

Supporting Information for:

Decomposition of A Key Intermediate In Ruthenium Catalyzed Olefin Metathesis Reactions

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General Considerations. Manipulation of organometallic compounds was performed using standard Schlenk techniques under an atmosphere of dry argon or in a nitrogen-filled Vacuum Atmospheres drybox ($O_2 < 2$ ppm). NMR spectra were recorded on a Varian Inova (499.85 MHz for 1H ; 202.34 MHz for ^{31}P ; 125.69 MHz for ^{13}C) or on a Varian Mercury 300 (299.817 MHz for 1H ; 121.39 MHz for ^{31}P ; 74.45 MHz for ^{13}C). ^{31}P NMR spectra were referenced using H_3PO_4 ($\delta = 0$ ppm) as an external standard. Elemental analyses were performed at Desert Analytics (Tucson, AZ). Mass spectra were recorded on JEOL JMS 600H spectrophotometer. GC spectra were recorded on Hewlett-Packard 5970B MSD with 5890 GC.

Materials and Methods. Benzene, benzene- d_6 , pentane, and methylene chloride were dried by passage through solvent purification columns.¹ CD_2Cl_2 was dried by vacuum transfer from CaH_2 . All solvents are degassed by standard procedure. Allylbenzene was obtained from Aldrich and used as received. $(IMesH_2)(PCy_3)(Cl)_2Ru=CH_2$ was prepared according to literature procedure.²

¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

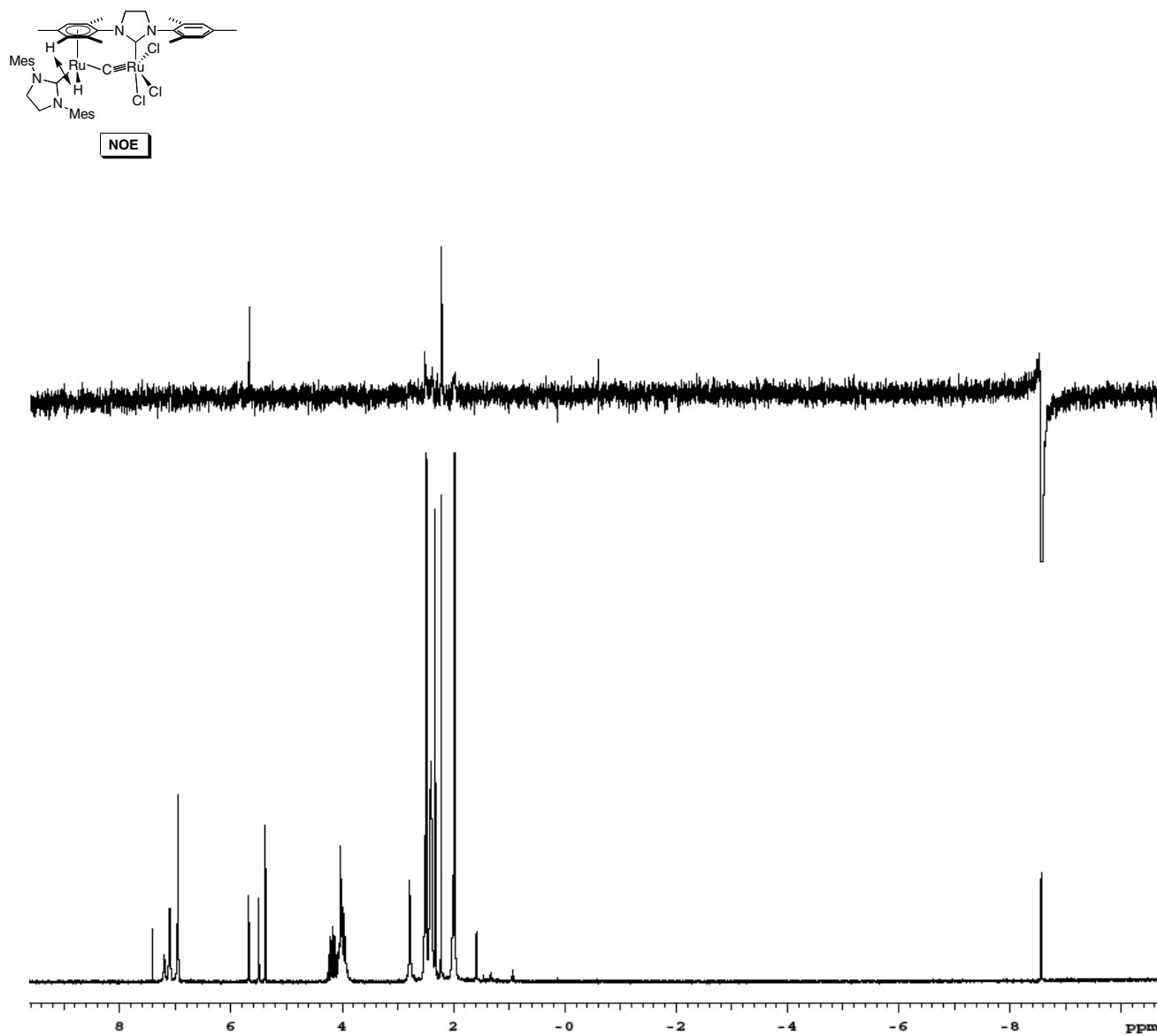
² Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543-6554.

Decomposition of complex 4. Complex **4** (48.3 mg, 0.06 mmol) was dissolved in benzene (2.7 mL) in a sealed tube. The reaction mixture was heated to 55 °C. Precipitation of orange-yellow crystalline solid was observed after 7 hrs. After 72 hrs, the precipitates were filtered, washed with benzene and dried under vacuum to afford complex **8** (13.2 mg, 46%). Methyltricyclohexylphosphonium chloride **9** was obtained along with some unidentified decomposed ruthenium species by the addition of pentane (5 mL) to the filtered benzene solution.

Dinuclear ruthenium complex 8. ^1H NMR (CD_2Cl_2): 7.14 (s, 1H), 7.05 (s, 1H), 7.04 (s, 1H), 6.90 (s, 3H), 5.62 (s, 1H), 5.44 (s, 1H), 4.19-4.06 (m, 2H), 3.99-3.86 (m, 6H), 2.73 (br s, 3H), 2.46 (br s, 3H), 2.45 (s, 3H), 2.43 (s, 3H), 2.4-2.3 (br, 9H), 2.27 (s, 3H), 2.17 (s, 3H), 1.96 (br s, 3H), 1.93 (s, 3H), 1.91 (s, 3H), -8.61 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): 413.98, 222.73, 207.87, 141.31, 140.11, 139.64, 139.04, 138.88, 138.86, 138.71, 138.44, 137.68, 135.13, 134.44, 133.65, 131.88, 130.60, 129.93, 129.89, 128.90, 128.68, 128.28, 120.30, 111.99, 111.85, 104.38, 100.60, 98.20, 51.63, 51.37, 48.81, 21.40, 20.99, 20.6-20.5 (br, m), 19.89, 19.25, 19.14, 18.53, 16.95. Anal. Calcd for $\text{C}_{43}\text{H}_{53}\text{N}_4\text{Cl}_3\text{Ru}_2$: C, 55.27; H, 5.72; N, 6.00. Found: C, 55.58; H, 5.64; N, 5.64. HRMS analysis (FAB) m/z : Calcd $[\text{M}^+]$ 936.1424, found 936.1434.

Methyltricyclohexylphosphonium Chloride 9. ^1H NMR (C_6D_6): 2.61 (m, $(\text{CHC}_5\text{H}_{10})_3\text{-PCH}_3^+$, 3H), 2.42 (d, 3H, $\text{CH}_3\text{-PCy}_3^+$, $J_{\text{HP}} = 12.6\text{Hz}$), 1.85-1.00 (m, 30H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 30.43 (d, $(\text{CHC}_5\text{H}_{10})_3\text{-PCH}_3^+$, $J_{\text{CP}} = 42.6\text{Hz}$), 27.11 (d, $J_{\text{CP}} = 3.1\text{Hz}$), 26.47 (d, $J_{\text{CP}} = 12.6\text{ Hz}$), 25.86, 1.5 (d, $\text{CH}_3\text{-PCy}_3^+$, $J_{\text{CP}} = 47.6\text{Hz}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): 34.5 ppm. HRMS analysis (FAB) m/z : Calcd for $\text{C}_{19}\text{H}_{36}\text{P}$ $[\text{M}^+]$: 295.2555, found: 295.2557.

Figure S1. NOE and ^1H NMR spectra of **8**



Isomerization reaction of allylbenzene. Allylbenzene (17.1 mg, 0.15 mmol) and complex **8** (2.0mg, 1.5 mol %) were dissolved in CD_2Cl_2 (0.6 mL) in an NMR tube fitted with a screw cap. The resulting solution was heated to 40 °C and reaction was monitored by measuring the peak heights of allylic protons of allylbenzene and methyl protons of 1-phenyl-1-propene by ^1H NMR spectroscopy. After 1 day, yield of 1-phenyl-1-propene was determined by GC (76%, trans:cis = 8:1).

Crystal Structure Analysis of Complex 8

Contents

Table S1. Crystal data

Figures

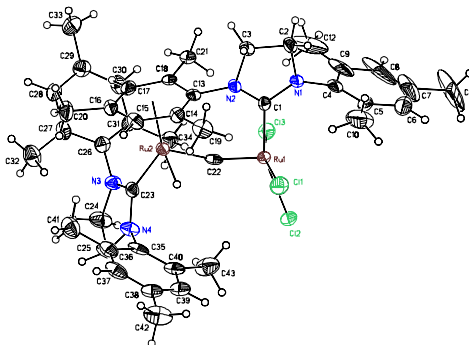
Table S2. Atomic Coordinates

Table S3. Selected bond distances and angles

Table S4. Full bond distances and angles (for deposit)

Table S5. Anisotropic displacement parameters

Table S6. Observed and calculated structure factors (for deposit)



Note: 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 223170.

Table S1. Crystal data and structure refinement for complex 8 (CCDC 223170).

| | |
|-------------------------|---|
| Empirical formula | C ₄₁ H ₅₃ Cl ₃ N ₄ Ru ₂ · 1½(C ₆ H ₆) |
| Formula weight | 1051.55 |
| Crystallization Solvent | Benzene |
| Crystal Habit | Needle |
| Crystal size | 0.38 x 0.07 x 0.04 mm ³ |
| Crystal color | Yellow/orange |

Data Collection

| | | |
|---|--|-------------------|
| Preliminary Photos | Rotation | |
| Type of diffractometer | Bruker SMART 1000 | |
| Wavelength | 0.71073 Å MoKα | |
| Data Collection Temperature | 100(2) K | |
| θ range for 10984 reflections used in lattice determination | 2.39 to 27.68° | |
| Unit cell dimensions | a = 12.4536(9) Å b = 16.1001(11) Å c = 24.7739(17) Å | β = 102.7980(10)° |
| Volume | 4843.9(6) Å ³ | |
| Z | 4 | |
| Crystal system | Monoclinic | |
| Space group | P2 ₁ /c | |
| Density (calculated) | 1.442 Mg/m ³ | |
| F(000) | 2164 | |
| Data collection program | Bruker SMART v5.054 | |
| θ range for data collection | 1.52 to 28.43° | |
| Completeness to θ = 28.43° | 92.5 % | |
| Index ranges | -15 ≤ h ≤ 16, -20 ≤ k ≤ 21, -32 ≤ l ≤ 32 | |
| Data collection scan type | ω scans at 3 φ settings | |
| Data reduction program | Bruker SAINT v6.022 | |
| Reflections collected | 42525 | |
| Independent reflections | 11284 [R _{int} = 0.0770] | |
| Absorption coefficient | 0.828 mm ⁻¹ | |
| Absorption correction | None | |
| Max. and min. transmission | 0.9676 and 0.7437 | |

Table S1 (cont.)**Structure solution and Refinement**

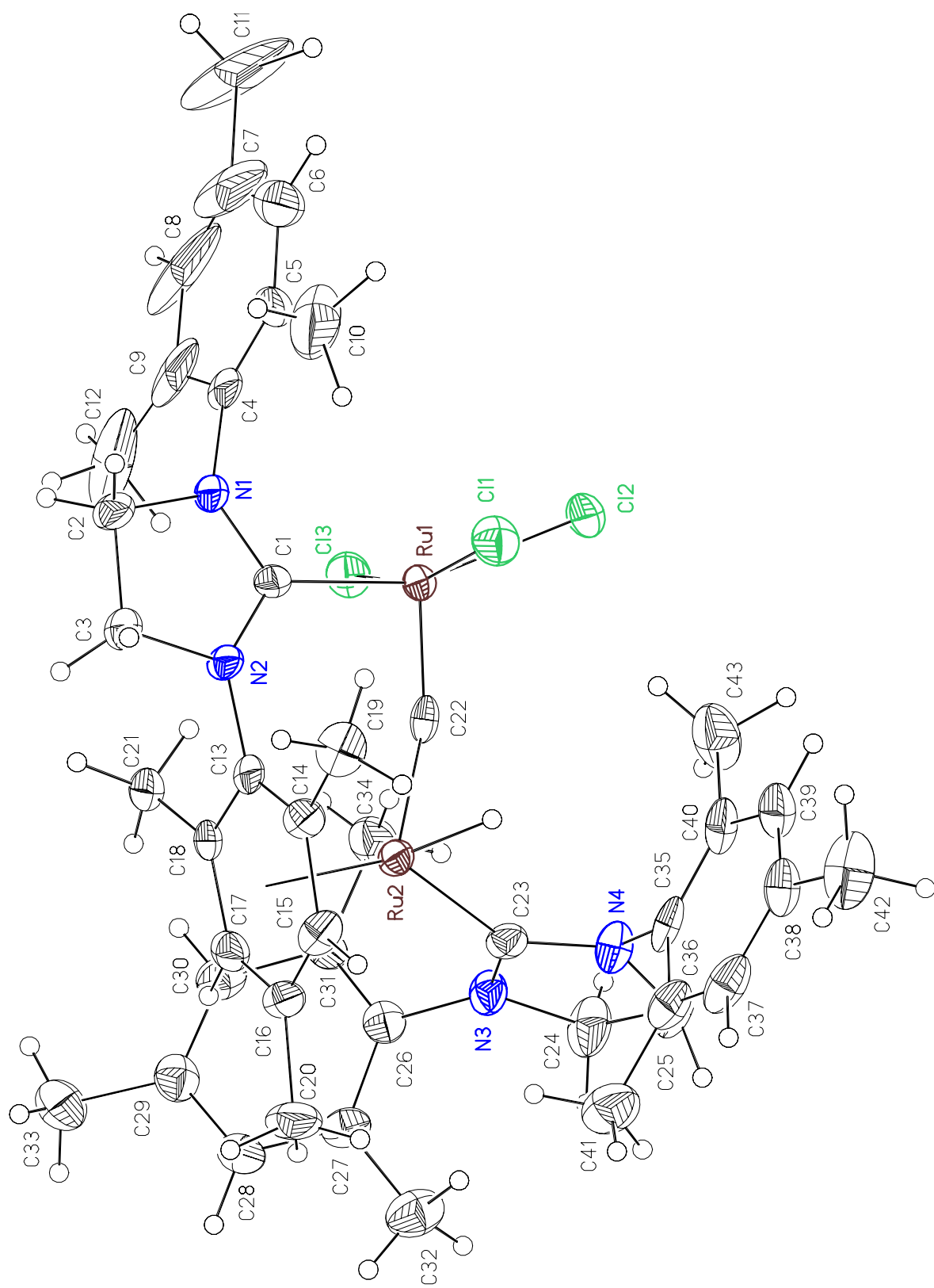
| | |
|--|---------------------------------------|
| Structure solution program | SHELXS-97 (Sheldrick, 1990) |
| Primary solution method | Patterson method |
| Secondary solution method | Difference Fourier map |
| Hydrogen placement | Difference Fourier map |
| Structure refinement program | SHELXL-97 (Sheldrick, 1997) |
| Refinement method | Full matrix least-squares on F^2 |
| Data / restraints / parameters | 11284 / 0 / 554 |
| Treatment of hydrogen atoms | Mixed |
| Goodness-of-fit on F^2 | 1.396 |
| Final R indices [$I > 2\sigma(I)$, 7073 reflections] | $R1 = 0.0488$, $wR2 = 0.0803$ |
| R indices (all data) | $R1 = 0.0952$, $wR2 = 0.0859$ |
| Type of weighting scheme used | Sigma |
| Weighting scheme used | $w = 1/\sigma^2(F_o^2)$ |
| Max shift/error | 0.005 |
| Average shift/error | 0.000 |
| Largest diff. peak and hole | 2.111 and -0.969 e. \AA^{-3} |

Special Refinement Details

All hydrogen atoms appear in the Fourier map and were refined as riding atoms with the exception of H2, a hydride on Ru2. This hydrogen was refined without restraints. However, care should be taken when interpreting the presence of this hydrogen based solely on the crystallographic data. Hydrides bound to metal atoms are notoriously difficult to resolve with x-ray diffraction data, therefore the results obtained here should be checked for consistency with data from other techniques. There is one residual peak in the final difference Fourier larger than $1\text{e}/\text{\AA}^3$ and it is impossibly close to a solvent of crystallization.

Refinement of F^2 against ALL reflections. The weighted R-factor (wR) 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.



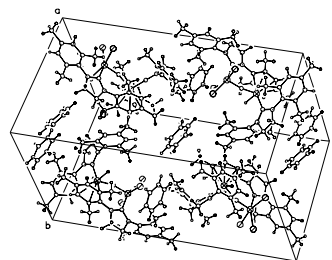
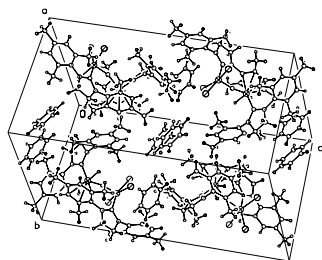


Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 8 (CCDC 223170). $U(\text{eq})$ is defined as the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U_{eq} |
|-------|-----------|---------|----------|-----------------|
| Ru(1) | 8847(1) | 2335(1) | 7123(1) | 22(1) |
| Ru(2) | 7130(1) | 1878(1) | 8038(1) | 22(1) |
| Cl(1) | 7366(1) | 2136(1) | 6352(1) | 36(1) |
| Cl(2) | 8966(1) | 3735(1) | 6794(1) | 32(1) |
| Cl(3) | 10589(1) | 2596(1) | 7711(1) | 32(1) |
| N(1) | 9591(3) | 635(2) | 6887(2) | 28(1) |
| N(2) | 8399(3) | 537(2) | 7400(1) | 22(1) |
| N(3) | 7501(3) | 3233(2) | 8932(1) | 28(1) |
| N(4) | 6234(3) | 3588(2) | 8219(2) | 29(1) |
| C(1) | 8985(3) | 1078(2) | 7160(2) | 21(1) |
| C(2) | 9455(4) | -272(2) | 6934(2) | 32(1) |
| C(3) | 8621(4) | -345(2) | 7291(2) | 29(1) |
| C(4) | 10388(5) | 929(3) | 6593(2) | 48(2) |
| C(5) | 10075(8) | 1003(4) | 6020(3) | 86(3) |
| C(6) | 10933(10) | 1261(5) | 5756(4) | 141(6) |
| C(7) | 12002(13) | 1354(6) | 6062(7) | 178(9) |
| C(8) | 12236(7) | 1252(4) | 6594(5) | 137(5) |
| C(9) | 11472(6) | 1016(3) | 6895(4) | 71(2) |
| C(10) | 8955(8) | 827(4) | 5699(3) | 124(4) |
| C(11) | 12919(11) | 1624(4) | 5757(6) | 331(11) |
| C(12) | 11786(5) | 832(3) | 7496(3) | 88(2) |
| C(13) | 7764(4) | 686(2) | 7796(2) | 22(1) |
| C(14) | 6605(4) | 677(2) | 7624(2) | 26(1) |
| C(15) | 5988(4) | 772(2) | 8038(2) | 29(1) |
| C(16) | 6496(4) | 872(2) | 8596(2) | 29(1) |
| C(17) | 7663(4) | 889(2) | 8749(2) | 28(1) |
| C(18) | 8318(3) | 769(2) | 8365(2) | 23(1) |
| C(19) | 6040(4) | 542(3) | 7032(2) | 37(1) |
| C(20) | 5817(4) | 895(3) | 9029(2) | 43(1) |
| C(21) | 9538(3) | 739(2) | 8524(2) | 29(1) |
| C(22) | 8059(3) | 2296(2) | 7601(2) | 22(1) |
| C(23) | 6927(3) | 2975(2) | 8434(2) | 25(1) |
| C(24) | 7289(4) | 4117(3) | 9048(2) | 43(1) |
| C(25) | 6299(4) | 4315(3) | 8586(2) | 38(1) |
| C(26) | 8193(4) | 2733(3) | 9345(2) | 27(1) |
| C(27) | 7739(4) | 2402(3) | 9769(2) | 30(1) |
| C(28) | 8395(4) | 1866(3) | 10149(2) | 33(1) |
| C(29) | 9455(4) | 1663(3) | 10110(2) | 33(1) |
| C(30) | 9898(4) | 2058(3) | 9714(2) | 33(1) |
| C(31) | 9289(4) | 2613(3) | 9333(2) | 28(1) |
| C(32) | 6613(4) | 2634(3) | 9840(2) | 44(1) |
| C(33) | 10096(4) | 1024(3) | 10491(2) | 46(1) |
| C(34) | 9802(4) | 3053(3) | 8919(2) | 39(1) |
| C(35) | 5311(3) | 3526(2) | 7756(2) | 28(1) |
| C(36) | 4318(4) | 3213(3) | 7844(2) | 33(1) |
| C(37) | 3419(4) | 3203(3) | 7402(2) | 39(1) |
| C(38) | 3472(4) | 3497(3) | 6884(2) | 35(1) |
| C(39) | 4458(4) | 3788(3) | 6812(2) | 37(1) |

| | | | | |
|-------|---------|---------|---------|-------|
| C(40) | 5392(4) | 3817(2) | 7237(2) | 32(1) |
| C(41) | 4222(4) | 2881(3) | 8390(2) | 48(1) |
| C(42) | 2457(4) | 3525(3) | 6422(2) | 57(2) |
| C(43) | 6462(4) | 4128(3) | 7126(2) | 53(2) |
| C(51) | 3888(5) | 861(4) | 9939(3) | 68(2) |
| C(52) | 3294(5) | 309(4) | 9557(3) | 75(2) |
| C(53) | 2542(4) | 603(4) | 9101(3) | 63(2) |
| C(54) | 2400(4) | 1455(4) | 9034(2) | 59(2) |
| C(55) | 2972(4) | 1979(4) | 9418(2) | 54(2) |
| C(56) | 3719(5) | 1682(4) | 9876(3) | 60(2) |
| C(61) | 4649(7) | 4204(4) | -47(4) | 77(2) |
| C(62) | 5441(7) | 4419(4) | 389(3) | 69(2) |
| C(63) | 5818(5) | 5224(6) | 439(3) | 86(2) |

Table S3. Selected bond lengths [Å] and angles [°] for complex 8 (CCDC 223170).

| | | | |
|-------------|------------|-------------------|------------|
| Ru(1)-C(22) | 1.698(4) | C(22)-Ru(1)-C(1) | 89.29(17) |
| Ru(1)-C(1) | 2.031(4) | C(22)-Ru(1)-Cl(1) | 95.19(13) |
| Ru(1)-Cl(1) | 2.3653(12) | C(1)-Ru(1)-Cl(1) | 86.80(12) |
| Ru(1)-Cl(3) | 2.3669(11) | C(22)-Ru(1)-Cl(3) | 99.79(13) |
| Ru(1)-Cl(2) | 2.4124(11) | C(1)-Ru(1)-Cl(3) | 95.29(12) |
| Ru(2)-H(2) | 1.45(3) | Cl(1)-Ru(1)-Cl(3) | 164.89(4) |
| Ru(2)-C(22) | 1.875(4) | C(22)-Ru(1)-Cl(2) | 110.97(13) |
| Ru(2)-C(23) | 2.063(4) | C(1)-Ru(1)-Cl(2) | 159.29(12) |
| | | Cl(1)-Ru(1)-Cl(2) | 87.09(4) |
| | | Cl(3)-Ru(1)-Cl(2) | 85.74(4) |
| | | H(2)-Ru(2)-C(22) | 74.1(13) |
| | | H(2)-Ru(2)-C(23) | 83.9(13) |
| | | C(22)-Ru(2)-C(23) | 97.12(16) |
| | | Ru(1)-C(22)-Ru(2) | 160.3(2) |

Table S4. Bond lengths [Å] and angles [°] for complex 8 (CCDC 223170).

| | | | |
|-------------|------------|-------------------|------------|
| Ru(1)-C(22) | 1.698(4) | C(29)-C(30) | 1.382(6) |
| Ru(1)-C(1) | 2.031(4) | C(29)-C(33) | 1.501(6) |
| Ru(1)-Cl(1) | 2.3653(12) | C(30)-C(31) | 1.396(6) |
| Ru(1)-Cl(3) | 2.3669(11) | C(31)-C(34) | 1.502(6) |
| Ru(1)-Cl(2) | 2.4124(11) | C(35)-C(40) | 1.394(6) |
| Ru(2)-H(2) | 1.45(3) | C(35)-C(36) | 1.396(6) |
| Ru(2)-C(22) | 1.875(4) | C(36)-C(37) | 1.382(6) |
| Ru(2)-C(23) | 2.063(4) | C(36)-C(41) | 1.483(6) |
| Ru(2)-C(13) | 2.207(4) | C(37)-C(38) | 1.384(6) |
| Ru(2)-C(14) | 2.219(4) | C(38)-C(39) | 1.362(6) |
| Ru(2)-C(15) | 2.280(4) | C(38)-C(42) | 1.506(6) |
| Ru(2)-C(18) | 2.345(4) | C(39)-C(40) | 1.385(6) |
| Ru(2)-C(17) | 2.357(4) | C(40)-C(43) | 1.503(6) |
| Ru(2)-C(16) | 2.375(4) | C(51)-C(56) | 1.343(7) |
| N(1)-C(1) | 1.328(5) | C(51)-C(52) | 1.387(8) |
| N(1)-C(4) | 1.435(6) | C(52)-C(53) | 1.382(8) |
| N(1)-C(2) | 1.478(5) | C(53)-C(54) | 1.389(7) |
| N(2)-C(1) | 1.357(5) | C(54)-C(55) | 1.351(7) |
| N(2)-C(13) | 1.411(5) | C(55)-C(56) | 1.382(7) |
| N(2)-C(3) | 1.483(5) | C(61)-C(62) | 1.337(8) |
| N(3)-C(23) | 1.346(5) | C(61)-C(63)#1 | 1.371(8) |
| N(3)-C(26) | 1.432(5) | C(62)-C(63) | 1.376(8) |
| N(3)-C(24) | 1.487(5) | C(63)-C(61)#1 | 1.371(8) |
| N(4)-C(23) | 1.341(5) | | |
| N(4)-C(35) | 1.437(5) | C(22)-Ru(1)-C(1) | 89.29(17) |
| N(4)-C(25) | 1.472(5) | C(22)-Ru(1)-Cl(1) | 95.19(13) |
| C(2)-C(3) | 1.510(5) | C(1)-Ru(1)-Cl(1) | 86.80(12) |
| C(4)-C(5) | 1.391(8) | C(22)-Ru(1)-Cl(3) | 99.79(13) |
| C(4)-C(9) | 1.398(8) | C(1)-Ru(1)-Cl(3) | 95.29(12) |
| C(5)-C(6) | 1.434(11) | Cl(1)-Ru(1)-Cl(3) | 164.89(4) |
| C(5)-C(10) | 1.473(10) | C(22)-Ru(1)-Cl(2) | 110.97(13) |
| C(6)-C(7) | 1.386(19) | C(1)-Ru(1)-Cl(2) | 159.29(12) |
| C(7)-C(8) | 1.296(17) | Cl(1)-Ru(1)-Cl(2) | 87.09(4) |
| C(7)-C(11) | 1.565(12) | Cl(3)-Ru(1)-Cl(2) | 85.74(4) |
| C(8)-C(9) | 1.385(9) | H(2)-Ru(2)-C(22) | 74.1(13) |
| C(9)-C(12) | 1.484(9) | H(2)-Ru(2)-C(23) | 83.9(13) |
| C(13)-C(14) | 1.411(6) | C(22)-Ru(2)-C(23) | 97.12(16) |
| C(13)-C(18) | 1.430(6) | H(2)-Ru(2)-C(13) | 110.6(13) |
| C(14)-C(15) | 1.420(6) | C(22)-Ru(2)-C(13) | 81.52(16) |
| C(14)-C(19) | 1.496(6) | C(23)-Ru(2)-C(13) | 164.18(17) |
| C(15)-C(16) | 1.394(6) | H(2)-Ru(2)-C(14) | 86.6(13) |
| C(16)-C(17) | 1.419(6) | C(22)-Ru(2)-C(14) | 101.67(16) |
| C(16)-C(20) | 1.506(6) | C(23)-Ru(2)-C(14) | 155.68(16) |
| C(17)-C(18) | 1.396(5) | C(13)-Ru(2)-C(14) | 37.19(15) |
| C(18)-C(21) | 1.484(5) | H(2)-Ru(2)-C(15) | 93.9(13) |
| C(24)-C(25) | 1.520(6) | C(22)-Ru(2)-C(15) | 138.18(16) |
| C(26)-C(31) | 1.385(5) | C(23)-Ru(2)-C(15) | 121.74(15) |
| C(26)-C(27) | 1.402(6) | C(13)-Ru(2)-C(15) | 65.25(15) |
| C(27)-C(28) | 1.400(6) | C(14)-Ru(2)-C(15) | 36.78(14) |
| C(27)-C(32) | 1.499(6) | H(2)-Ru(2)-C(18) | 147.0(13) |
| C(28)-C(29) | 1.384(6) | C(22)-Ru(2)-C(18) | 92.88(15) |

| | | | |
|-------------------|------------|-------------------|----------|
| C(23)-Ru(2)-C(18) | 128.46(16) | N(2)-C(13)-Ru(2) | 128.7(3) |
| C(13)-Ru(2)-C(18) | 36.47(14) | C(18)-C(13)-Ru(2) | 77.0(2) |
| C(14)-Ru(2)-C(18) | 66.10(15) | C(13)-C(14)-C(15) | 117.4(4) |
| C(15)-Ru(2)-C(18) | 75.57(15) | C(13)-C(14)-C(19) | 121.7(4) |
| H(2)-Ru(2)-C(17) | 156.6(13) | C(15)-C(14)-C(19) | 120.8(4) |
| C(22)-Ru(2)-C(17) | 124.48(16) | C(13)-C(14)-Ru(2) | 71.0(2) |
| C(23)-Ru(2)-C(17) | 105.47(16) | C(15)-C(14)-Ru(2) | 73.9(2) |
| C(13)-Ru(2)-C(17) | 63.70(15) | C(19)-C(14)-Ru(2) | 127.3(3) |
| C(14)-Ru(2)-C(17) | 76.23(15) | C(16)-C(15)-C(14) | 121.9(4) |
| C(15)-Ru(2)-C(17) | 62.89(16) | C(16)-C(15)-Ru(2) | 76.3(2) |
| C(18)-Ru(2)-C(17) | 34.55(13) | C(14)-C(15)-Ru(2) | 69.3(2) |
| H(2)-Ru(2)-C(16) | 122.8(13) | C(15)-C(16)-C(17) | 118.7(4) |
| C(22)-Ru(2)-C(16) | 155.20(16) | C(15)-C(16)-C(20) | 120.4(4) |
| C(23)-Ru(2)-C(16) | 102.43(15) | C(17)-C(16)-C(20) | 120.8(4) |
| C(13)-Ru(2)-C(16) | 75.50(15) | C(15)-C(16)-Ru(2) | 68.9(2) |
| C(14)-Ru(2)-C(16) | 64.68(15) | C(17)-C(16)-Ru(2) | 71.9(2) |
| C(15)-Ru(2)-C(16) | 34.78(14) | C(20)-C(16)-Ru(2) | 135.2(3) |
| C(18)-Ru(2)-C(16) | 62.97(15) | C(18)-C(17)-C(16) | 122.3(4) |
| C(17)-Ru(2)-C(16) | 34.89(14) | C(18)-C(17)-Ru(2) | 72.2(2) |
| C(1)-N(1)-C(4) | 128.1(3) | C(16)-C(17)-Ru(2) | 73.2(2) |
| C(1)-N(1)-C(2) | 113.8(3) | C(17)-C(18)-C(13) | 117.1(4) |
| C(4)-N(1)-C(2) | 118.0(3) | C(17)-C(18)-C(21) | 122.8(4) |
| C(1)-N(2)-C(13) | 129.4(3) | C(13)-C(18)-C(21) | 120.0(4) |
| C(1)-N(2)-C(3) | 113.2(3) | C(17)-C(18)-Ru(2) | 73.2(2) |
| C(13)-N(2)-C(3) | 116.6(3) | C(13)-C(18)-Ru(2) | 66.5(2) |
| C(23)-N(3)-C(26) | 126.5(3) | C(21)-C(18)-Ru(2) | 130.4(3) |
| C(23)-N(3)-C(24) | 113.1(3) | Ru(1)-C(22)-Ru(2) | 160.3(2) |
| C(26)-N(3)-C(24) | 120.2(3) | N(4)-C(23)-N(3) | 107.5(4) |
| C(23)-N(4)-C(35) | 126.6(3) | N(4)-C(23)-Ru(2) | 125.3(3) |
| C(23)-N(4)-C(25) | 113.5(3) | N(3)-C(23)-Ru(2) | 127.1(3) |
| C(35)-N(4)-C(25) | 118.2(3) | N(3)-C(24)-C(25) | 101.7(3) |
| N(1)-C(1)-N(2) | 107.4(3) | N(4)-C(25)-C(24) | 102.8(3) |
| N(1)-C(1)-Ru(1) | 124.4(3) | C(31)-C(26)-C(27) | 121.7(4) |
| N(2)-C(1)-Ru(1) | 127.8(3) | C(31)-C(26)-N(3) | 120.2(4) |
| N(1)-C(2)-C(3) | 103.2(3) | C(27)-C(26)-N(3) | 118.1(4) |
| N(2)-C(3)-C(2) | 102.3(3) | C(28)-C(27)-C(26) | 117.8(4) |
| C(5)-C(4)-C(9) | 123.8(6) | C(28)-C(27)-C(32) | 119.7(4) |
| C(5)-C(4)-N(1) | 118.5(6) | C(26)-C(27)-C(32) | 122.4(4) |
| C(9)-C(4)-N(1) | 117.2(5) | C(29)-C(28)-C(27) | 121.4(4) |
| C(4)-C(5)-C(6) | 115.0(9) | C(30)-C(29)-C(28) | 118.5(4) |
| C(4)-C(5)-C(10) | 123.5(6) | C(30)-C(29)-C(33) | 121.5(4) |
| C(6)-C(5)-C(10) | 121.5(8) | C(28)-C(29)-C(33) | 120.0(4) |
| C(7)-C(6)-C(5) | 120.2(11) | C(29)-C(30)-C(31) | 122.1(4) |
| C(8)-C(7)-C(6) | 121.0(11) | C(26)-C(31)-C(30) | 117.7(4) |
| C(8)-C(7)-C(11) | 120.2(16) | C(26)-C(31)-C(34) | 121.3(4) |
| C(6)-C(7)-C(11) | 118.7(14) | C(30)-C(31)-C(34) | 120.9(4) |
| C(7)-C(8)-C(9) | 123.7(12) | C(40)-C(35)-C(36) | 120.9(4) |
| C(8)-C(9)-C(4) | 115.9(8) | C(40)-C(35)-N(4) | 120.3(4) |
| C(8)-C(9)-C(12) | 122.4(8) | C(36)-C(35)-N(4) | 118.6(4) |
| C(4)-C(9)-C(12) | 121.7(5) | C(37)-C(36)-C(35) | 118.0(5) |
| C(14)-C(13)-N(2) | 118.7(4) | C(37)-C(36)-C(41) | 120.2(4) |
| C(14)-C(13)-C(18) | 122.5(4) | C(35)-C(36)-C(41) | 121.7(4) |
| N(2)-C(13)-C(18) | 118.6(4) | C(38)-C(37)-C(36) | 122.3(4) |
| C(14)-C(13)-Ru(2) | 71.8(2) | C(39)-C(38)-C(37) | 117.9(4) |

| | | | |
|-------------------|----------|---------------------|----------|
| C(39)-C(38)-C(42) | 121.3(5) | C(52)-C(53)-C(54) | 118.7(6) |
| C(37)-C(38)-C(42) | 120.7(5) | C(55)-C(54)-C(53) | 120.0(6) |
| C(38)-C(39)-C(40) | 122.9(5) | C(54)-C(55)-C(56) | 121.1(6) |
| C(39)-C(40)-C(35) | 117.9(4) | C(51)-C(56)-C(55) | 119.7(6) |
| C(39)-C(40)-C(43) | 120.2(5) | C(62)-C(61)-C(63)#1 | 121.3(6) |
| C(35)-C(40)-C(43) | 121.9(4) | C(61)-C(62)-C(63) | 119.6(6) |
| C(56)-C(51)-C(52) | 120.3(6) | C(62)-C(63)-C(61)#1 | 119.1(6) |
| C(53)-C(52)-C(51) | 120.1(6) | | |

Symmetry transformations used to generate equivalent atoms:

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

Table S5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for complex 8 (CCDC 223170). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U ¹¹ | U ²² | U ³³ | U ²³ | U ¹³ | U ¹² |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ru(1) | 257(2) | 162(2) | 251(2) | 26(2) | 99(2) | 14(2) |
| Ru(2) | 232(2) | 168(2) | 283(2) | 3(2) | 104(2) | -7(2) |
| Cl(1) | 428(7) | 360(7) | 269(7) | -25(5) | 14(5) | 10(5) |
| Cl(2) | 436(7) | 191(6) | 378(7) | 60(5) | 164(6) | 7(5) |
| Cl(3) | 248(6) | 314(6) | 402(7) | 57(5) | 91(5) | -23(5) |
| N(1) | 370(20) | 165(19) | 350(20) | 47(17) | 195(19) | 58(17) |
| N(2) | 280(20) | 132(18) | 280(20) | -26(16) | 136(17) | -6(16) |
| N(3) | 350(20) | 210(20) | 270(20) | -36(17) | 45(18) | 38(17) |
| N(4) | 250(20) | 220(20) | 360(20) | -42(18) | -14(18) | 22(17) |
| C(1) | 260(30) | 220(20) | 180(20) | -12(19) | 69(19) | 11(19) |
| C(2) | 430(30) | 200(20) | 390(30) | -20(20) | 240(20) | 20(20) |
| C(3) | 390(30) | 150(20) | 370(30) | -10(20) | 170(20) | 10(20) |
| C(4) | 720(40) | 130(30) | 780(40) | 170(30) | 570(40) | 180(30) |
| C(5) | 1720(80) | 420(40) | 770(50) | 380(40) | 940(60) | 620(50) |
| C(6) | 2940(150) | 510(50) | 1350(90) | 560(50) | 1700(110) | 950(90) |
| C(7) | 2960(170) | 290(50) | 3100(200) | 510(80) | 2770(180) | 600(90) |
| C(8) | 1060(70) | 160(40) | 3430(160) | -90(60) | 1650(100) | 10(40) |
| C(9) | 640(50) | 90(30) | 1640(70) | 40(40) | 730(50) | 80(30) |
| C(10) | 2250(110) | 1160(60) | 330(40) | 100(40) | 300(50) | 1210(70) |
| C(11) | 5100(200) | 460(50) | 6400(200) | 740(90) | 5600(200) | 590(80) |
| C(12) | 420(40) | 360(40) | 1690(80) | -100(40) | -100(40) | 120(30) |
| C(13) | 300(30) | 70(20) | 310(30) | -7(18) | 110(20) | 2(18) |
| C(14) | 250(30) | 200(20) | 360(30) | -10(20) | 120(20) | -62(19) |
| C(15) | 220(30) | 200(20) | 500(30) | -50(20) | 150(20) | -76(19) |
| C(16) | 380(30) | 140(20) | 410(30) | -20(20) | 240(20) | -60(20) |
| C(17) | 400(30) | 180(20) | 270(30) | 12(19) | 120(20) | -10(20) |
| C(18) | 310(30) | 110(20) | 280(30) | 41(18) | 90(20) | 41(19) |
| C(19) | 290(30) | 320(30) | 460(30) | -70(20) | 20(20) | -90(20) |
| C(20) | 590(40) | 340(30) | 480(30) | -30(20) | 360(30) | -90(30) |
| C(21) | 370(30) | 200(20) | 320(30) | 30(20) | 110(20) | 60(20) |
| C(22) | 220(20) | 100(20) | 310(30) | -22(19) | -6(19) | 13(18) |
| C(23) | 230(20) | 230(20) | 310(30) | 0(20) | 130(20) | -31(19) |
| C(24) | 550(40) | 260(30) | 430(30) | -110(20) | 10(30) | 70(20) |
| C(25) | 300(30) | 260(30) | 530(30) | -110(20) | -10(20) | 70(20) |
| C(26) | 310(30) | 260(20) | 210(20) | -50(20) | 20(20) | -20(20) |
| C(27) | 290(30) | 320(30) | 310(30) | -70(20) | 110(20) | -40(20) |
| C(28) | 370(30) | 370(30) | 280(30) | 20(20) | 110(20) | -20(20) |
| C(29) | 340(30) | 350(30) | 270(30) | -10(20) | 10(20) | 10(20) |
| C(30) | 260(30) | 440(30) | 310(30) | -40(20) | 60(20) | 0(20) |
| C(31) | 330(30) | 270(30) | 250(30) | 30(20) | 70(20) | -30(20) |
| C(32) | 320(30) | 590(30) | 400(30) | -90(30) | 90(20) | 0(30) |
| C(33) | 500(40) | 540(30) | 310(30) | 90(30) | 50(30) | 70(30) |
| C(34) | 340(30) | 390(30) | 460(30) | 80(20) | 110(20) | -50(20) |
| C(35) | 180(30) | 150(20) | 470(30) | -90(20) | -20(20) | 47(19) |
| C(36) | 280(30) | 250(30) | 460(30) | -100(20) | 90(20) | 10(20) |
| C(37) | 190(30) | 300(30) | 680(40) | -120(30) | 80(30) | -10(20) |
| C(38) | 350(30) | 190(20) | 460(30) | 0(20) | -10(20) | 20(20) |

| | | | | | | |
|-------|----------|----------|----------|----------|----------|---------|
| C(39) | 420(30) | 220(30) | 470(30) | 50(20) | 70(30) | 50(20) |
| C(40) | 230(30) | 170(20) | 530(30) | 40(20) | 30(20) | 30(20) |
| C(41) | 400(30) | 510(40) | 570(40) | -40(30) | 200(30) | -20(30) |
| C(42) | 500(40) | 370(30) | 700(40) | -140(30) | -140(30) | 10(30) |
| C(43) | 340(30) | 460(30) | 780(40) | 240(30) | 80(30) | -40(30) |
| C(51) | 560(40) | 860(50) | 590(40) | 290(40) | 60(30) | -40(40) |
| C(52) | 550(40) | 620(40) | 1130(60) | 370(40) | 280(40) | 30(40) |
| C(53) | 340(40) | 800(50) | 740(50) | 60(40) | 110(30) | -90(30) |
| C(54) | 320(30) | 770(50) | 630(40) | 200(40) | 50(30) | -40(30) |
| C(55) | 340(30) | 550(40) | 750(50) | 40(30) | 160(30) | -50(30) |
| C(56) | 490(40) | 770(50) | 600(40) | 10(40) | 250(30) | 10(30) |
| C(61) | 910(60) | 570(50) | 900(60) | 70(50) | 340(50) | 30(40) |
| C(62) | 1100(60) | 600(50) | 460(40) | 80(30) | 340(40) | 390(40) |
| C(63) | 560(50) | 1170(70) | 810(60) | -340(50) | 90(40) | 250(50) |
