.94 (m, 4 H, Mes), 4.10–3.96 (m, 4 H, NCH_2CH_2N), 3.08 (d, *J* = 5.4 Hz, 2 H, Ru=CHCH_2CMe_2), 2.59 (br s, 6 H, Mes–CH_3), 2.34 (s, 6 H, Mes–CH_3), 2.26 (br s, 6 H, Mes–CH_3), 1.01 (s, 9 H, NCMe_3), 0.92 (s, 6 H, CMe_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.71 MHz, δ): 345.22 (Ru=*C*HCH_2), 219.82 (Ru–*C*$(N)_2$), 172.97 (Ru–N=*C*), 139.83, 139.13, 138.55, 137.92, 136.09, 129.83, 129.74, 64.05, 63.66, 51.75, 51.27, 43.02, 28.89, 26.77, 21.37, 20.21, 18.58. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1638.6. HRMS–FAB (m/z): $[M]^+$ calcd for $C_{31}H_{45}Cl_2N_3Ru$, 631.2035; found, 631.2031.

R=Me (**15e**)

Ru complex **3** (143 mg, 0.196 mmol), imine **14e** (30.4 mg, 0.242 mmol) and CH_2Cl_2 (5 mL) gave **15e** (92.5 mg, 0.164 mmol) as a green–brown solid. Yield: 84 %. ^{1}H NMR (CD_2Cl_2, 299.87 MHz, δ): 18.80 (t, *J* = 5.1 Hz, 1 H, Ru=C*H*CH_2), 7.42 (m, 1 H, C*H*=N), 7.00 (br s, 4 H, Mes), 4.05 (s, 4 H, NCH_2CH_2N), 2.73 (d, *J* = 1.2 Hz, 1H, N*Me*), 2.69 (d, *J* = 5.1 Hz, 2 H, Ru=CHCH_2CMe_2), 2.41 (s, 12 H, Mes–CH_3), 2.34 (s, 6 H, Mes–CH_3), 0.93 (s, 6 H, CMe_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.71 MHz, δ): 342.54 (Ru=*C*HCH_2), 218.93 (Ru–*C*$(N)_2$), 175.29 (Ru–N=*C*), 139.04, 138.87, 136.52, 129.61, 64.46, 51.85, 46.76, 41.83, 26.88, 21.37, 19.56. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1635.4. HRMS–FAB (m/z): $[M]^+$ calcd for $C_{28}H_{39}Cl_2N_3Ru$, 589.1565; found, 589.1560.

General procedure for the synthesis of imines $CH_2{=}CHCH_2CMe_2CH{=}NCH_2CH_2XMe$ (**16a–16c**)



The condensation of 2,2-dimethyl-4-pentenal (**S2**) with various primary amines was carried out in CH_2Cl_2 over activated 4Å molecular sieves at r.t. for 12 h. The sieves were removed by filtration and the solution concentrated under vacuum to give the desired imines.

X=CH_2 **(16a)**

Aldehyde **S2** (1.00 mL, 0.825 g, 7.35 mmol) and n-butylamine (1.09 mL, 0.806 g, 11.0 mmol) in CH_2Cl_2 (15 mL) gave **16a** (0.705 g, 4.22 mmol) as a clear liquid. Yield: 57 %. ^{1}H NMR ($CDCl_3$, 300.09 MHz, δ): 7.47 (t, *J* = 1.2 Hz, 1 H, C*H*=N), 5.82–5.66 (m, 1 H, $CH_2{=}C\mathit{H}CH_2$), 5.06–4.94 (m, 2 H, $C\mathit{H}_2{=}CH$), 3.36 (td, *J* = 7.2, 1.2 Hz, 2 H, $CH{=}NC\mathit{H}_2CH_2$), 2.14 (d, *J* = 7.5 Hz, 2 H, $=CHC\mathit{H}_2CMe_2$), 1.54 (quint., *J* = 7.5 Hz, 2 H, $NCH_2C\mathit{H}_2CH_2$), 1.27 (sext., *J* = 7.8 Hz, $CH_2C\mathit{H}_2Me$), 1.03 (s, 6 H, $C\mathit{Me}_2$), 0.89 (t, *J* = 7.2 Hz, 3 H, Bu-*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.46 MHz, δ): 171.12, 134.87, 117.51, 61.33, 44.92, 39.02, 33.15, 24.82, 20.40, 14.04. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1665.6.

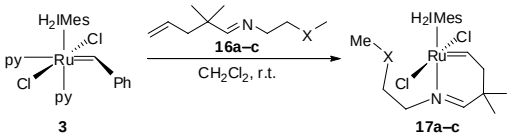
X=O **(16b)**

Aldehyde **S2** (1.00 mL, 0.825 g, 7.35 mmol) and 2-methoxyethylamine (0.77 mL, 0.662 g, 8.82 mmol) in CH_2Cl_2 (15 mL) gave **16b** (0.946 g, 5.59 mmol) as a clear liquid. Yield: 76 %. ^{1}H NMR ($CDCl_3$, 299.82 MHz, δ): 7.53 (s, 1 H, C*H*=N), 5.83–5.67 (m, 1 H, $CH_2{=}C\mathit{H}CH_2$), 5.06–4.97 (m, 2 H, $C\mathit{H}_2{=}CH$), 3.55 (s, 4 H, $CH{=}NC\mathit{H}_2C\mathit{H}_2$), 3.34 (s, 3 H, O*Me*), 2.15 (d, *J* = 7.2 Hz, 2 H, $=CHC\mathit{H}_2CMe_2$), 1.05 (s, 6 H, $C\mathit{Me}_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz, δ): 173.29, 134.80, 117.50, 72.29, 60.98, 58.98, 44.84, 39.19. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1666.6.

X=S (**16c**)

Aldehyde **S2** (1.00 mL, 0.825 g, 7.35 mmol) and 2-thiomethylethylamine (0.69 mL, 0.67 g, 7.37 mmol) in CH_2Cl_2 (15 mL) gave **16c** (1.150 g, 6.20 mmol) as a pale yellow liquid. Yield: 84 %. ^{1}H NMR ($CDCl_3$, 299.82 MHz, δ): 7.53 (t, *J* = 1.2 Hz, 1 H, C*H*=N), 5.84–5.70 (m, 1 H, $CH_2{=}C\mathit{H}CH_2$), 5.06–4.98 (m, 2 H, $C\mathit{H}_2{=}CH$), 3.58 (td, *J* = 7.2, 1.2 Hz, 2 H, $CH{=}NC\mathit{H}_2CH_2$), 2.71 (t, *J* = 7.2 Hz, 2 H, $NCH_2C\mathit{H}_2SMe$), 2.16 (td, *J* = 7.5, 1.2 Hz, 2 H, $=CHC\mathit{H}_2CMe_2$), 2.12 (s, 3 H, $CH_2S\mathit{Me}$), 1.05 (s, 6 H, $C\mathit{Me}_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.46 MHz, δ): 172.93, 134.71, 117.66, 60.97, 44.81, 39.23, 35.23, 24.69, 16.09. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1664.6.

General procedure for the synthesis of catalysts **17a–c**



In the glove box, a Schlenk flask was charged with **3** and CH_2Cl_2. The corresponding imine was then added via syringe and the reaction stirred at r.t. for 30 min. The volatiles were removed under vacuum, the residue redissolved in C_6H_6 (2 mL), and precipitated with pentane (20 mL), cooling to -5 ºC. The solid was collected, washed with pentane (3 x 5 mL) and dried under vacuum to give the imine-substituted ruthenium compounds in good yields. Any modifications are described below for each reaction.

X=CH_2 **(17a)**

Ru complex **3** (140 mg, 0.192 mmol), imine **16a** (48.0 mg, 0.219 mmol) and CH_2Cl_2 (5 mL) gave **17a** (85.3 mg, 0.135 mmol) as a light green solid. Yield: 70 %. ^{1}H NMR (CD_2Cl_2, 299.87 MHz, δ): 18.71 (t, *J* = 5.4 Hz, 1 H, Ru=C*H*CH_2), 7.38 (t, *J* = 1.2 Hz, 1 H, C*H*=N), 7.00 (br s, 4 H, Mes), 4.03 (s, 4 H, NC*H*$_2$C*H*$_2$N), 3.03 (td, *J* = 7.8, 1.2 Hz, 2 H, CH=NC*H*$_2$$CH_2$), 2.84 (d, *J* = 5.4 Hz, 2 H, Ru=CHC*H*$_2$$CMe_2$), 2.42 (br s, 12 H, Mes-*CH*$_3$), 2.34 (s, 6 H, Mes-*CH*$_3$), 1.19 (m, 2 H, NC*H*$_2$C*H*$_2$$CH_2$), 1.04 (sext., *J* = 7.8 Hz, CH_2C*H*$_2$Me), 0.93 (s, 6 H, C*Me*$_2$), 0.77 (t, *J* = 7.5 Hz, 3 H, Bu-*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.71 MHz, δ): 344.20 (Ru=*C*HCH_2), 219.23 (Ru–*C*(N)$_2$), 174.25 (Ru–N=*C*), 138.84, 129.74, 64.54, 61.70, 51.72 (br), 42.00, 31.14, 27.04, 21.40, 20.89, 19.58 (br), 13.61. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1634.9. HRMS–FAB (m/z): [M]$^+$ calcd for $C_{31}H_{45}Cl_2N_3Ru$, 631.2035; found, 631.2042.

X=O **(17b)**

Ru complex **3** (160 mg, 0.220 mmol), imine **16b** (46.8 mg, 0.276 mmol) and CH_2Cl_2 (5 mL) gave **17b** (115.8 mg, 0.182 mmol) as a light green solid. Yield: 83 %. ^{1}H NMR (CD_2Cl_2, 299.87 MHz, δ): 18.64 (t, *J* = 5.7 Hz, 1 H, Ru=C*H*CH_2), 7.47 (t, *J* = 1.5 Hz, 1 H, C*H*=N), 7.00 (s, 4 H, Mes), 3.93 (s, 4 H, NC*H*$_2$C*H*$_2$N), 3.53 (t, *J* = 5.4 Hz, 2 H, NCH_2C*H*$_2$OMe), 3.14 (td, *J* = 5.8, 1.5 Hz, 2 H, CH=NC*H*$_2$$CH_2$), 2.92 (d, *J* = 5.4 Hz, 2 H, Ru=CHC*H*$_2$$CMe_2$), 2.83 (s, 3 H, O*Me*), 2.44 (s, 12 H, Mes-C*H*$_3$), 2.35 (s, 6 H, Mes-C*H*$_3$), 0.95 (s, 6 H, C*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.42 MHz, δ): 341.29 (Ru=*C*HCH_2), 218.88 (Ru–*C*(N)$_2$), 176.24 (Ru–N=*C*), 139.03, 138.64, 137.40, 129.73, 70.46, 63.31, 59.33, 58.61, 51.95, 40.89, 26.96, 21.35, 19.49. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1645.8. HRMS–FAB (m/z): [M]$^+$ calcd for $C_{30}H_{43}Cl_2N_3RuO$, 633.1827; found, 633.1845.

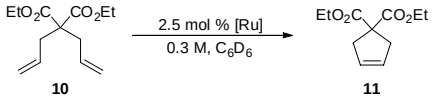
X=S **(17c)**

Ru complex **3** (149 mg, 0.205 mmol), imine **16c** (47.0 mg, 0.253 mmol) and CH_2Cl_2 (5 mL) gave **17c** (110.2 mg, 0.169 mmol) as a light green solid. Yield: 83 %. ^{1}H NMR (CD_2Cl_2, 299.82 MHz, δ): 18.45 (t, *J* = 7.5 Hz, 1 H, Ru=C*H*CH_2), 7.47 (s, 1 H, C*H*=N), 7.01 (s, 4 H, Mes), 3.79 (s, 4 H, NC*H*$_2$C*H*$_2$N), 3.13 (m, 4 H, NC*H*$_2$$CH_2$ and Ru=CHC*H*$_2$$CMe_2$), 2.5–2.4 (m, 2 H, NCH_2C*H*$_2$SMe), 2.42 (s, 12 H, Mes-C*H*$_3$), 2.37 (s, 6 H, Mes-C*H*$_3$), 1.43 (s, 3 H, CH_2S*Me*), 0.95

(s, 6 H, C*Me*$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.42 MHz, δ): 342.16 (Ru=*C*HCH$_2$), 219.28 (Ru–*C*(N)$_2$), 175.04 (Ru–N=*C*), 139.14, 138.90, 138.44, 129.96, 61.52, 60.61, 51.89, 38.58, 35.32, 27.04, 21.40, 19.40, 14.44. IR (CH_2Cl_2 soln, $\nu_{C=N}$, cm^{-1}): 1641.3. HRMS–FAB (m/z): $[M]^+$ calcd for $C_{30}H_{43}Cl_2N_3RuS$, 649.1599; found, 649.1626.

Catalysis Procedures

RCM of Diethyldiallyl Malonate (**10**) at elevated temperature



A stock solution was prepared to deliver the catalyst solution. Inside a glovebox, a volumetric flask was charged with catalyst (0.026 mmol) and C_6D_6 added to prepare 2.0 mL of stock solution (0.013 M). An NMR tube with a screwcap septum top was charged with catalyst stock solution (0.013 M, 0.40 mL, 5.2 μmol, 2.5 mol%) and C_6D_6 (0.25 mL). The sample was equilibrated at the desired temperature in the NMR probe before **10** (50 μL, 50 mg, 0.21 mmol, 0.3 M) was added via syringe. Data points were collected over an appropriate period of time using the Varian array function. The conversion to **11** was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ 2.84 (dt), with those in the product, δ 3.14 (s).

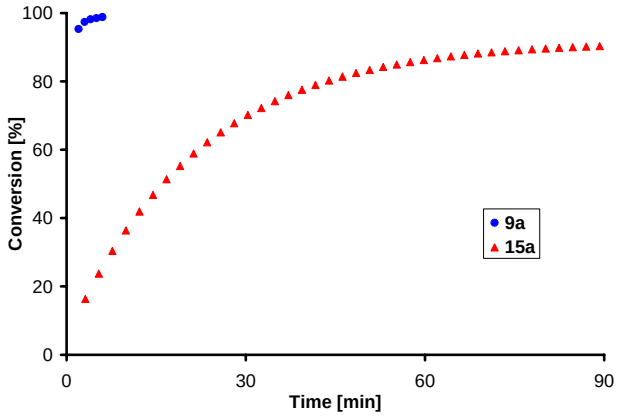
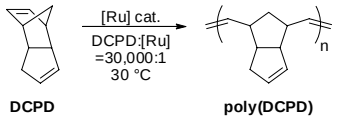


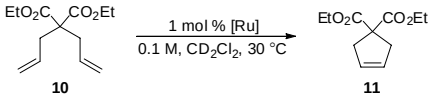
Figure S1. Conversion plot for RCM of **10** with **9a, 15a** (2.5 mol %, 30 ºC, 0.3M C_6D_6)

ROMP of Dicyclopentadiene (DCPD).



DCPD containing 3.5% of tricyclopentadiene (100 g) was polymerized by addition of catalyst (0.025 mmol, monomer/catalyst = 30,000) in a minimal amount of CH_2Cl_2 at 30 ºC. The reaction was monitored by measuring the polymerization exotherm with a temperature probe.

RCM of Diethyldiallyl Malonate (**10**) to test latency



A stock solution was prepared to deliver the catalyst solution. Inside a glovebox, a volumetric flask was charged with catalyst (0.016 mmol) and CD_2Cl_2 added to prepare 1.0 mL of stock solution (0.016 M). An NMR tube with a screwcap septum top was charged with catalyst stock solution (0.016 M, 50 µL, 0.80 µmol, 1.0 mol%) and CD_2Cl_2 (0.75 mL). The sample was equilibrated at 30 º C in the NMR probe before **10** (19.3 µL, 19.2 mg, 0.080 mmol, 0.1 M) was added via syringe. Data points were collected over an appropriate period of time using the Varian array function. The conversion to **11** was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ 2.61 (dt), with those in the product, δ 2.98 (s).

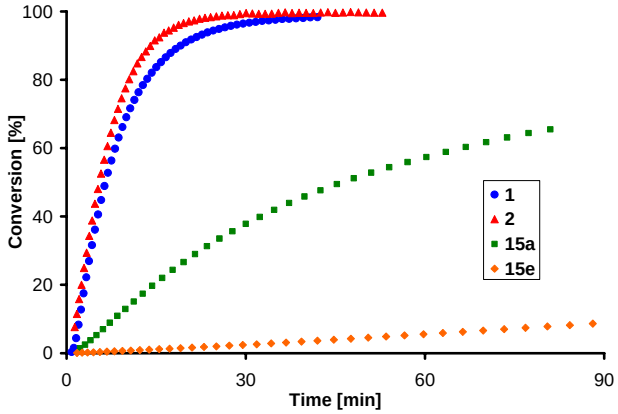
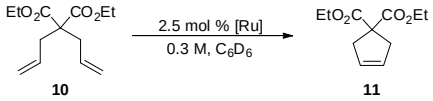


Figure S2. Conversion plot for RCM of **10** with **1**, **2**, **15a**, **15e** (1 mol %, 30 ºC, 0.1 M CD_2Cl_2)

Test of sulfur inhibition



A stock solution was prepared to deliver the catalyst solution. Inside a glovebox, a volumetric flask was charged with catalyst **17a** (0.026 mmol) and C_6D_6 added to prepare 2.0 mL of catalyst stock solution (0.013 M). A stock solution of SMe_2 was prepared by dissolving SMe_2 (30.3 μL, 25.6 mg, 0.41 mmol) and C_6D_6 added to prepare 2.0 mL of solution (0.21 M). An NMR tube with a screwcap septum top was charged with catalyst stock solution (0.013 M, 0.40 mL, 5.2 μmol, 2.5 mol%), SMe_2 stock solution (25 μL, 5.2 μmol) and C_6D_6 (0.25 mL). The sample was equilibrated at 60 ºC in the NMR probe before **10** (50 μL, 50 mg, 0.21 mmol, 0.3 M) was added via syringe. Data points were collected over an appropriate period of time using the Varian array function. The conversion to **11** was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ 2.84 (dt), with those in the product, δ 3.14 (s). Corresponding NMR samples were prepared with **17a** and **17c** in the absence of SMe_2.

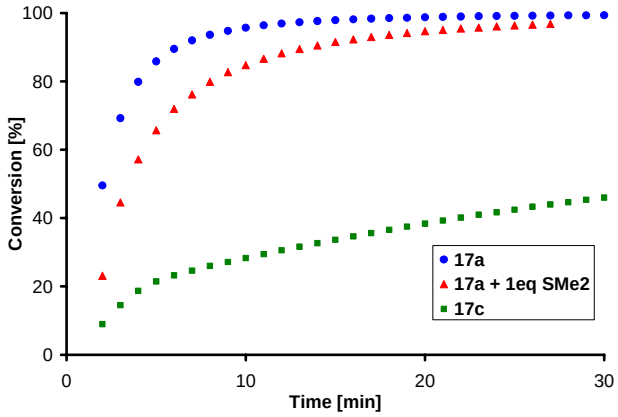


Figure S3. Conversion plot for RCM of **10** with **17a, 17a** + SMe_2**, 17c** (2.5 mol %, 65 ºC, 0.3M C_6D_6)

X-ray Crystallography

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number - **9a** (CCDC 278062), **15a** (CCDC 254980), **15e** (CCDC 272587), **17c** (CCDC 281471).

Table S1. Crystal data and structure refinement for 9a (CCDC 278062).

Empirical formula	$C_{34}H_{43}N_3Cl_2Ru$
Formula weight	665.68
Crystallization Solvent	THF/pentane
Crystal Habit	Olive brown
Crystal size	0.28 x 0.17 x 0.15 mm^3
Crystal color	Block

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 14476 reflections used in lattice determination	2.33 to 32.02°
Unit cell dimensions	a = 13.7555(7) Å b = 11.4276(6) Å β= 98.6480(10)° c = 20.4538(11) Å
Volume	3178.6(3) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/n$
Density (calculated)	1.391 Mg/m^3
F(000)	1384
Data collection program	Bruker SMART v5.630
θ range for data collection	1.67 to 27.55°
Completeness to θ = 27.55°	99.6 %
Index ranges	$-17 \leq h \leq 17$, $-14 \leq k \leq 14$, $-26 \leq l \leq 26$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	42974
Independent reflections	7309 [R_{int}= 0.0840]
Absorption coefficient	0.689 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9037 and 0.8305

Table S1 (cont.)

Structure solution and Refinement

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	7309 / 0 / 369
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.222
Final R indices [I>2σ(I), 5586 reflections]	R1 = 0.0593, *w*R2 = 0.1034
R indices (all data)	R1 = 0.0831, *w*R2 = 0.1064
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	2.767 and -1.273 e.Å^{-3}

Special Refinement Details

All peaks in the final electron difference Fourier map representing more than one electron lie within 1Å of Ru.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

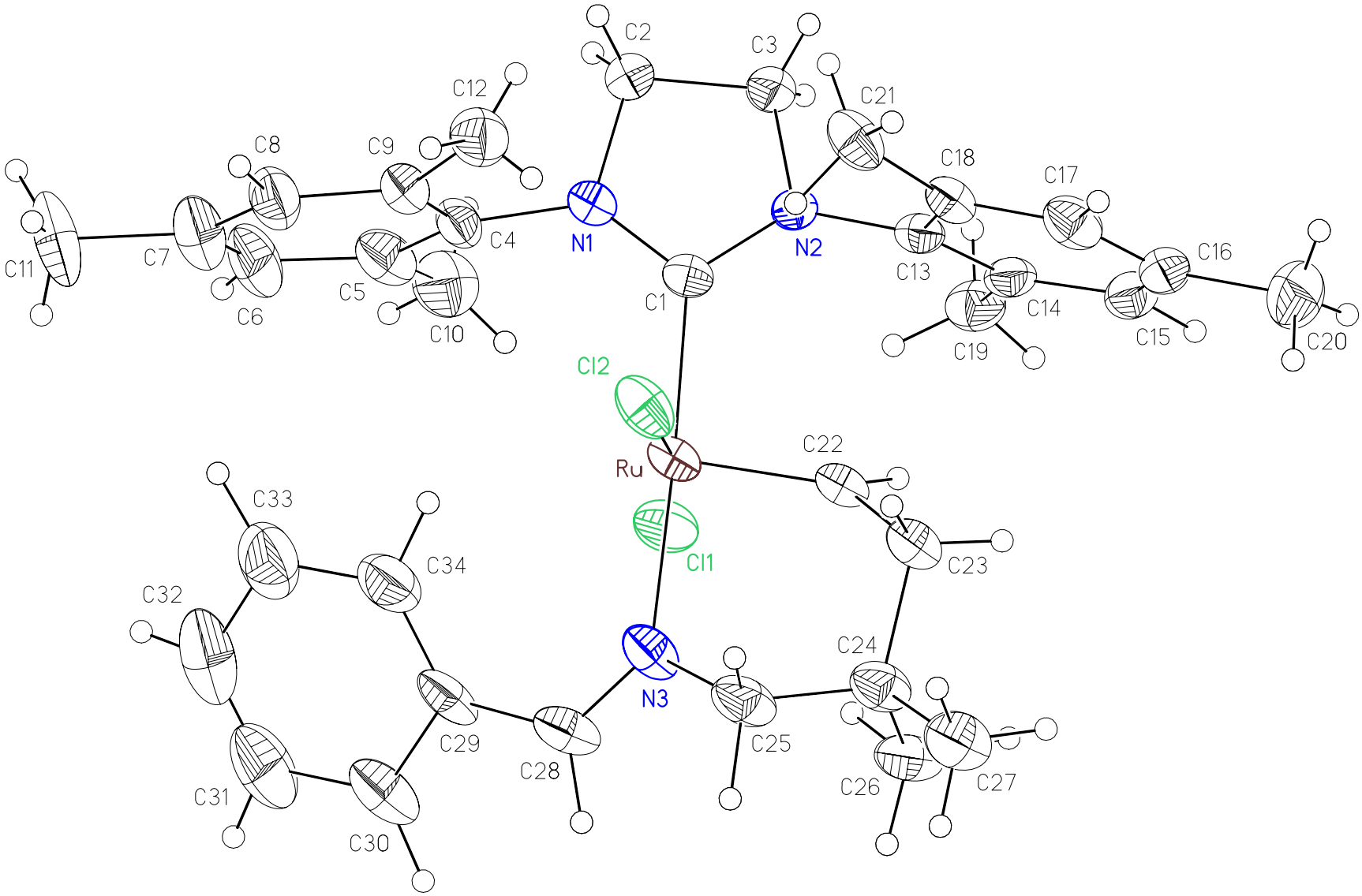


Figure S4. Labeled view of **9a**

Table S2. Crystal data and structure refinement for 15a (CCDC 254980).

Empirical formula	$C_{33}H_{41}N_3Cl_2Ru$
Formula weight	651.66
Crystallization Solvent	THF/pentane
Crystal Habit	Block
Crystal size	0.33 x 0.31 x 0.27 mm^3
Crystal color	Dichroic Green/brown

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 19323 reflections used in lattice determination	2.32 to 45.20°
Unit cell dimensions	a = 13.5715(4) Å b = 11.6530(4) Å β= 100.8070(10)° c = 20.2953(6) Å
Volume	3152.75(17) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/n$
Density (calculated)	1.373 Mg/m^3
F(000)	1352
θ range for data collection	1.67 to 47.34°
Completeness to θ = 47.34°	80.2 %
Index ranges	$-28 \leq h \leq 24$, $-24 \leq k \leq 24$, $-41 \leq l \leq 41$
Data collection scan type	ω scans at 3 ϕ settings for 2θ=-28º and 2 for 2θ=-70º
Reflections collected	62469
Independent reflections	23433 [R_{int}= 0.0583]
Absorption coefficient	0.693 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.8350 and 0.8036

Table S2 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	23433 / 0 / 390
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.358
Final R indices [I>2σ(I), 13403 reflections]	R1 = 0.0514, *w*R2 = 0.0848
R indices (all data)	R1 = 0.0974, *w*R2 = 0.0898
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.004
Average shift/error	0.000
Largest diff. peak and hole	2.906 and -2.223 e.Å^{-3}

Special Refinement Details

The molecule exhibits disorder in the link between C22 and N3 where both possible pucker orientations are observed. The methylene carbon of the linkage (C23) adopts two different positions which correlate to alternate positions for the two methyl groups (C25 and C26) bonded to C24. The ratio between both conformations is 0.68:0.32 (see Table 2). The third figure illustrates both, the minor component in blue with dashed bonds.

All hydrogen atoms were restrained to ride the respective carbon but methyl groups were allowed to rotate about the C-C bond to provide maximum fit to the observed electron density. A cluster of difference electron density peaks (greater than 1e-/Å^3) appear within 1Å of Ru in the final map.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

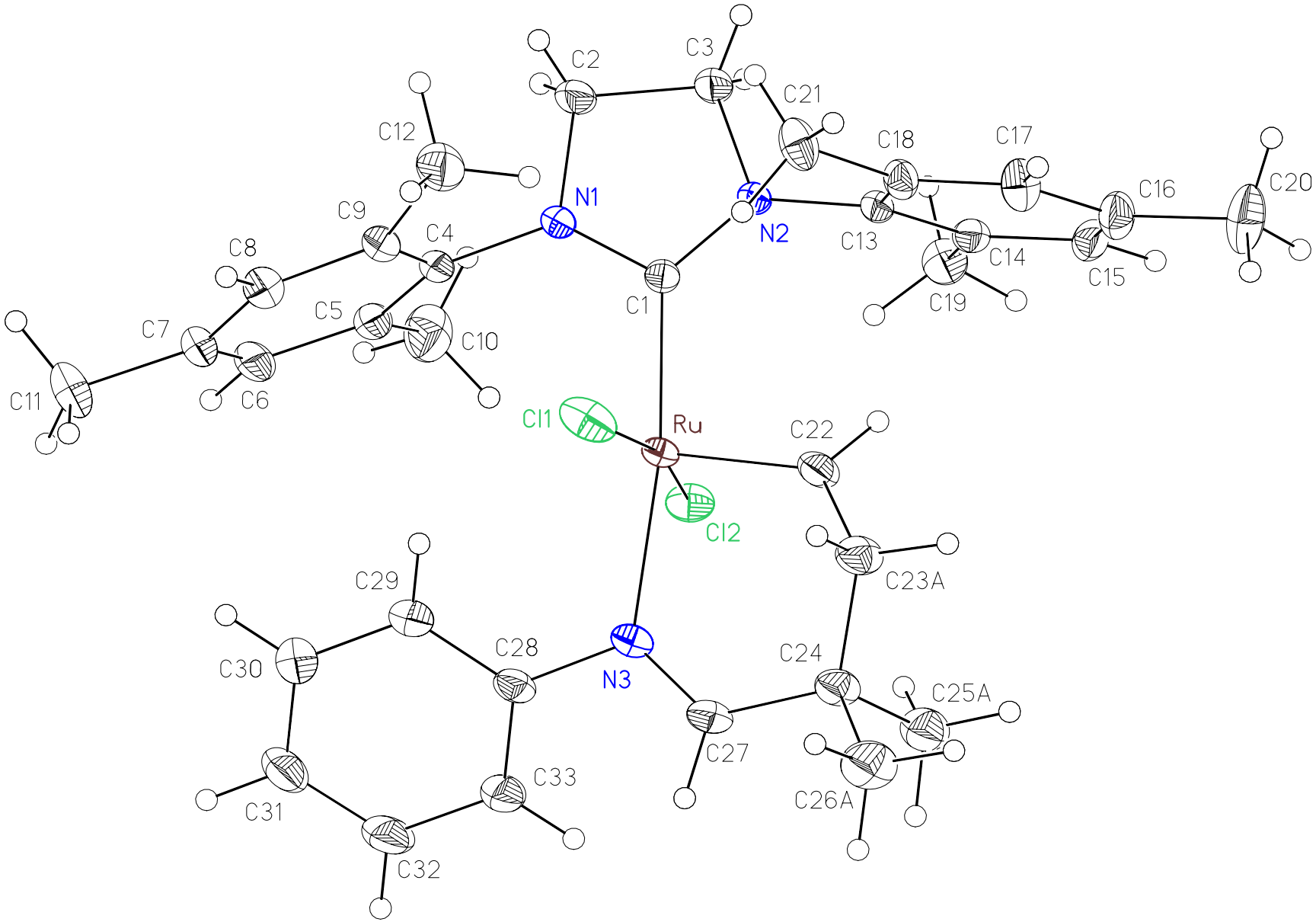


Figure S5. Labeled view of **15a**, conformation A

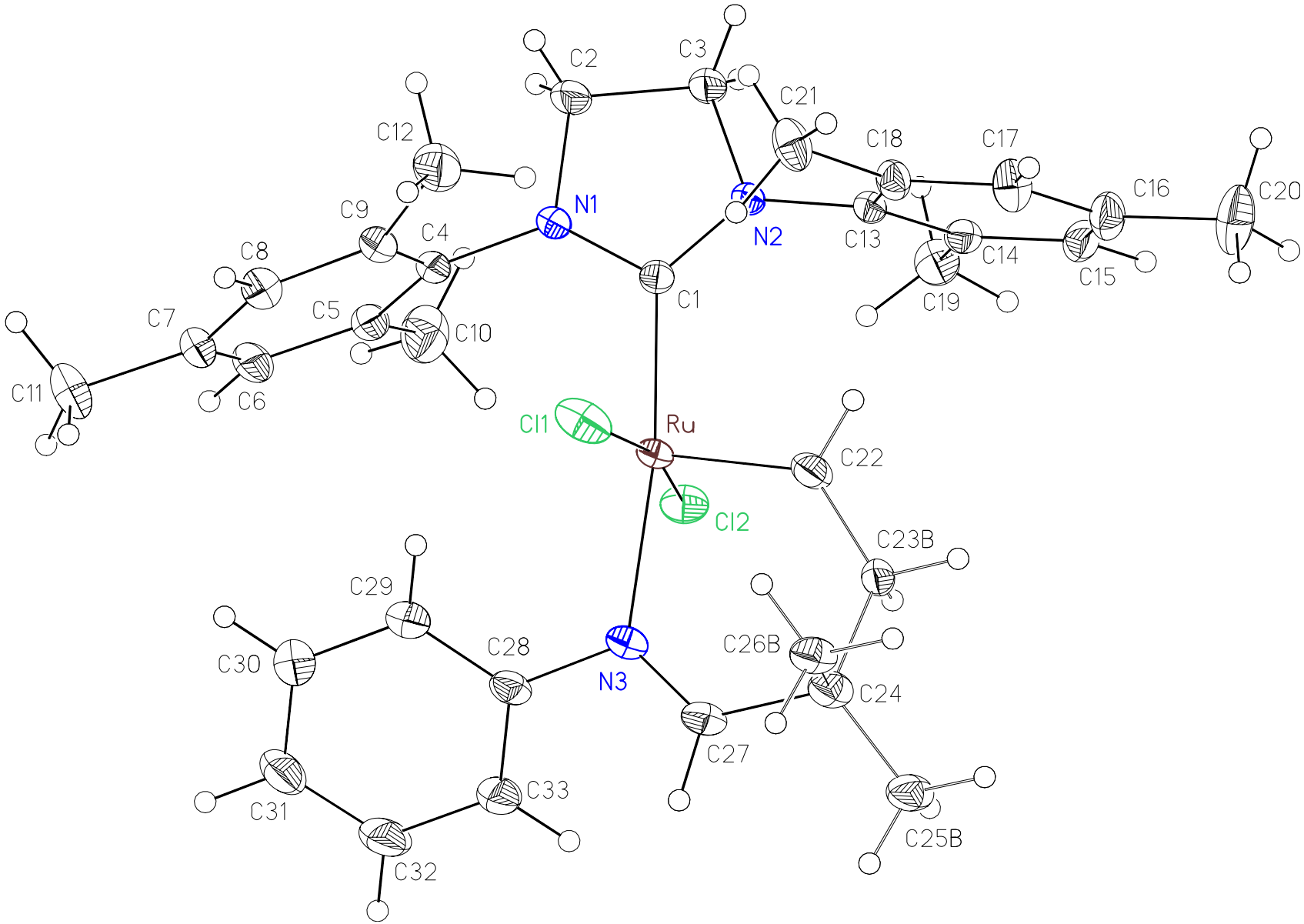


Figure S6. Labeled view of **15a**, conformation B

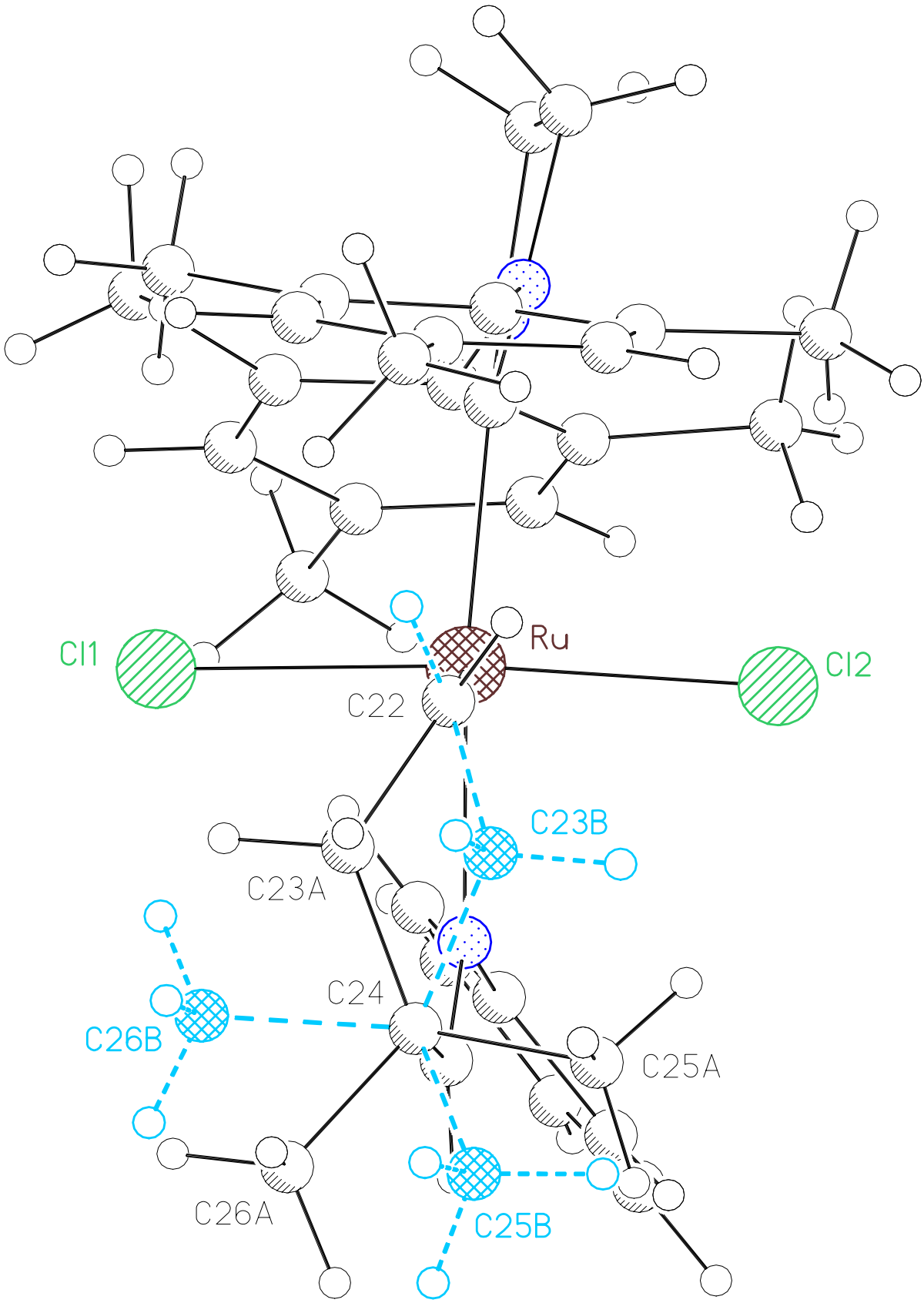


Figure S7. Labeled side view of **15a**, conformations A and B overlaid

Table S3. Crystal data and structure refinement for 15e (CCDC 272587).

Empirical formula	$C_{28}H_{39}N_3Cl_2Ru$
Formula weight	589.59
Crystallization Solvent	THF/hexanes
Crystal Habit	Fragment
Crystal size	0.33 x 0.20 x 0.10 mm^3
Crystal color	Trichroic - green/purple/blue

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 10966 reflections used in lattice determination	2.26 to 32.71°
Unit cell dimensions	a = 14.9244(9) Å b = 16.4672(10) Å c = 11.2788(7) Å
Volume	2771.9(3) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	Pnnm
Density (calculated)	1.413 Mg/m^3
F(000)	1224
Data collection program	Bruker SMART v5.630
θ range for data collection	1.84 to 33.52°
Completeness to θ = 33.52°	95.0 %
Index ranges	$-20 \leq h \leq 22$, $-24 \leq k \leq 25$, $-17 \leq l \leq 17$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	44687
Independent reflections	5402 [R_{int}= 0.1233]
Absorption coefficient	0.779 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9261 and 0.7830

Table S3 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	5402 / 0 / 209
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.576
Final R indices [I>2σ(I), 3250 reflections]	R1 = 0.0575, *w*R2 = 0.0784
R indices (all data)	R1 = 0.1089, *w*R2 = 0.0843
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.010
Average shift/error	0.001
Largest diff. peak and hole	1.599 and -2.701 e.Å^{-3}

Special Refinement Details

The molecule sits on a special position, astride the mirror plane at *z*=0. Therefore, atoms Ru(1), N(1), N(2), N(3), C(1), C(4), C(7), C(9), C(10), C(13), C(15), C(16), C(21) and C(22) have coordinates with *z*=0; the mirror plane generates equivalent positions for all other atoms. For Cl(1), C(5), C(6), C(8), C(11), C(12) and C(14) the mirror supplies positions to complete the unique molecule. For C(2), C(3), C(17), C(18), C(19) and C(20) the mirror produces an alternate conformation of the molecule.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

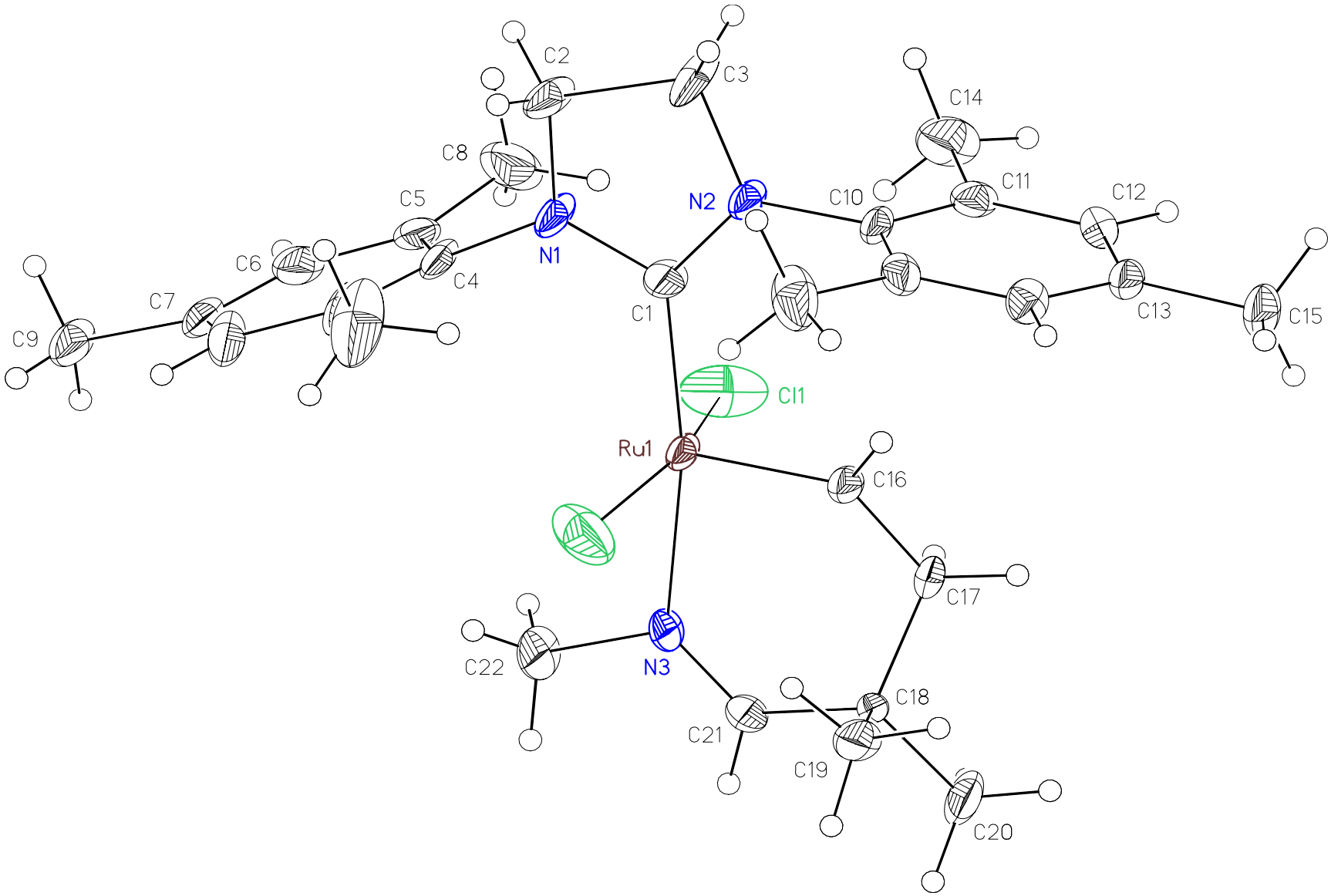


Figure S8. Labeled view of **15e**

Table S4. Crystal data and structure refinement for 17c (CCDC 281471).

Empirical formula	$C_{30}H_{43}N_3SCl_2Ru \cdot ½(C_4H_8O)$
Formula weight	685.76
Crystallization Solvent	Pentane/THF
Crystal Habit	Block
Crystal size	0.31 x 0.29 x 0.29 mm^3
Crystal color	Greenblue

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 42363 reflections used in lattice determination	2.22 to 37.63°
Unit cell dimensions	a = 11.1365(3) Å b = 17.4341(4) Å β= 93.7070(10)° c = 34.7895(9) Å
Volume	6740.4(3) $Å^3$
Z	8
Crystal system	Monoclinic
Space group	Pc
Density (calculated)	1.352 Mg/m^3
F(000)	2864
θ range for data collection	1.17 to 38.31°
Completeness to θ = 38.31°	88.6 %
Index ranges	$-18 \leq h \leq 18$, $-30 \leq k \leq 30$, $-52 \leq l \leq 52$
Data collection scan type	ω scans at 5 ϕ settings
Reflections collected	129948
Independent reflections	58933 [R_{int}= 0.0684]
Absorption coefficient	0.712 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.8201 and 0.8094

Table S4 (cont.)

Structure solution and Refinement

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XS v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	58933 / 372 / 1573
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.302
Final R indices [I>2σ(I), 41916 reflections]	R1 = 0.0580, *w*R2 = 0.0946
R indices (all data)	R1 = 0.0900, *w*R2 = 0.1005
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Absolute structure parameter	0.044(18)
Largest diff. peak and hole	2.556 and -2.245 e.$Å^{-3}$

Special Refinement Details

There are four Ru molecules and two molecules of THF in the asymmetric unit. An approximate center of symmetry exists at *x*=0.45, *y*=0.25 and *z*=0.38 and if actually present would result in space group $P2_1/c$. The four Ru molecules are identical with the exception that one site (molecule C) is disordered about an approximate mirror plane through C(1C), Ru(3), Cl(1C) and Cl(2C) to give molecule G (see Figures 3-7.). The atomic positions of S(1C), N(3C) and C(22C)-C(30C) were modeled to give an approximate mirror image composed of atomic positions for S(1G), N(3G) and C(22G)-C(30G) in a ratio of 61:39 (see Table 1.)

Restraints were required to maintain satisfactory geometry in the disordered ligand of molecule G and were applied as follows; 1) all similar bonds (1-2 distances) in each molecule were assigned a target value, 2) all similar angles (1-3 distances) were assigned a target value and 3) target values were refined as free variables during least squares. As a result the model target values are an average of the distances in all four molecules. In this way the model is allowed to define its own geometry without introducing undo bias. The assignment and final target values follow;

Bond type	Atoms	Distance
Ru=C*sp*^{2}	Ru*-C(22*)	1.884(5)
C*sp*^{2}-C*sp*^{3}, N-C*sp*^{3}	C(22*)-C(23*), C(24*)-C(27*) and N(3*)-C(28*)	1.497(5)
C*sp*^{3}-C*sp*^{3}	C(23*)-C(24*), C(24*)-C(25*), C(24*)-C(26*) and C(28*)-C(29*)	1.538(3)
N=C*sp*^{2}	N(3*)-C(27*)	1.277(5)
S-C*sp*^{3}	S(1*)-C(29*) and S(1*)-C(30*)	1.802(6)
Ru-S	Ru*-S(1*)	2.561(2)
Ru-Cl	Ru*-Cl(*)	2.409(4)

The anisotropic displacement parameters (ADP's) of the disordered atoms were restrained to simulate isotropic

behavior. The same restraint was applied to the ADP's of the THF molecules and the occupancy of both were refined together as one value, Occ=0.89 (see Table 1.). Additionally, the ADP's for C(22C) and C(23C) were constrained to be equal. All hydrogen atoms were restrained to ride the corresponding carbon with optimized geometry.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

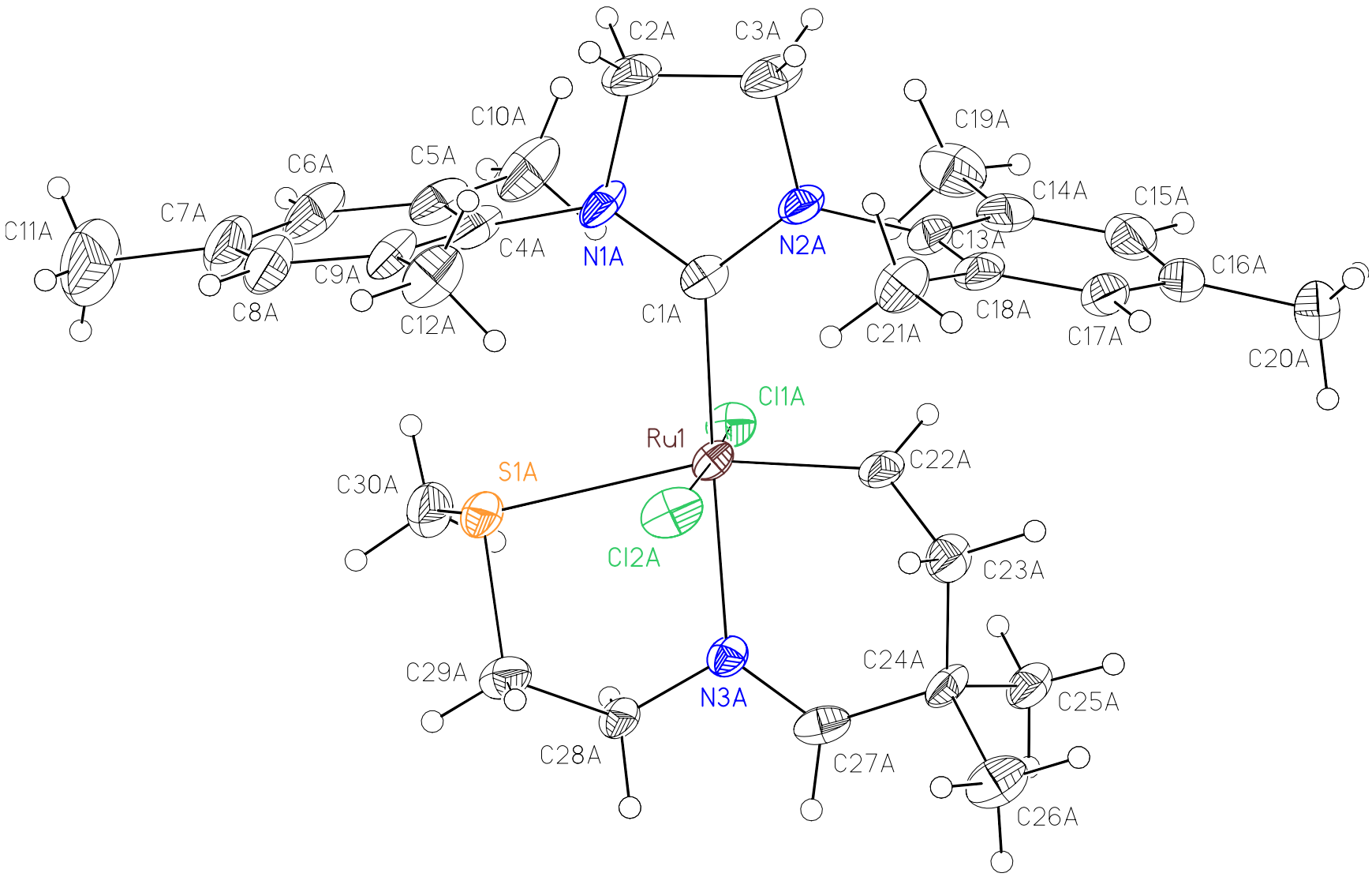


Figure S9. Labeled view of **17c**, molecule A

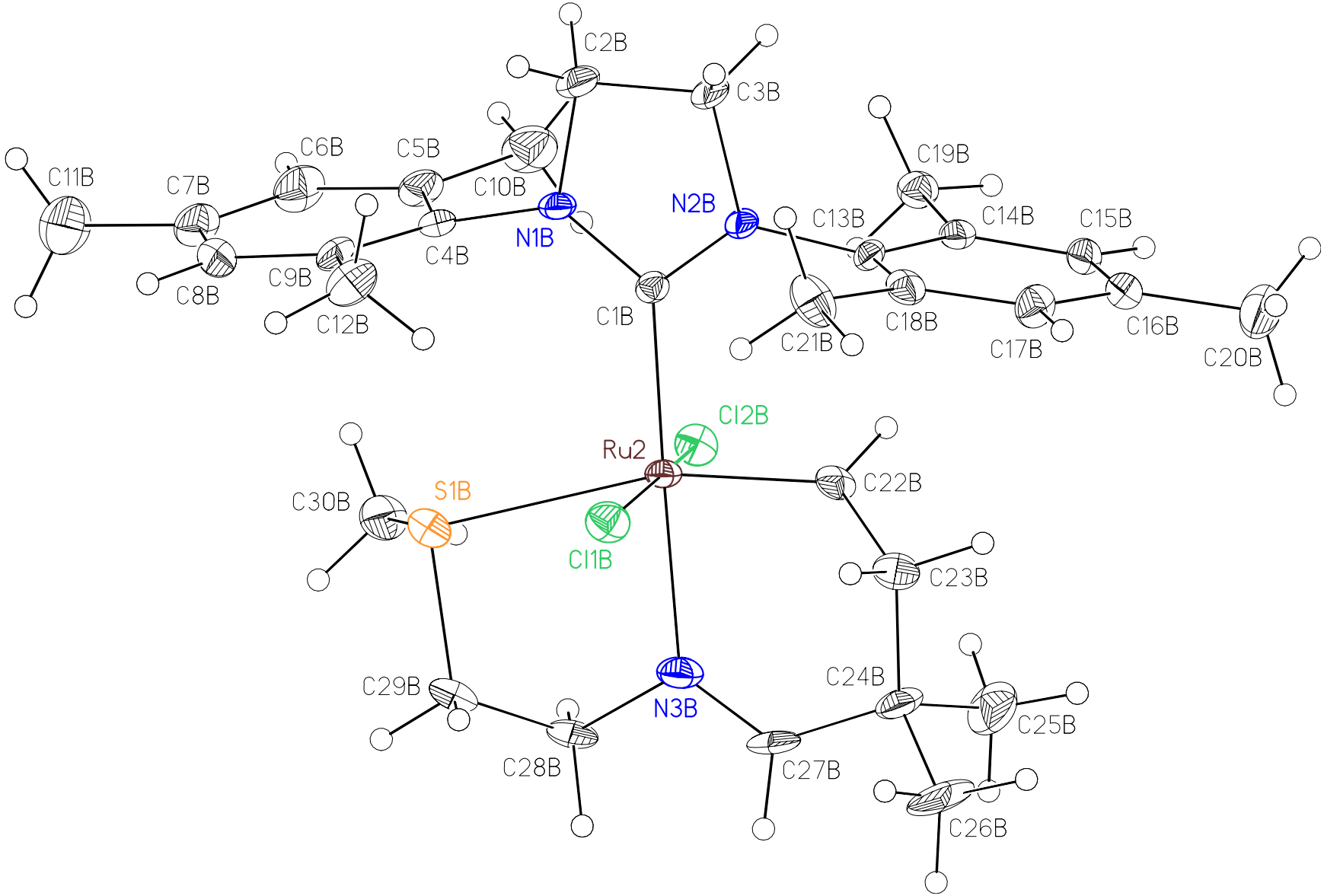


Figure S10. Labeled view of **17c**, molecule B

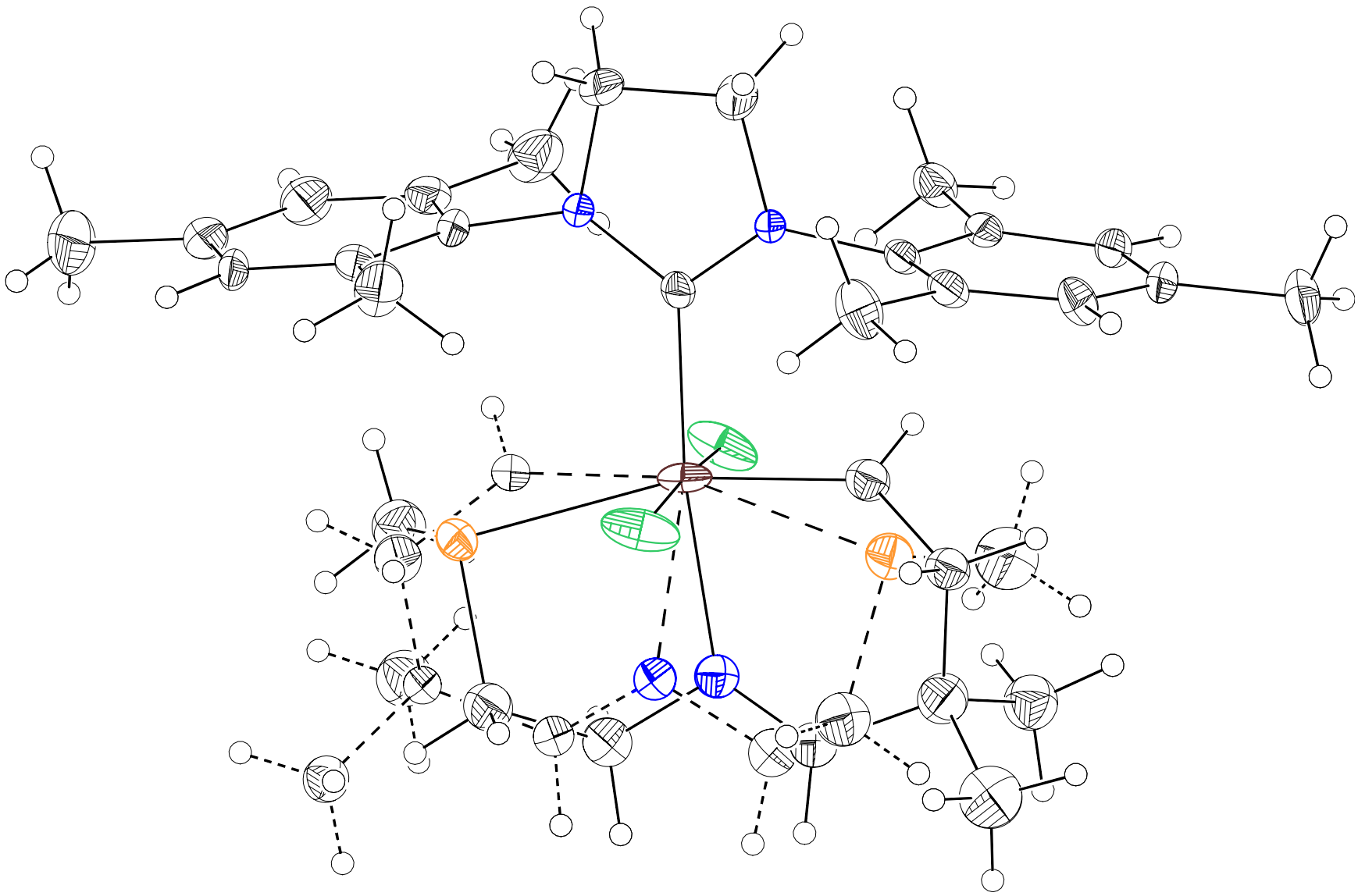


Figure S11. Unlabeled view of **17c**, molecule C with minor component (molecule G, dashed lines).

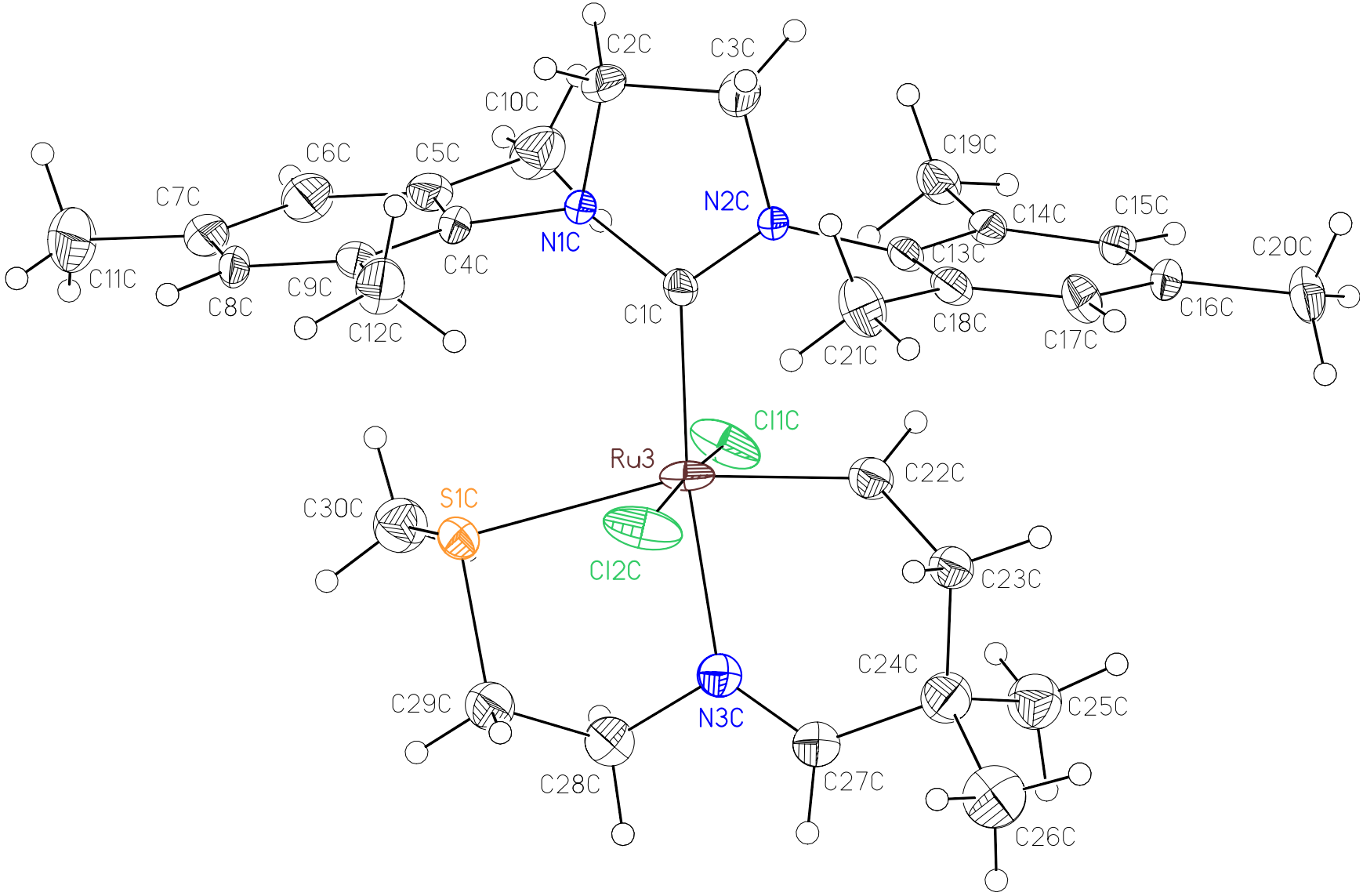


Figure S12. Labeled view of **17c**, molecule C (major component).

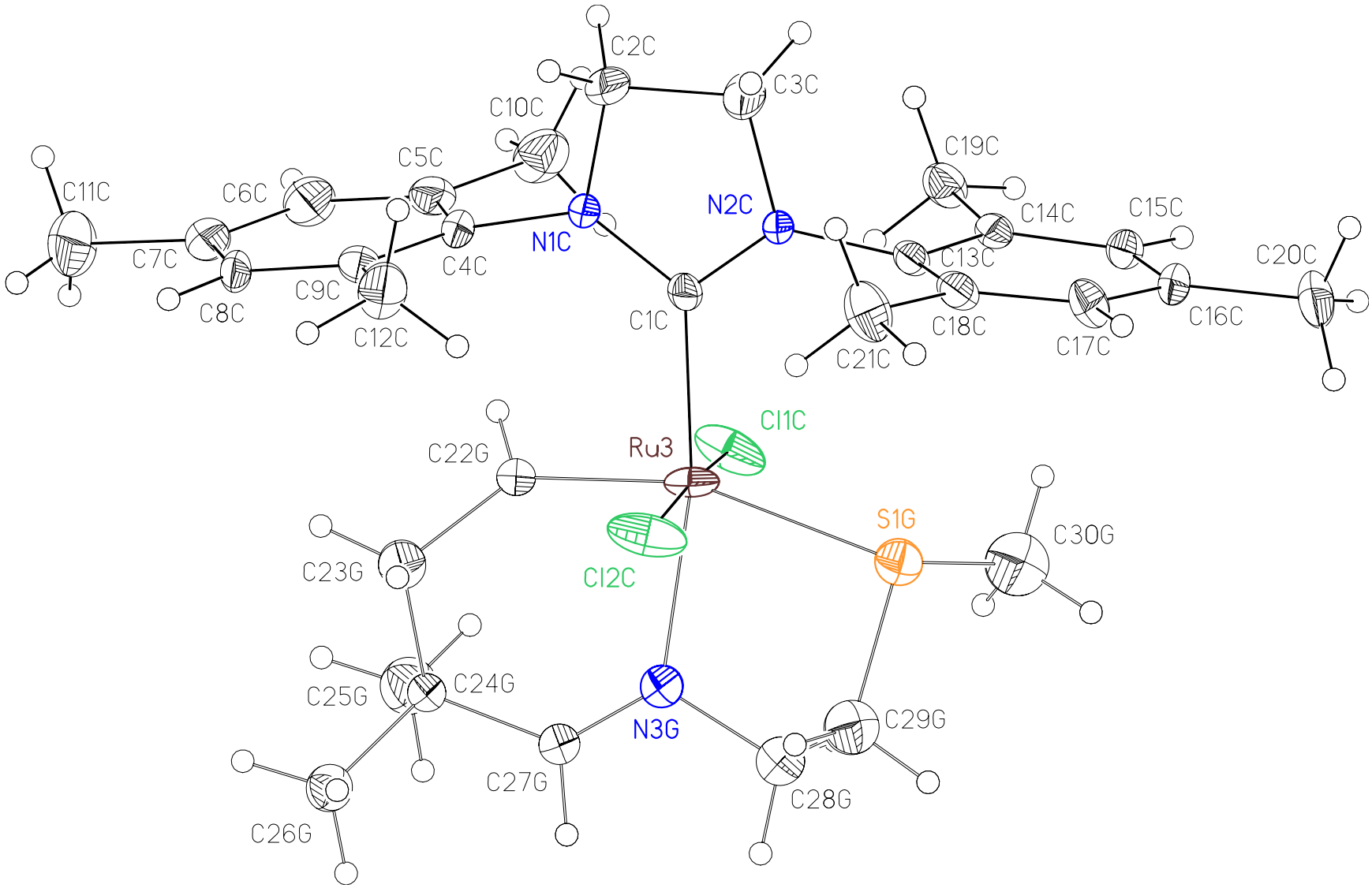


Figure S13. Labeled view of **17c**, molecule G (minor component).

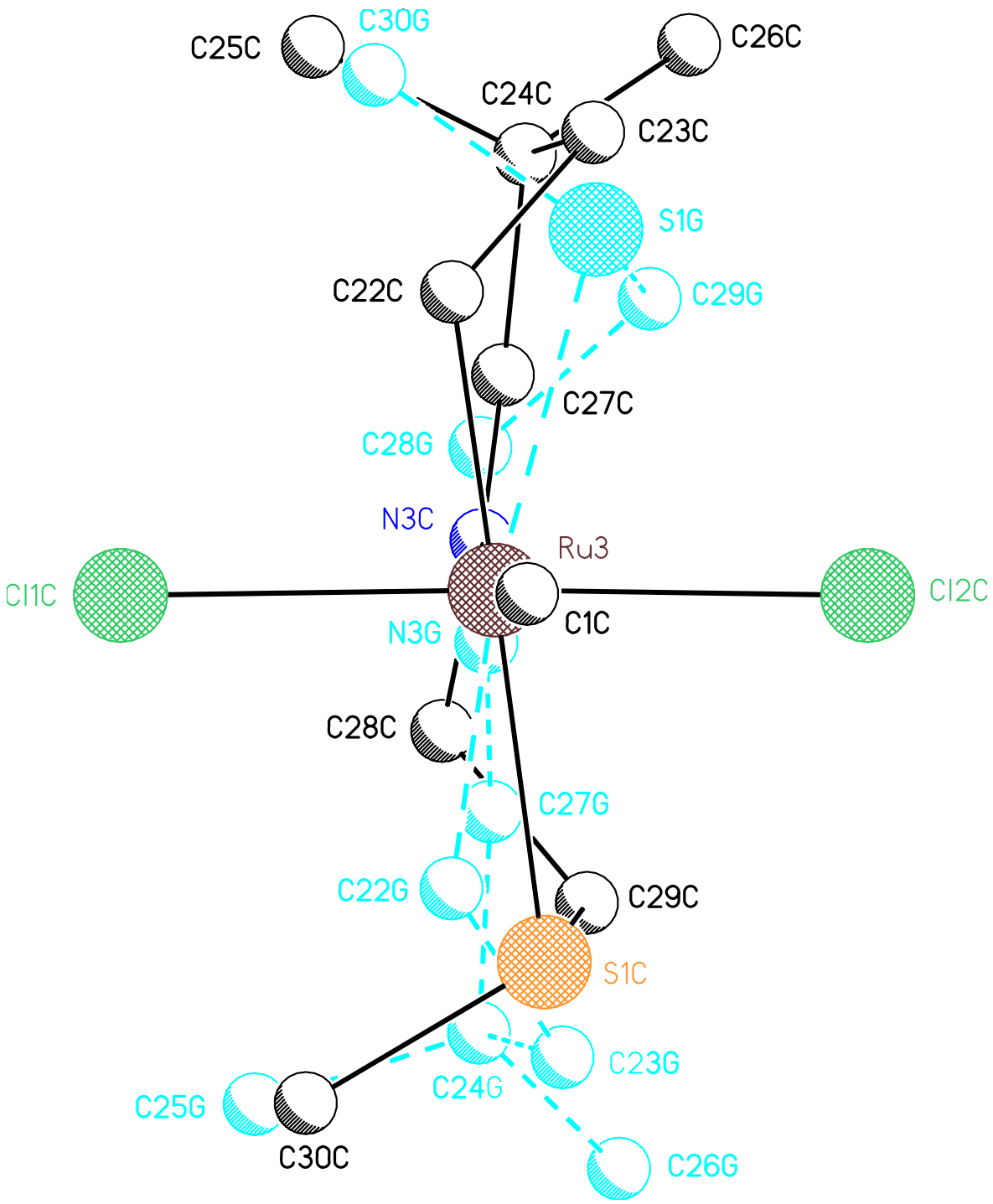


Figure S14. Labeled view of 17c, disordered ligand (hydrogens omitted). The mirror plane is horizontal, normal to the page. The minor component is shown in cyan with dashed bonds.

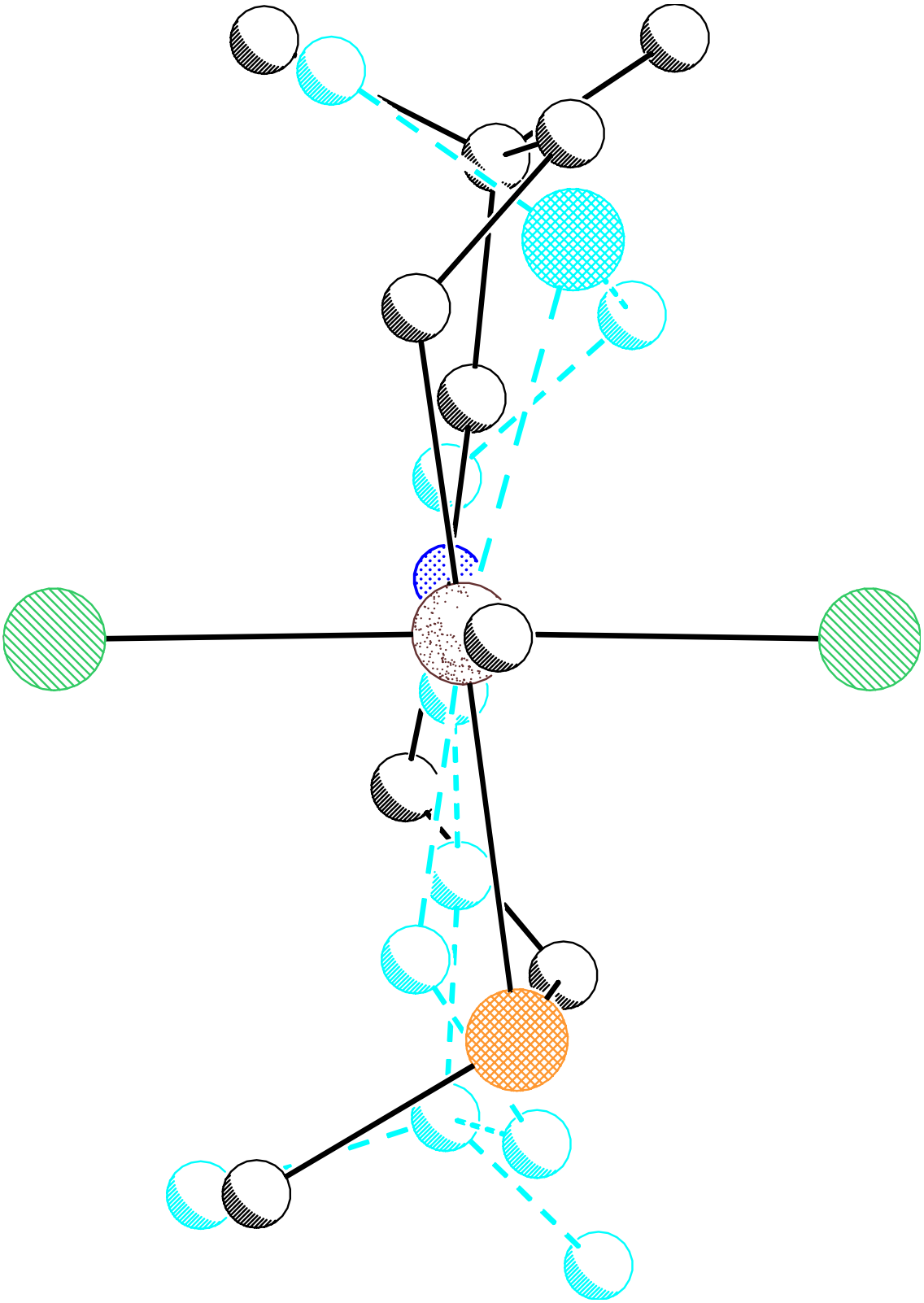


Figure S15. Unlabeled view of **17c** disordered ligand (hydrogens omitted). The mirror plane is horizontal, normal to the page. The minor component is shown in cyan with dashed bonds.

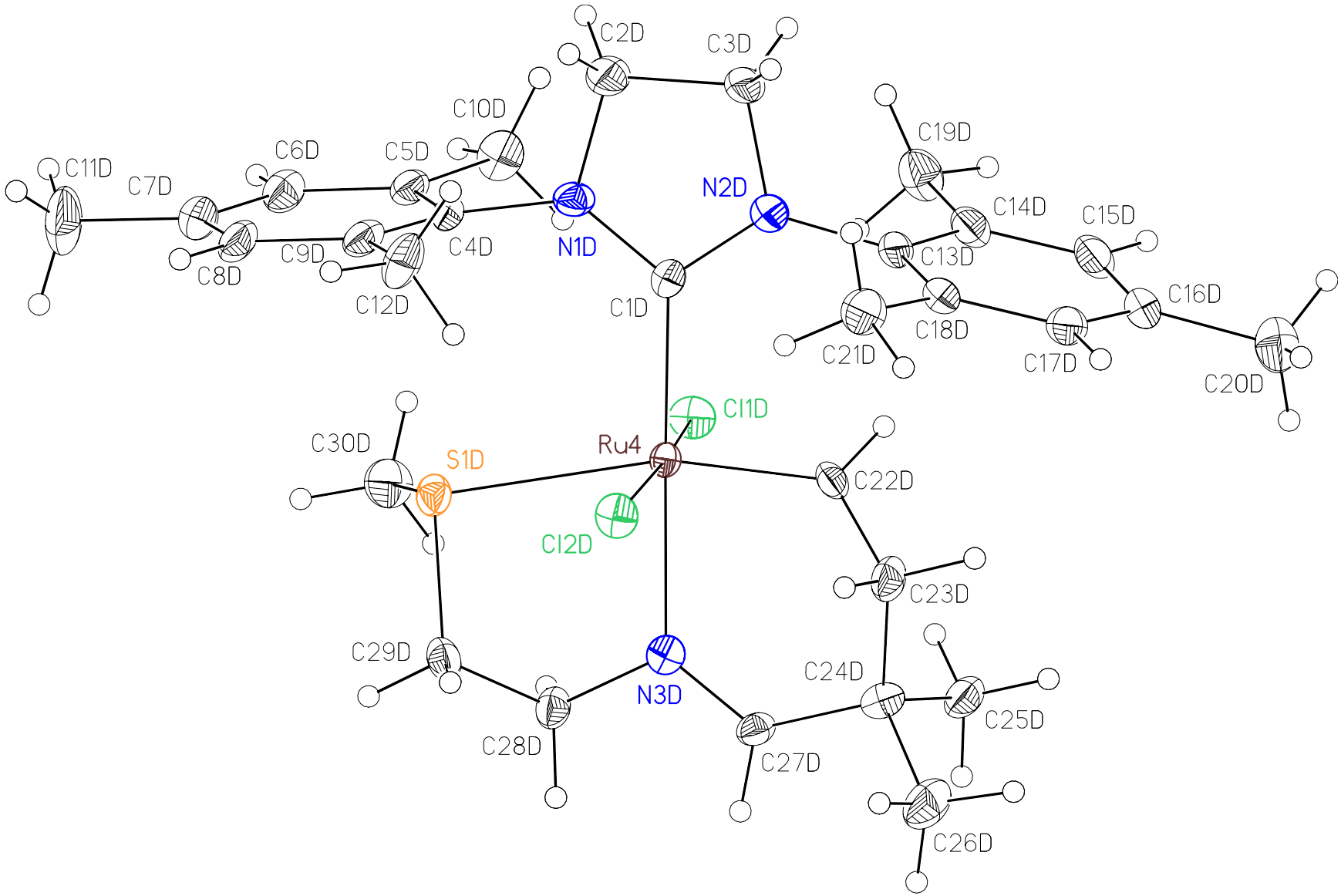


Figure S16. Labeled view of **17c**, molecule D