

The Effects of NHC-Backbone Substitution on Efficiency in Ruthenium-based Olefin Metathesis

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Supporting Information

General Information.

NMR spectra were recorded using a Varian Mercury 300 or Varian Inova 500 MHz spectrometer. NMR chemical Shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent for ¹H and ¹³C, and H₃PO₄ (δ 0.0) for ³¹P. Spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. IR spectra were recorded on a Perkin-Elmer Paragon 1000 Spectrophotometer. Gas chromatography data was obtained using an Agilent 6850 FID gas chromatograph equipped with a DB-Wax Polyethylene Glycol capillary column (J&W Scientific). High-resolution mass spectroscopy (FAB) was completed at the California Institute of Technology Mass Spectrometry Facility. X-ray crystallographic structures were obtained by the Beckman Institute X-ray Crystallography Laboratory of the California Institute of Technology. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 670930 (**17**) and 651007 (**20**).

All reactions involving metal complexes were conducted in oven-dried glassware under a nitrogen atmosphere with anhydrous and degassed solvents, using standard Schlenk and glovebox techniques. Anhydrous solvents were obtained via elution through a solvent column drying system.ⁱ Silica gel used for the purification of organometallic complexes was obtained from TSI Scientific, Cambridge, MA (60 Å, pH 6.5–7.0). RuCl₂(PCy₃)₂(=CH-*o*-OiPrC₆H₄), **2**, and **3** were obtained from Materia, Inc. Unless otherwise indicated, all compounds were purchased from Aldrich or Fisher and used as obtained. The compounds **6**,ⁱⁱ **7**,ⁱⁱⁱ **12**,ⁱⁱⁱ **21**,^{iv} **24**–**29**,⁵ have been described previously and were prepared according to literature procedures or

identified by comparison of their spectroscopic data. The initial screening of the catalysts, in ring-closing metathesis (RCM) via ^1H NMR was conducted according to literature procedures. Error! Bookmark not defined.

Low Catalyst Loading Assay.

Experiments on the RCM of **24**, **26**, and **28** using the catalysts described were conducted using a SymyxTM Technologies Core Module (Santa Clara, CA) housed in a Braun nitrogen-filled glovebox and equipped with Julabo LH45 and LH85 temperature-control units for separate positions of the robot tabletop.

For experiments where aliquots were not taken during the course of the reaction, up to 576 reactions (6x96 well plates) could be performed simultaneously in 1 mL vials by an Epoch software-based protocol as follows. To prepare catalyst stock solutions (0.25 mM), 20 mL glass scintillation vials were charged with catalyst (5 μmole) and diluted to 20.0 mL total volume in THF. Catalyst solutions, 6 to 800 μL depending on desired final catalyst loading, were transferred to reaction vials and solvent was removed via centrifugal evaporation. The catalysts were preheated to the desired temperature using the LH45 unit, and stirring was started. Substrates (0.1 mmol), containing dodecane (0.025 mmol) as an internal standard, were dispensed simultaneously to 4 reactions at a time using one arm of the robot equipped with a 4-needle assembly. Immediately following substrate addition, solvent was added to reach the desired reaction molarity, generally 1 M. All reactions were quenched by injection of 0.1 mL 5% v/v ethyl vinyl ether in toluene at a preprogrammed time.

Alternatively, where aliquots were taken during the course of the reaction, the entire operation was performed on 12 reactions simultaneously (4 catalyst loadings in triplicate or 2 catalysts at 3 catalyst loadings in duplicate) by an Epoch software-based protocol as follows. To prepare catalyst stock solutions (1.0 mM), 20 mL glass scintillation vials were charged with catalyst (5 μmole) and diluted to 5.0 mL total volume in toluene. Catalyst solutions, 10 to 400 μL depending on desired final catalyst loading, were transferred to glass 20 mL scintillation vials each capped with a septum having a 3 mm hole for the purpose of needle access, and were diluted to 10 mL total volume in toluene. The catalysts were preheated to 50.0 $^{\circ}\text{C}$ using the LH45 unit and stirred. Substrates (1 mmol), containing dodecane (0.25 mmol) as an internal standard, were dispensed simultaneously to 4 reactions at a time using one arm of the robot equipped with a 4-needle assembly. After the 2 minutes required for completion of the transfer,

50 μL aliquots of each reaction were withdrawn using the other robot arm and dispensed to 1.2 mL septa-covered vials containing 5% v/v ethyl vinyl ether in toluene cooled to $-20\text{ }^\circ\text{C}$ in two 96 well plates. The needle was flushed and washed between dispenses to prevent transfer of the quenching solution into the reaction vials. 16 timepoints were sampled at preprogrammed intervals and the exact times were recorded by the Epoch protocol.

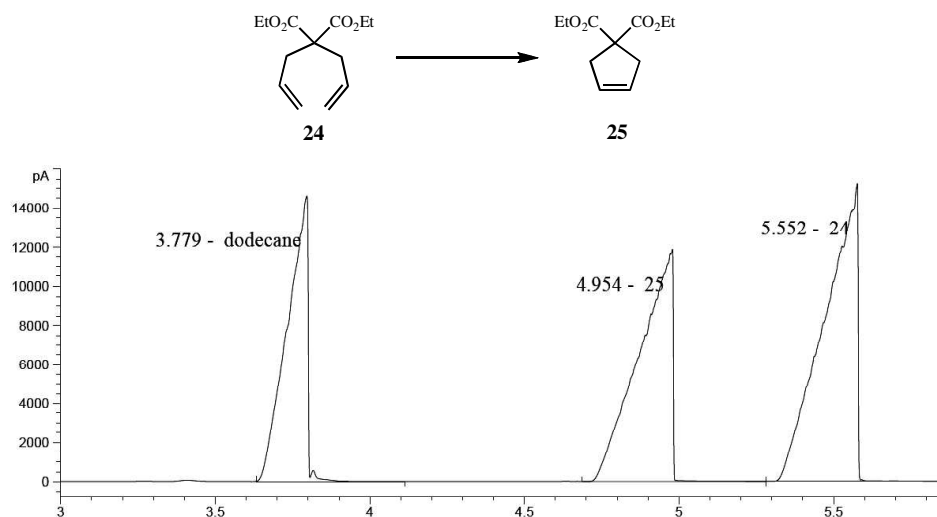
GC Data Analysis.

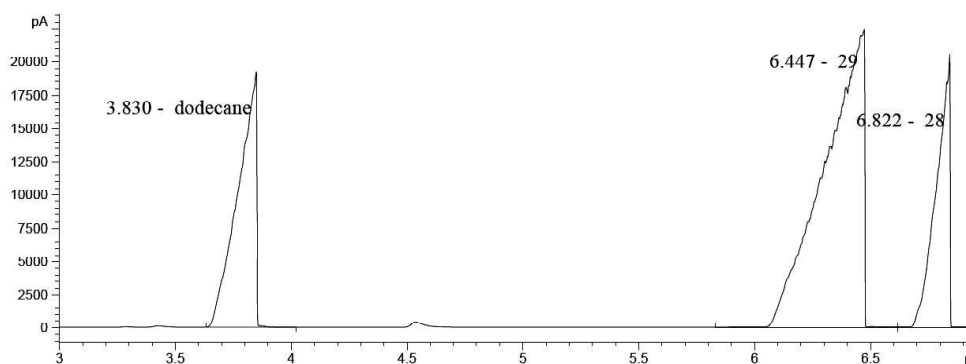
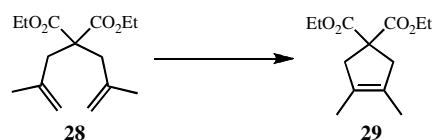
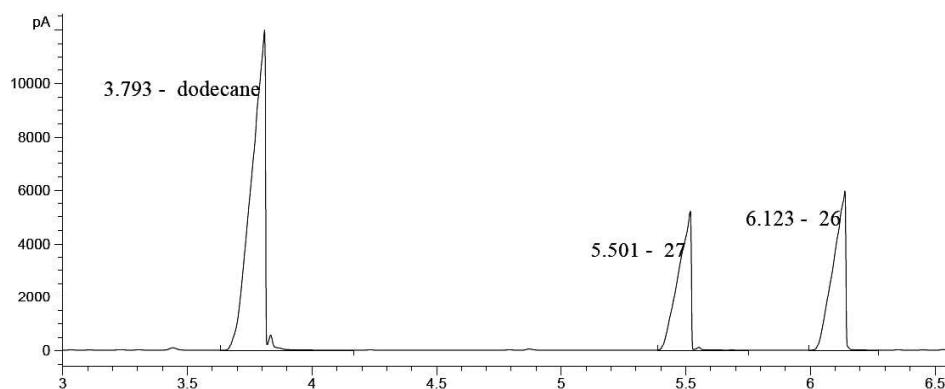
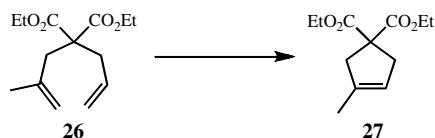
Samples were analyzed by gas chromatography with dodecane as an internal standard, measuring the change in the amounts of substrate and product with time. To obtain accurate conversion data, GC response factors were obtained for all starting materials and products. **Error! Bookmark not defined.**

Relevant instrument conditions: Inlet temperature = $250\text{ }^\circ\text{C}$; detector temperature = $250\text{ }^\circ\text{C}$; hydrogen flow = 32 mL/min ; air flow = 400 mL/min ; constant col + makeup flow = 30 mL/min .

GC Method: $85\text{ }^\circ\text{C}$ for 1.5 minutes, followed by a temperature increase of $15\text{ }^\circ\text{C/min}$ to $160\text{ }^\circ\text{C}$, followed by a temperature increase of $80\text{ }^\circ\text{C/min}$ to $200\text{ }^\circ\text{C}$ and a subsequent isothermal period at $210\text{ }^\circ\text{C}$ for one minute (total run time = 8 minutes).

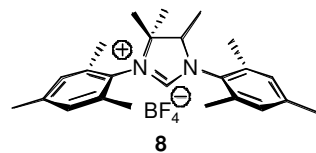
Representative GC traces.





Experimentals.

1,3-dimesityl-4,4,5-trimethyl-imidazolinium tetrafluoroborate (**8**)



A solution of the diimine **12** (2.00 g, 6.24 mmol) in dry benzene was placed in a flask equipped with a reflux condenser, and added a solution of methylmagnesium chloride in tetrahydrofuran (3.0 M, 8.3 ml, 24.96 mmol). The resulting solution was stirred at refluxing temperature for one day. The solvents were removed under vacuum, the residue was dissolved in diethyl ether and treated Lithium aluminium hydride (120 mg, 3.1 mmol). After work-up and purification by column chromatography, the diamine was obtained as a white solid in 69% yield. A mixture of diamine (1.62 g, 4.78 mmol), ammonium tetrafluoroborate (0.75 g, 7.17 mmol), and triethyl orthoformate (12 ml) was stirred at 120 °C for 10 min and cooled to room temperature. The precipitation was collected by filtration, and the solid was redissolved in

CH₂Cl₂. After the insoluble material was filtered off, the filtrate was evaporated under vacuum, and the residue was recrystallized in ethyl acetate to give **8** as a white solid (543 mg, 1.24 mmol, Y = 26%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.00 (s, 1H), 7.13 (s, 2H), 7.11 (s, 2H), 4.71 (q, J = 6.9 Hz, 1H), 2.34-2.29 (m, 18H), 1.52 (s, 3H), 1.36 (s, 3H), 1.19 (d, J = 6.9 Hz, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 159.0, 139.7, 137.5, 136.9, 136.0, 135.8, 130.2, 130.1, 129.8, 129.2, 128.3, 73.5, 67.7, 26.3, 20.5, 20.5, 19.3, 19.1, 18.2, 17.9, 11.9. ¹⁹F NMR (282 MHz, DMSO-*d*₆): δ -148.7. HRMS Calc'd for C₂₄H₃₃N₂: 349.2644. Meas: 349.2648.

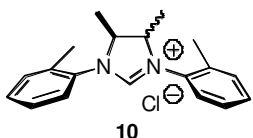
1,3-Ditolyl-4,4-Dimethyl-imidazolium chloride (**9**)



To a THF solution (40 mL) of the formamidine (1 eq) at -78 °C was added a solution of *n*-BuLi in hexanes (1 eq). The mixture was stirred for 30 minutes, then was allowed to warm to r.t. and stirred for a further 12 hours. The mixture was again cooled to -78 °C, and 3-bromopropene (1 eq) or 3-bromo-2-methylpropene (1 eq) was slowly added. The mixture was stirred for 30 minutes at -78 °C then heated at 50 °C for 12 hours. Removal of the volatiles under vacuum and extraction with hexanes afforded the corresponding alkylated derivative.

An oven dried, argon flushed, sealable Schlenk tube with a Teflon stopcock was loaded with the alkylated derivative (1 eq), toluene and was cooled to 0°C, at which point was added a solution of HCl in Et₂O (2.0 M, 1 eq). Precipitation of a white powder was immediately observed. After 15 minutes at 0°C the mixture was left to warm to r.t. and stirred for an additional 15 minutes. The mixture was heated at 110°C for 24 hours, after which time the volatiles were removed under vacuum and the resulting salt washed with toluene and ether to afford salt **9** (overall yield = 77%). ¹H NMR (300 MHz, CDCl₃): δ 9.00 (s, 1H), 7.86 (d, J = 7.2 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.37-7.15 (m, 6H), 4.32 (s, 2H), 2.42 (s, 3H), 2.40 (s, 3H), 1.62 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): 157.8, 136.2, 134.6, 133.6, 131.9, 131.7, 131.1, 130.6, 130.1, 130.0, 128.0, 127.3.0, 127.1, 69.8, 64.6, 26.4, 18.8, 18.3.

1,3-Ditolyl-4,5-Dimethyl-imidazolium chloride (**10**)



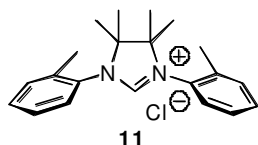
A mixture of 2,3-butandione (2.00 g, 23.23 mmol), *o*-toluidine (5.00 g, 46.66 mmol), and ethanol (ca. 2 ml) was stirred at room temperature for 1 day. The yellow crystalline solid was collected by filtration and rinsed

with a small amount of ethanol to yield 3.42 g (12.97 mmol, Y = 56%) of the desired diimine. After reduction, the diamine was obtained as a mixture of isomers. A diethyl ether solution of the diamine was treated with a solution of hydrogen chloride (2 eq) to precipitate the diamine hydrochloride salt. The white solid was collected by filtration and washed with copious amount of diethyl ether. The solid was placed in a flask and triethyl orthoformate (large excess) was added. The resulting mixture was stirred at 130 °C for 5 to 10 min then cooled. After cooling to room temperature, the white solid was collected by filtration washing with large amount of diethyl ether and then with acetone to give the desired imidazolidinium chloride salt **10**.

^1H NMR (300 MHz, CDCl_3): δ 9.04 (s, 0.3H, *trans*), 8.45 (s, 0.7H, *cis*), 8.00-7.93 (m, 2H), 7.39-7.25 (m, 6H), 5.54 (m, 1.4H, *cis*), 4.64 (m, 0.6H, *trans*), 2.47 (s, 4.2H, *cis*), 2.45 (s, 1.8H, *trans*), 1.53 (d, J = 6.0 Hz, 1.8H, *trans*), 1.32 (d, J = 5.7 Hz, 4.2H, *cis*).

^{13}C NMR (75 MHz, CDCl_3): δ 157.2 (*trans*), 156.2 (*cis*), 134.4 (*cis*), 134.3 (*trans*), 132.8 (*cis*), 132.6 (*trans*), 131.7 (*trans*), 131.6 (*cis*), 130.0 (*trans*), 129.8 (*cis*), 127.9 (*trans*), 127.6 (*cis*), 127.55 (*trans*), 127.5 (*cis*), 66.9 (*trans*), 62.8 (*cis*), 18.3 (*cis*), 18.2 (*trans*), 17.6 (*trans*), 12.5 (*cis*). HRMS Calc'd for $\text{C}_{19}\text{H}_{23}\text{N}_2$: 279.1861. Meas: 279.1853.

1,3-Ditolyl-4,4,5,5-Tetramethyl-imidazolinium chloride (11)



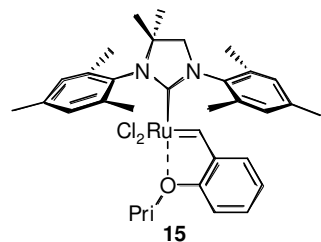
A solution of the diimine (3.00 g, 11.35 mmol) in dry benzene was placed in a flask equipped with a reflux condenser, and added a solution of methylmagnesium chloride in tetrahydrofuran (3.0 M, 11.3 ml, 45.4 mmol). The resulting solution was stirred at refluxing temperature for overnight. After cooled to room temperature, the reaction mixture was slowly added saturated aqueous solution of ammonium chloride. The organic layer was separated and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine, dried over magnesium sulfate, and purified by flash chromatography on silica (eluent: hexanes/ethyl acetate = 30/1) to yield the desired diamine as a yellow oil (2.25 g, 7.60 mmol, Y = 67%). The diamine was dissolved in diethyl ether (10 ml) and treated with a solution of hydrogen chloride (4 M in dioxane) to precipitate the diamine hydrochloride salt. The solid was collected by filtration and rinsed with ample amount of diethyl ether then with acetone to give the desired amine salt as a white powder (2.19 g, 5.93 mmol, Y = 78%). A mixture of the diamine salt (330 mg, 0.89 mmol) and triethyl orthoformate (1.5 ml) was placed in a vial and stirred at 120 °C for 18 hours. After cooled to room temperature, the tan colored solid was collected by

filtration and washed with diethyl ether. (**11**, 64 mg, 0.187 mmol, Y = 21%). ^1H NMR (300 MHz, CDCl_3): δ 9.38 (br s, 1H), 7.58 (deformed d, 2H), 7.40-7.30 (m, 6H), 2.47 (s, 6H), 1.50 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3): δ 157.9, 136.3, 131.8, 131.3, 130.4, 130.4, 127.2, 74.0, 21.6, 18.8. HRMS Calc'd for $\text{C}_{21}\text{H}_{27}\text{N}_2$: 307.2174. Meas: 307.2162.

General procedure for the preparation of catalysts 15-20:

To a solution of imidazolium salt in toluene (or benzene) was added KHMDS, and the resulting solution was stirred at room temperature for a few minutes. $\text{RuCl}_2(\text{PCy}_3)(=\text{CH}-o\text{-OiPrC}_6\text{H}_4)$ was then added, and the mixture was stirred for the designated time and temperature (*vide infra*). After cooling to room temperature, the mixture was purified by column chromatography on TSI silica (eluent: hexane/diethyl ether = 2/1 \rightarrow 1/1) to give the titled compounds as a green solid.

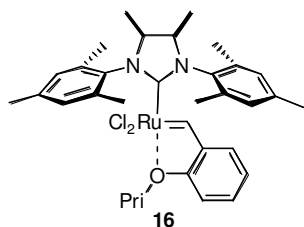
$\text{RuCl}_2(4,4\text{-dimethyl-1,3-dimesitylimidazolin-2-ylidene})(=\text{CH}-o\text{-OiPrC}_6\text{H}_4)$ (**15**)



6 (200 mg, 0.54 mmol), potassium hexamethyldisilazide (140 mg, 0.70 mmol), and $\text{RuCl}_2(\text{PCy}_3)(=\text{CH}-o\text{-OiPrC}_6\text{H}_4)$ (250 mg, 0.42 mmol) was reacted according to the general procedure (stirred for 2 hours at 70 $^\circ\text{C}$) to give the desired ruthenium complex **15** as a green powder (135 mg, 0.21 mmol, 49%).

^1H NMR (500 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$): δ 16.46 (br s, 1H), 7.55 (ddd, J = 8.3 Hz, J = 2.0 Hz, 1H), 7.10 (br s, 2H), 7.05 (br s, 2H), 6.95 (dd, J = 7.5 Hz, J = 2.0 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 4.86 (sept, J = 6.1 Hz, 1H), 3.93 (s, 2H), 2.50-2.25 (m, 18H), 1.47 (s, 6H), 1.21 (d, J = 6.1 Hz, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 293.3 (m), 213.3, 153.0, 146.4, 141.3, 139.0, 138.6, 130.7, 130.0, 129.3, 122.7, 122.5, 113.6, 75.4, 68.2 (br), 65.6 (br), 28.1, 21.8, 21.5, 21.4. HRMS Calc'd for $\text{C}_{33}\text{H}_{42}\text{Cl}_2\text{N}_2\text{ORu}$: 654.1718. Meas: 654.1725.

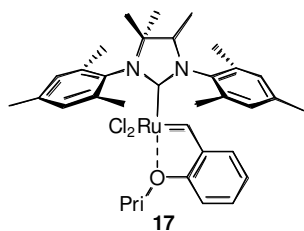
$\text{RuCl}_2(1,3\text{-dimesityl-4,5-dimethylimidazolin-2-ylidene})(=\text{CH}-o\text{-OiPrC}_6\text{H}_4)$ (**16**)



7 (100 mg, 0.27 mmol), potassium hexamethyldisilazide (70 mg, 0.35 mmol), and $\text{RuCl}_2(\text{PCy}_3)(=\text{CH}-o\text{-O}i\text{PrC}_6\text{H}_4)$ (100 mg, 0.17 mmol) was reacted according to the general procedure (stirred for 2 hours at 70 °C) to give the desired ruthenium complex **16** as a green powder (60 mg, 0.092 mmol, 54%).

^1H NMR (500 MHz, C_6D_6 , 25 °C): δ 16.74 (s, 1H), 7.14 (dd, $J = 7.5$ Hz, $J = 1.5$ Hz, 1H), 7.11 (ddd, $J = 7.5$ Hz, $J = 1.5$ Hz, 1H), 7.00 (br s, 4H), 6.65 (dt, $J = 7.5$ Hz, $J = 1.0$ Hz, 1H), 6.32 (d, $J = 8.0$ Hz, 1H), 4.49 (sept, $J = 6.1$ Hz, 1H), 4.12 (s, 2H), 3.00-2.30 (br s, 12H), 2.25 (s, 6H), 1.31 (br s, 6H), 0.81 (d, $J = 6.5$ Hz, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 293.8, 213.4, 153.0, 146.4, 140.7, 138.7, 130.2, 129.9, 128.8, 122.8, 122.5, 113.6, 75.3, 62.4 (br), 21.8, 21.4, 13.9 (br). HRMS Calc'd for $\text{C}_{33}\text{H}_{42}\text{Cl}_2\text{N}_2\text{ORu}$: 654.1718. Meas: 654.1738.

$\text{RuCl}_2(1,3\text{-dimesityl-4,4,5-trimethyl-imidazolin-2-ylidene})(=\text{CH}-o\text{-O}i\text{PrC}_6\text{H}_4)$ (**17**)

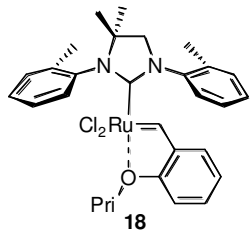


8 (200 mg, 0.46 mmol), potassium hexamethyldisilazide (120 mg, 0.60 mmol), and $\text{RuCl}_2(\text{PCy}_3)(=\text{CH}-o\text{-O}i\text{PrC}_6\text{H}_4)$ (200 mg, 0.33 mmol) was reacted according to the general procedure (stirred for 2.5 hrs at room temperature and 4 hrs at 60 °C) to give the desired ruthenium complex **17** as a green powder (97 mg, 0.15 mmol, 44%). Crystals suitable for X-ray crystallography were grown at room temperature by slow

diffusion of pentane into a solution of **17** in benzene. ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ 16.65 (br s, 1H), 7.13-7.07 (m, 3H), 6.94 (br m, 3H), 6.63 (td, $J = 7.6$, 0.8 Hz, 1H), 6.31 (d, $J = 8.0$ Hz, 1H), 4.46 (sept, $J = 6.1$ Hz, 1H), 4.20 (br s, 1H), 2.85-2.47 (m, 12H), 2.24 (s, 3H), 2.21 (s, 3H), 1.28 (d, $J = 6.1$ Hz, 6H), 1.15 (br s, 3H), 0.88 (br s, 3H), 0.69 (br d, $J = 6.9$ Hz, 3H).

^{13}C NMR (125 MHz, C_6D_6): δ 293.8 (m), 213.4 (br), 152.9, 146.5, 140.7, 138.7, 138.6, 130.9, 130.6, 130.3, 129.4, 122.7, 122.4, 113.6, 75.3, 71.0 (br), 68.4 (br), 25.1, 23.1 (br), 21.8, 21.5, 21.4, 12.1. HRMS Calc'd for $\text{C}_{34}\text{H}_{44}\text{Cl}_2\text{N}_2\text{ORu}$: 668.1875. Meas: 668.1898.

$\text{RuCl}_2(1,3\text{-ditolyl-4,4-dimethyl-imidazolin-2-ylidene})(=\text{CH}-o\text{-O}i\text{PrC}_6\text{H}_4)$ (**18**)

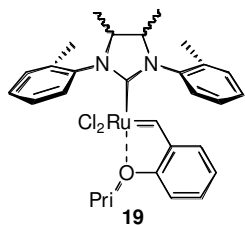


9 (190 mg, 0.60 mmol), potassium hexamethyldisilazide (157 mg, 0.78 mmol), and $\text{RuCl}_2(\text{PCy}_3)(=\text{CH}-o\text{-OiPrC}_6\text{H}_4)$ (200 mg, 0.33 mmol) was reacted according to the general procedure (stirred for 2 hours at 70 °C) to give the desired ruthenium complex **18** as a green powder (112 mg, 0.19 mmol, 57%). ^1H NMR (500 MHz, CD_2Cl_2 , 25 °C): δ 16.41 (br s, 0.40H),

16.24 (br s, 0.60H), 8.59 (br s, 1.20H), 8.59 (br s, 0.80H), 7.60-7.20 (m, 7H), 6.88-6.81 (m, 3H), 4.91 (m, 1H), 4.40-3.60 (m, 2H), 2.62-2.40 (m, 6H), 1.64-1.07 (m, 12H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 232.5, 152.2, 144.3, 141.9, 138.6, 134.3, 132.5, 131.4, 129.9, 129.5, 129.2, 128.9, 128.8, 127.6, 126.9, 122.3, 122.0, 121.8, 112.9, 74.8, 68.1, 66.6, 29.7, 27.3, 27.0, 26.9, 26.3, 24.6, 23.9, 21.5, 19.5.

HRMS Calc'd for $\text{C}_{29}\text{H}_{34}\text{Cl}_2\text{N}_2\text{ORu}$: 598.1092. Meas: 598.1064.

$\text{RuCl}_2(1,3\text{-ditolyl-4,5-dimethyl-imidazolin-2-ylidene})(=\text{CH}-o\text{-OiPrC}_6\text{H}_4)$ (**19**)

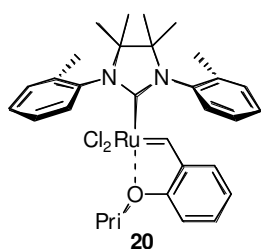


10 (100 mg, 0.32 mmol), potassium hexamethyldisilazide (70 mg, 0.35 mmol), and $\text{RuCl}_2(\text{PCy}_3)(=\text{CH}-o\text{-OiPrC}_6\text{H}_4)$ (100 mg, 0.17 mmol) was reacted according to the general procedure (stirred for 2 hours at 70 °C) to give the desired ruthenium complex **19** as a green (39 mg, 0.065 mmol, 38%). ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ 16.64-16.41 (m, 1H), 9.00 (br s, 2H), 7.11-6.71 (m, 8H), 6.65 (m, 1H), 6.42 (t, $J = 7.8$ Hz, 1H), 4.57 (sept, $J = 6.4$ Hz, 1H),

4.29-3.55 (m, 2H), 2.65-2.25 (m, 6H), 1.20-1.60 (m, 6H), 1.05-0.60 (m, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 291.7, 290.9, 232.5, 210.74, 152.8, 144.2, 140.0, 139.6, 138.6, 137.4, 132.4, 132.2, 131.5, 131.3, 130.6, 130.3, 121.9, 121.8, 113.0, 112.8, 74.4, 61.1, 61.0, 60.4, 21.7, 21.6, 13.2, 12.9.

HRMS Calc'd for $\text{C}_{29}\text{H}_{34}\text{Cl}_2\text{N}_2\text{ORu}$: 598.1092. Meas: 598.1097.

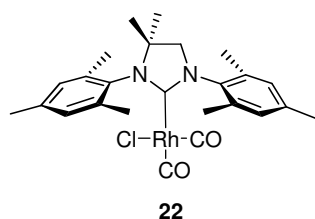
$\text{RuCl}_2(1,3\text{-ditolyl-4,4,5,5-tetramethyl-imidazolin-2-ylidene})(=\text{CH}-o\text{-OiPrC}_6\text{H}_4)$ (**20**)



11 (41 mg, 0.12 mmol), potassium hexamethyldisilazide (24 mg, 0.12 mmol), and $\text{RuCl}_2(\text{PCy}_3)(=\text{CH}-o\text{-OiPrC}_6\text{H}_4)$ (60 mg, 0.1 mmol) was reacted according to the general procedure described above to give the desired ruthenium complex **20** as a green powder as a ca. 3:1 mixture of isomers (45 mg, 0.072 mmol, 72%). Crystals suitable for X-ray crystallography were grown at room temperature by slow diffusion of

pentane into a solution of **20** in benzene. ^1H NMR (500 MHz, C_6D_6): δ 16.64 (s, 0.75H), 16.33 (s, 0.25H), 8.89 (d, $J = 7.7$ Hz, 0.75H), 8.84 (d, $J = 7.9$ Hz, 0.25H), 7.43-7.25 (m, 4H), 7.20-7.05 (m, 4H), 6.99-6.94 (m, 1H), 6.70-6.62 (m, 1H), 6.34 (d, $J = 8.3$ Hz, 1H), 4.45 (sept, $J = 6.1$ Hz, 1H), 2.74 (s, 0.75H), 2.68 (s, 2.25H), 2.47 (s, 0.75H), 2.44 (s, 2.25H), 1.38-1.20 (m, 10H), 1.04 (s, 2H), 0.76-0.70 (m, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 214.0, 211.5, 153.1, 153.0, 145.8, 143.3, 143.2, 141.6, 140.8, 140.3, 139.8, 137.3, 136.5, 136.0, 134.7, 134.4, 132.3, 132.2, 131.9, 129.6, 129.5, 129.4, 129.1, 128.9, 127.6, 127.3, 126.9, 126.6, 122.7, 122.6, 122.6, 122.5, 113.5, 75.2, 75.1, 72.3, 71.8, 71.7, 71.4, 24.9, 24.3, 24.1, 23.9, 22.7, 22.5, 22.4, 22.2, 22.1, 22.0, 20.3, 20.1, 19.7, 19.4, 19.3. HRMS Calc'd for $\text{C}_{31}\text{H}_{38}\text{Cl}_2\text{N}_2\text{ORu}$: 626.1405. Meas: 626.1427.

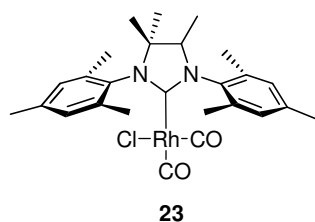
$\text{RhCl}(\text{CO})_2(4,4\text{-dimethyl-1,3-dimesitylimidazolin-2-ylidene})$ (**22**)



The imidazolidinium salt **6** (40 mg, 0.10 mmol), KHMDS (22 mg, 0.11 mmol), and toluene (2 ml) was stirred at room temperature under N_2 for 5 min, and added to a suspension of $[\text{RhCl}(\text{COD})]_2$ (25 mg, 0.05 mmol) in toluene (1 ml). The resulting mixture was stirred at room temperature for 1 hour, and then the solvent was removed under vacuum.

The residue was purified by column chromatography on TSI silica (eluent: 2% EtOH in CH_2Cl_2) to give $[(\text{NHC})\text{RhCl}(\text{COD})]$ as a yellow powder. A solution of the prepared complex in CH_2Cl_2 (3 ml) was bubbled with CO for 1 hour. The mixture was then concentrated under vacuum and the residue was washed with dry hexane (2 ml \times 3). The resulting solid was dried under vacuum to give **22** (38 mg, 0.071 mmol, $Y = 71\%$ two steps). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.01 (s, 2H), 6.97 (s, 2H), 3.74 (s, 2H), 2.43 (s, 12H), 2.33 (s, 6H), 1.41 (s, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 205.6 ($J_{\text{C-Rh}} = 41$ Hz), 185.7 ($J_{\text{C-Rh}} = 53$ Hz), 183.4 ($J_{\text{C-Rh}} = 75$ Hz), 138.6, 138.3, 135.5, 132.8, 130.0, 129.7, 69.7, 69.7, 65.0, 25.0, 21.4, 21.0, 20.9, 18.8. IR (CD_2Cl_2): 2079, 1995 cm^{-1} . HRMS Calc'd for $\text{C}_{25}\text{H}_{29}\text{ClN}_2\text{O}_2\text{Rh}$: 527.0973. Meas: 527.0960.

$\text{RhCl}(\text{CO})_2(1,3\text{-dimesityl-4,4,5-trimethylimidazolin-2-ylidene})$ (**23**)



The imidazolidinium **8** (46 mg, 0.10 mmol) was treated as described above to give **23** (36 mg, 0.066 mmol, $Y = 66\%$ two steps). IR (CD_2Cl_2): 2078, 1994 cm^{-1} . HRMS Calc'd for $\text{C}_{26}\text{H}_{32}\text{ClN}_2\text{O}_2\text{Rh}$: 542.1207. Meas: 542.1228.

X-Ray Structural Analysis

Compound 17 (CCDC 670930)

Table 1. Crystal data and structure refinement for 17 (CCDC 670930).

Empirical formula	C ₃₄ H ₄₄ N ₂ OCl ₂ Ru, 1/2(C ₅ H ₁₂)
Formula weight	704.25
Crystallization Solvent	Benzene/ <i>n</i> -pentane
Crystal Habit	Plate
Crystal size	0.36 x 0.29 x 0.17 mm ³
Crystal color	Blue

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoK α	
Data Collection Temperature	100(2) K	
θ range for 9852 reflections used in lattice determination	2.37 to 30.72°	
Unit cell dimensions	a = 11.5182(8) Å b = 12.3831(8) Å c = 12.4144(8) Å	α = 99.737(3)° β = 92.627(4)° γ = 92.065(4)°
Volume	1741.6(2) Å ³	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.343 Mg/m ³	
F(000)	737	
θ range for data collection	1.67 to 31.98°	
Completeness to $\theta = 31.98^\circ$	83.2 %	

Index ranges	$-17 \leq h \leq 12, -18 \leq k \leq 18, -18 \leq l \leq 17$
Data collection scan type	ω and ϕ scans; 6 settings
Reflections collected	29761
Independent reflections	10056 [$R_{\text{int}} = 0.0430$]
Absorption coefficient	0.634 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.8999 and 0.8040

Table 1 (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	10056 / 6 / 428
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.665
Final R indices [$I > 2\sigma(I)$, 7915 reflections]	$R_1 = 0.0605$, $wR_2 = 0.0916$
R indices (all data)	$R_1 = 0.0797$, $wR_2 = 0.0928$
Type of weighting scheme used	Sigma
Weighting scheme used	$w = 1/\sigma^2(F_o^2)$
Max shift/error	0.002
Average shift/error	0.000
Largest diff. peak and hole	2.037 and -1.337 e.Å ⁻³

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

The difference electron density maps contained three peaks consistent with ~10% of a Cl-Ru-Cl center. These were incorporated into the model and refined anisotropically such that the total sum of Cl-Ru-Cl centers equaled one. The result is shown in the second figure; occupancy of the minor component refined to 6.4%.

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.

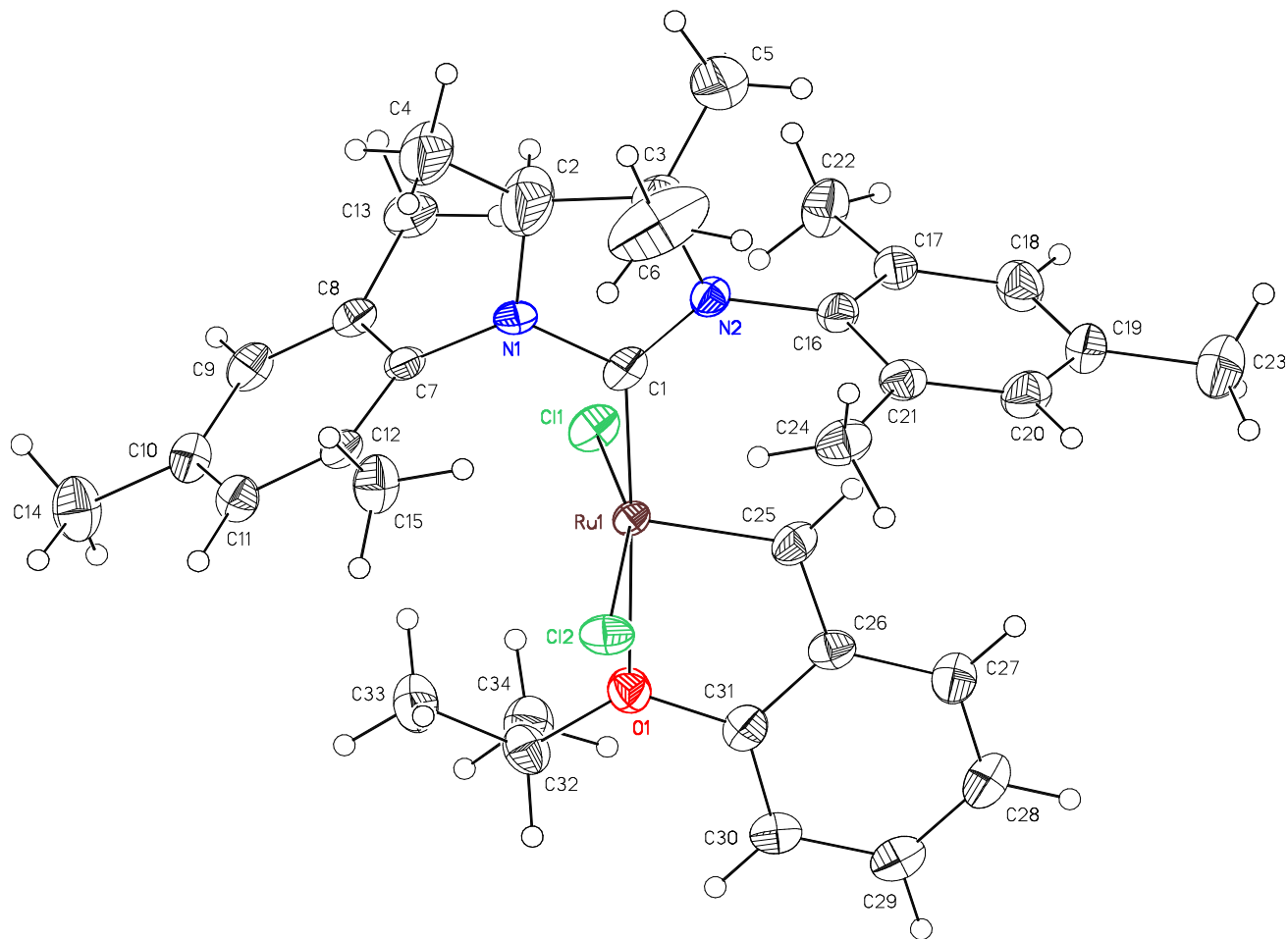


Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 17 (CCDC 670930). U_{eq} is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Ru(1)	8058(1)	7612(1)	7031(1)	16(1)	0.937(2)
Cl(1)	8783(1)	7941(1)	8844(1)	26(1)	0.937(2)
Cl(2)	7894(1)	7596(1)	5139(1)	27(1)	0.937(2)
Ru(2)	7541(7)	7243(7)	7395(9)	74(4)	0.064(2)
Cl(1B)	7204(17)	6709(16)	5509(17)	100(9)	0.064(2)
Cl(2B)	7560(20)	7187(19)	9288(18)	96(8)	0.064(2)
O(1)	9619(2)	6591(2)	6666(2)	27(1)	1
N(1)	6922(2)	9681(2)	7493(2)	20(1)	1
N(2)	5572(2)	8378(2)	7433(2)	21(1)	1
C(1)	6739(3)	8563(2)	7342(2)	20(1)	1
C(2)	5890(4)	10264(3)	7839(4)	65(1)	1
C(3)	4913(3)	9400(3)	7582(3)	35(1)	1
C(4)	5810(3)	11385(3)	7690(4)	57(1)	1
C(5)	4006(4)	9447(3)	8387(4)	61(1)	1
C(6)	4303(4)	9539(4)	6494(3)	79(2)	1
C(7)	8056(3)	10194(2)	7529(2)	20(1)	1
C(8)	8671(3)	10567(2)	8544(2)	22(1)	1
C(9)	9771(3)	11027(2)	8532(3)	26(1)	1
C(10)	10296(3)	11157(2)	7576(3)	26(1)	1
C(11)	9661(3)	10832(2)	6588(3)	26(1)	1
C(12)	8529(3)	10393(2)	6557(2)	20(1)	1
C(13)	8142(3)	10502(3)	9625(2)	31(1)	1
C(14)	11507(3)	11653(3)	7622(3)	39(1)	1
C(15)	7823(3)	10230(3)	5472(2)	33(1)	1
C(16)	5029(3)	7317(2)	7424(3)	24(1)	1
C(17)	5022(3)	6888(3)	8393(3)	26(1)	1
C(18)	4516(3)	5840(3)	8378(3)	32(1)	1
C(19)	4037(3)	5218(3)	7419(3)	33(1)	1
C(20)	4082(3)	5649(3)	6467(3)	32(1)	1
C(21)	4577(3)	6683(3)	6430(3)	25(1)	1
C(22)	5636(3)	7491(3)	9453(2)	35(1)	1
C(23)	3501(3)	4086(3)	7432(3)	49(1)	1
C(24)	4681(3)	7047(3)	5336(2)	34(1)	1
C(25)	7405(3)	6229(2)	7004(2)	26(1)	1
C(26)	8145(3)	5311(2)	6769(2)	24(1)	1
C(27)	7719(3)	4225(3)	6698(3)	32(1)	1
C(28)	8438(3)	3371(3)	6453(3)	37(1)	1
C(29)	9607(3)	3576(3)	6261(3)	35(1)	1
C(30)	10048(3)	4646(3)	6306(2)	29(1)	1
C(31)	9314(3)	5494(3)	6584(2)	25(1)	1
C(32)	10861(3)	6953(3)	6711(3)	29(1)	1
C(33)	10864(3)	8133(3)	6573(3)	37(1)	1
C(34)	11446(3)	6783(3)	7776(3)	35(1)	1
C(41)	9615(7)	4542(5)	9716(4)	115(3)	1
C(42)	8323(8)	4854(7)	9783(5)	136(3)	1
C(43)	7714(12)	3904(12)	9430(9)	109(5)	0.50

Table 3. Selected bond lengths [\AA] and angles [$^\circ$] for 17 (CCDC 670930).

Ru(1)-C(25)	1.840(3)	C(25)-Ru(1)-C(1)	103.09(14)
Ru(1)-C(1)	1.969(3)	C(25)-Ru(1)-O(1)	79.52(12)
Ru(1)-O(1)	2.255(2)	C(1)-Ru(1)-O(1)	177.38(11)
Ru(1)-Cl(1)	2.3288(8)	C(25)-Ru(1)-Cl(1)	98.12(10)
Ru(1)-Cl(2)	2.3446(8)	C(1)-Ru(1)-Cl(1)	93.31(8)
		O(1)-Ru(1)-Cl(1)	86.49(6)
		C(25)-Ru(1)-Cl(2)	96.93(9)
		C(1)-Ru(1)-Cl(2)	94.09(8)
		O(1)-Ru(1)-Cl(2)	85.34(6)
		Cl(1)-Ru(1)-Cl(2)	161.26(4)
Ru(2)-Cl(1B)	2.33(2)	Cl(1B)-Ru(2)-Cl(2B)	160.3(10)
Ru(2)-Cl(2B)	2.36(3)		

Table 4. Bond lengths [Å] and angles [°] for 17 (CCDC 670930).

Ru(1)-C(25)	1.840(3)	C(19)-C(20)	1.379(4)
Ru(1)-C(1)	1.969(3)	C(19)-C(23)	1.514(4)
Ru(1)-O(1)	2.255(2)	C(20)-C(21)	1.391(4)
Ru(1)-Cl(1)	2.3288(8)	C(21)-C(24)	1.510(4)
Ru(1)-Cl(2)	2.3446(8)	C(25)-C(26)	1.444(4)
Cl(2B)-Ru(2)	2.36(3)	C(26)-C(31)	1.394(4)
Cl(1B)-Ru(2)	2.33(2)	C(26)-C(27)	1.401(4)
O(1)-C(31)	1.376(3)	C(27)-C(28)	1.369(4)
O(1)-C(32)	1.479(4)	C(28)-C(29)	1.400(5)
N(1)-C(1)	1.373(4)	C(29)-C(30)	1.393(4)
N(1)-C(7)	1.427(4)	C(30)-C(31)	1.380(4)
N(1)-C(2)	1.457(4)	C(32)-C(33)	1.499(4)
N(2)-C(1)	1.368(4)	C(32)-C(34)	1.506(4)
N(2)-C(16)	1.433(4)	C(41)-C(41)#1	1.473(12)
N(2)-C(3)	1.488(4)	C(41)-C(42)	1.554(9)
C(2)-C(4)	1.438(5)	C(42)-C(43)	1.344(13)
C(2)-C(3)	1.509(5)		
C(3)-C(5)	1.474(5)	C(25)-Ru(1)-C(1)	103.09(14)
C(3)-C(6)	1.532(5)	C(25)-Ru(1)-O(1)	79.52(12)
C(7)-C(12)	1.402(4)	C(1)-Ru(1)-O(1)	177.38(11)
C(7)-C(8)	1.415(4)	C(25)-Ru(1)-Cl(1)	98.12(10)
C(8)-C(9)	1.371(4)	C(1)-Ru(1)-Cl(1)	93.31(8)
C(8)-C(13)	1.513(4)	O(1)-Ru(1)-Cl(1)	86.49(6)
C(9)-C(10)	1.387(4)	C(25)-Ru(1)-Cl(2)	96.93(9)
C(10)-C(11)	1.390(4)	C(1)-Ru(1)-Cl(2)	94.09(8)
C(10)-C(14)	1.499(4)	O(1)-Ru(1)-Cl(2)	85.34(6)
C(11)-C(12)	1.390(4)	Cl(1)-Ru(1)-Cl(2)	161.26(4)
C(12)-C(15)	1.521(4)	Cl(1B)-Ru(2)-Cl(2B)	160.3(10)
C(16)-C(17)	1.394(4)	C(31)-O(1)-C(32)	119.9(2)
C(16)-C(21)	1.413(4)	C(31)-O(1)-Ru(1)	110.35(19)
C(17)-C(18)	1.400(4)	C(32)-O(1)-Ru(1)	128.72(18)
C(17)-C(22)	1.528(4)	C(1)-N(1)-C(7)	122.4(3)
C(18)-C(19)	1.383(4)	C(1)-N(1)-C(2)	112.5(3)

C(7)-N(1)-C(2)	123.9(3)	C(30)-C(31)-C(26)	122.2(3)
C(1)-N(2)-C(16)	124.1(2)	O(1)-C(32)-C(33)	105.3(3)
C(1)-N(2)-C(3)	113.3(3)	O(1)-C(32)-C(34)	109.9(3)
C(16)-N(2)-C(3)	122.6(3)	C(33)-C(32)-C(34)	113.3(3)
N(2)-C(1)-N(1)	106.1(3)	C(41)#1-C(41)-C(42)	110.2(8)
N(2)-C(1)-Ru(1)	134.4(2)	C(43)-C(42)-C(41)	104.3(9)
N(1)-C(1)-Ru(1)	119.5(2)		
C(4)-C(2)-N(1)	118.7(3)		
C(4)-C(2)-C(3)	124.9(4)		
N(1)-C(2)-C(3)	104.1(3)		
C(5)-C(3)-N(2)	115.0(3)		
C(5)-C(3)-C(2)	116.0(3)		
N(2)-C(3)-C(2)	101.2(3)		
C(5)-C(3)-C(6)	106.7(4)		
N(2)-C(3)-C(6)	110.0(3)		
C(2)-C(3)-C(6)	107.7(4)		
C(12)-C(7)-C(8)	119.8(3)		
C(12)-C(7)-N(1)	119.6(3)		
C(8)-C(7)-N(1)	120.4(3)		
C(9)-C(8)-C(7)	118.1(3)		
C(9)-C(8)-C(13)	119.8(3)		
C(7)-C(8)-C(13)	122.1(3)		
C(8)-C(9)-C(10)	123.1(3)		
C(9)-C(10)-C(11)	118.1(3)		
C(9)-C(10)-C(14)	120.4(3)		
C(11)-C(10)-C(14)	121.5(3)		
C(10)-C(11)-C(12)	121.0(3)		
C(11)-C(12)-C(7)	119.4(3)		
C(11)-C(12)-C(15)	117.9(3)		
C(7)-C(12)-C(15)	122.6(3)		
C(17)-C(16)-C(21)	120.4(3)		
C(17)-C(16)-N(2)	119.3(3)		
C(21)-C(16)-N(2)	120.2(3)		
C(16)-C(17)-C(18)	119.3(3)		
C(16)-C(17)-C(22)	121.8(3)		
C(18)-C(17)-C(22)	118.8(3)		
C(19)-C(18)-C(17)	121.3(3)		
C(20)-C(19)-C(18)	118.3(3)		
C(20)-C(19)-C(23)	121.8(3)		
C(18)-C(19)-C(23)	119.9(3)		
C(19)-C(20)-C(21)	123.0(3)		
C(20)-C(21)-C(16)	117.7(3)		
C(20)-C(21)-C(24)	119.3(3)		
C(16)-C(21)-C(24)	122.9(3)		
C(26)-C(25)-Ru(1)	117.8(2)		
C(31)-C(26)-C(27)	118.3(3)		
C(31)-C(26)-C(25)	119.8(3)		
C(27)-C(26)-C(25)	121.9(3)		
C(28)-C(27)-C(26)	120.5(3)		
C(27)-C(28)-C(29)	120.1(3)		
C(30)-C(29)-C(28)	120.5(3)		
C(31)-C(30)-C(29)	118.3(3)		
O(1)-C(31)-C(30)	125.2(3)		
O(1)-C(31)-C(26)	112.6(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+2

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for 17 (CCDC 670930). 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)	181(2)	159(1)	128(2)	6(1)	-9(1)	8(1)
Cl(1)	315(6)	276(4)	171(5)	1(3)	-82(4)	28(4)
Cl(2)	326(6)	334(5)	141(4)	43(3)	29(4)	71(4)
Ru(2)	330(40)	400(40)	1300(80)	-370(40)	-230(50)	60(40)
Cl(1B)	650(130)	720(130)	1250(180)	-810(130)	-140(120)	-130(120)
Cl(2B)	910(110)	980(110)	1020(110)	280(80)	-100(80)	210(80)
O(1)	223(13)	251(12)	340(14)	55(10)	24(11)	5(10)
N(1)	189(16)	194(13)	214(15)	15(11)	30(12)	59(12)
N(2)	195(16)	184(13)	233(15)	9(11)	-12(12)	11(12)
C(1)	290(20)	214(15)	70(15)	-10(12)	-96(14)	-4(15)
C(2)	350(30)	320(20)	1260(40)	90(30)	60(30)	40(20)
C(3)	260(20)	262(18)	490(20)	-27(16)	46(19)	63(17)
C(4)	330(20)	290(20)	1070(40)	80(20)	60(20)	80(19)
C(5)	620(30)	390(20)	820(30)	60(20)	320(30)	40(20)
C(6)	1040(40)	690(30)	560(30)	-110(20)	-370(30)	450(30)
C(7)	196(18)	179(14)	212(18)	-29(13)	19(15)	25(14)
C(8)	280(20)	181(15)	196(18)	18(13)	4(15)	46(14)
C(9)	320(20)	239(16)	205(19)	5(13)	-84(16)	-1(15)
C(10)	250(20)	218(16)	300(20)	60(14)	-60(16)	-4(15)
C(11)	320(20)	237(16)	219(18)	62(13)	-9(16)	-8(15)
C(12)	242(19)	179(14)	163(17)	12(12)	-30(14)	32(14)
C(13)	380(20)	344(19)	193(19)	-13(14)	-13(16)	18(17)
C(14)	350(20)	430(20)	370(20)	107(17)	-111(18)	-114(18)
C(15)	360(20)	343(19)	270(20)	79(15)	-86(17)	-83(17)
C(16)	200(19)	231(16)	272(19)	-21(14)	11(15)	-6(14)
C(17)	280(20)	269(17)	219(19)	24(14)	24(16)	-22(15)
C(18)	360(20)	327(19)	290(20)	98(15)	36(17)	-27(17)
C(19)	320(20)	247(17)	410(20)	13(16)	40(18)	-53(16)
C(20)	270(20)	325(19)	320(20)	-64(16)	-45(17)	-15(17)
C(21)	198(19)	283(17)	255(19)	12(14)	-8(15)	35(15)
C(22)	510(30)	316(18)	212(19)	45(14)	-65(17)	-91(18)
C(23)	540(30)	340(20)	560(30)	5(19)	20(20)	-120(20)
C(24)	400(20)	356(19)	240(20)	-36(15)	-13(17)	27(18)
C(25)	290(20)	231(16)	243(19)	-29(13)	-28(15)	0(15)
C(26)	280(20)	245(17)	184(17)	35(13)	9(15)	51(15)
C(27)	330(20)	273(18)	350(20)	45(15)	5(17)	-26(17)
C(28)	440(30)	229(17)	430(20)	14(16)	-16(19)	-12(18)
C(29)	400(20)	282(18)	350(20)	-6(15)	31(18)	80(18)
C(30)	300(20)	304(18)	250(19)	17(14)	23(16)	59(16)
C(31)	320(20)	230(16)	205(18)	61(13)	-15(16)	15(16)
C(32)	200(20)	339(19)	340(20)	98(16)	-9(17)	6(16)

C(33)	300(20)	330(20)	470(20)	117(17)	-14(18)	-48(17)
C(34)	320(20)	339(19)	400(20)	72(16)	-33(18)	-15(17)
C(41)	1810(90)	1140(60)	690(50)	440(40)	700(50)	420(60)
C(42)	2070(100)	1610(80)	550(40)	440(50)	460(50)	560(70)
C(43)	1300(120)	1470(130)	490(80)	180(80)	70(70)	-80(110)

Compound 20 (CCDC 651007).

Table 1. Crystal data and structure refinement for 20 (CCDC 651007).

Empirical formula	C ₃₁ H ₃₈ N ₂ OCl ₂ Ru
Formula weight	626.60
Crystallization Solvent	Benzene/pentane
Crystal Habit	Blade
Crystal size	0.32 x 0.20 x 0.11 mm ³
Crystal color	Dichroic - light green / dark blue

Data Collection

Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoK α	
Data Collection Temperature	100(2) K	
θ range for 17086 reflections used in lattice determination	2.37 to 41.27°	
Unit cell dimensions	a = 9.1757(3) Å b = 10.6130(4) Å c = 16.2638(6) Å	α = 85.3300(10)° β = 77.2650(10)° γ = 72.2060(10)°
Volume	1470.76(9) Å ³	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.415 Mg/m ³	
F(000)	648	
Data collection program	Bruker SMART v5.630	
θ range for data collection	2.02 to 41.86°	
Completeness to θ = 41.86°	79.4 %	
Index ranges	-17 ≤ h ≤ 15, -18 ≤ k ≤ 18, -28 ≤ l ≤ 27	
Data collection scan type	ω scans at 8 ϕ settings	
Data reduction program	Bruker SAINT v6.45A	
Reflections collected	45559	
Independent reflections	16192 [R _{int} = 0.0938]	
Absorption coefficient	0.741 mm ⁻¹	
Absorption correction	None	
Max. and min. transmission	0.9229 and 0.7975	

Table 1 (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	16192 / 0 / 342
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.187
Final R indices [$I > 2\sigma(I)$, 11711 reflections]	$R_1 = 0.0444$, $wR_2 = 0.0893$
R indices (all data)	$R_1 = 0.0677$, $wR_2 = 0.0937$
Type of weighting scheme used	Sigma
Weighting scheme used	$w = 1/\sigma^2(F_o^2)$
Max shift/error	0.002
Average shift/error	0.000
Largest diff. peak and hole	2.317 and -1.637 e.Å ⁻³

Special Refinement Details

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.

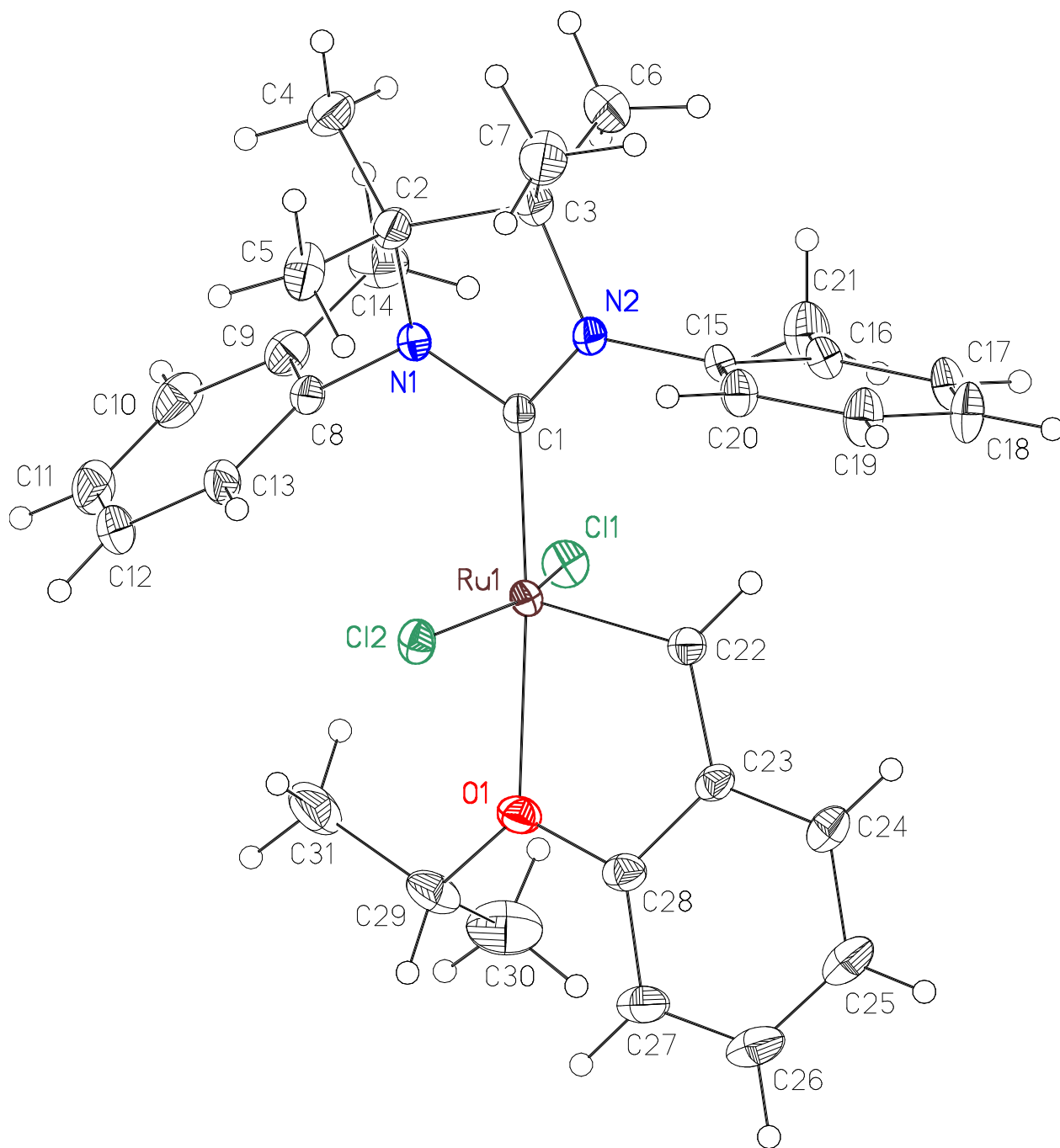


Figure 1. Minimum overlap view.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 20 (CCDC 651007). $U(\text{eq})$ is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	7217(1)	8130(1)	7087(1)	13(1)
Cl(1)	7853(1)	9439(1)	7976(1)	21(1)
Cl(2)	5754(1)	7111(1)	6490(1)	18(1)
O(1)	6169(2)	9943(1)	6337(1)	20(1)
N(1)	7110(2)	6264(2)	8484(1)	17(1)
N(2)	9086(2)	5315(2)	7494(1)	17(1)
C(1)	7962(2)	6481(2)	7713(1)	15(1)
C(2)	7361(2)	4802(2)	8671(1)	22(1)
C(3)	9058(2)	4234(2)	8143(1)	23(1)
C(4)	7200(3)	4483(2)	9611(1)	29(1)
C(5)	6155(2)	4369(2)	8333(1)	27(1)
C(6)	10317(2)	4117(3)	8642(2)	32(1)
C(7)	9337(3)	2896(2)	7753(2)	31(1)
C(8)	5690(2)	7222(2)	8890(1)	17(1)
C(9)	5673(2)	7835(2)	9632(1)	23(1)
C(10)	4247(3)	8692(2)	10039(1)	29(1)
C(11)	2898(2)	8961(2)	9721(1)	29(1)
C(12)	2934(2)	8370(2)	8981(1)	27(1)
C(13)	4331(2)	7490(2)	8575(1)	21(1)
C(14)	7122(3)	7606(2)	9982(2)	32(1)
C(15)	10418(2)	5168(2)	6807(1)	15(1)
C(16)	11629(2)	5698(2)	6841(1)	17(1)
C(17)	12890(2)	5493(2)	6155(1)	21(1)
C(18)	12956(2)	4773(2)	5464(1)	26(1)
C(19)	11750(2)	4251(2)	5443(1)	25(1)
C(20)	10474(2)	4454(2)	6116(1)	19(1)
C(21)	11574(2)	6529(2)	7555(1)	30(1)
C(22)	8794(2)	7995(2)	6151(1)	16(1)
C(23)	8491(2)	8880(2)	5440(1)	16(1)
C(24)	9541(2)	8743(2)	4654(1)	22(1)
C(25)	9170(3)	9595(2)	3988(1)	27(1)
C(26)	7752(3)	10590(2)	4103(1)	28(1)
C(27)	6693(2)	10766(2)	4875(1)	25(1)
C(28)	7079(2)	9909(2)	5538(1)	19(1)
C(29)	4874(2)	11139(2)	6616(1)	28(1)
C(30)	5537(3)	12254(2)	6730(2)	42(1)
C(31)	3925(3)	10739(3)	7424(2)	35(1)

Table 3. Selected bond lengths [Å] and angles [°] for 20 (CCDC 651007).

Ru(1)-C(22)	1.8360(17)	C(22)-Ru(1)-C(1)	103.04(7)
Ru(1)-C(1)	1.9633(18)	C(22)-Ru(1)-O(1)	79.01(7)
Ru(1)-O(1)	2.2621(14)	C(1)-Ru(1)-O(1)	174.03(6)
Ru(1)-Cl(1)	2.3559(4)	C(22)-Ru(1)-Cl(1)	101.89(5)
Ru(1)-Cl(2)	2.3559(4)	C(1)-Ru(1)-Cl(1)	94.04(5)
		O(1)-Ru(1)-Cl(1)	90.99(4)
		C(22)-Ru(1)-Cl(2)	95.85(5)
		C(1)-Ru(1)-Cl(2)	88.98(5)
		O(1)-Ru(1)-Cl(2)	85.21(4)
		Cl(1)-Ru(1)-Cl(2)	160.813(16)

Table 4. Bond lengths [Å] and angles [°] for 20 (CCDC 651007).

Ru(1)-C(22)	1.8360(17)	C(26)-C(27)	1.394(3)
Ru(1)-C(1)	1.9633(18)	C(27)-C(28)	1.388(3)
Ru(1)-O(1)	2.2621(14)	C(29)-C(31)	1.516(3)
Ru(1)-Cl(1)	2.3559(4)	C(29)-C(30)	1.527(3)
Ru(1)-Cl(2)	2.3559(4)		
O(1)-C(28)	1.378(2)	C(22)-Ru(1)-C(1)	103.04(7)
O(1)-C(29)	1.472(2)	C(22)-Ru(1)-O(1)	79.01(7)
N(1)-C(1)	1.366(2)	C(1)-Ru(1)-O(1)	174.03(6)
N(1)-C(8)	1.444(2)	C(22)-Ru(1)-Cl(1)	101.89(5)
N(1)-C(2)	1.513(2)	C(1)-Ru(1)-Cl(1)	94.04(5)
N(2)-C(1)	1.360(2)	O(1)-Ru(1)-Cl(1)	90.99(4)
N(2)-C(15)	1.441(2)	C(22)-Ru(1)-Cl(2)	95.85(5)
N(2)-C(3)	1.497(3)	C(1)-Ru(1)-Cl(2)	88.98(5)
C(2)-C(4)	1.524(3)	O(1)-Ru(1)-Cl(2)	85.21(4)
C(2)-C(5)	1.535(3)	Cl(1)-Ru(1)-Cl(2)	160.813(16)
C(2)-C(3)	1.564(2)	C(28)-O(1)-C(29)	119.65(15)
C(3)-C(6)	1.522(3)	C(28)-O(1)-Ru(1)	110.00(11)
C(3)-C(7)	1.529(3)	C(29)-O(1)-Ru(1)	129.75(12)
C(8)-C(13)	1.393(3)	C(1)-N(1)-C(8)	123.11(15)
C(8)-C(9)	1.412(3)	C(1)-N(1)-C(2)	111.54(14)
C(9)-C(10)	1.402(3)	C(8)-N(1)-C(2)	120.22(14)
C(9)-C(14)	1.506(3)	C(1)-N(2)-C(15)	124.44(15)
C(10)-C(11)	1.387(3)	C(1)-N(2)-C(3)	114.11(14)
C(11)-C(12)	1.391(3)	C(15)-N(2)-C(3)	119.97(14)
C(12)-C(13)	1.395(3)	N(2)-C(1)-N(1)	106.23(15)
C(15)-C(20)	1.389(2)	N(2)-C(1)-Ru(1)	133.02(12)
C(15)-C(16)	1.403(2)	N(1)-C(1)-Ru(1)	119.76(12)
C(16)-C(17)	1.396(2)	N(1)-C(2)-C(4)	112.12(16)
C(16)-C(21)	1.497(3)	N(1)-C(2)-C(5)	108.57(16)
C(17)-C(18)	1.389(3)	C(4)-C(2)-C(5)	109.54(16)
C(18)-C(19)	1.389(3)	N(1)-C(2)-C(3)	99.90(14)
C(19)-C(20)	1.391(2)	C(4)-C(2)-C(3)	114.01(17)
C(22)-C(23)	1.450(3)	C(5)-C(2)-C(3)	112.30(16)
C(23)-C(28)	1.403(3)	N(2)-C(3)-C(6)	109.06(16)
C(23)-C(24)	1.409(2)	N(2)-C(3)-C(7)	112.41(17)
C(24)-C(25)	1.387(3)	C(6)-C(3)-C(7)	108.98(18)
C(25)-C(26)	1.388(3)	N(2)-C(3)-C(2)	99.85(15)

C(6)-C(3)-C(2)	113.13(17)
C(7)-C(3)-C(2)	113.16(16)
C(13)-C(8)-C(9)	120.25(16)
C(13)-C(8)-N(1)	120.29(15)
C(9)-C(8)-N(1)	119.39(16)
C(10)-C(9)-C(8)	117.76(19)
C(10)-C(9)-C(14)	120.06(19)
C(8)-C(9)-C(14)	122.17(18)
C(11)-C(10)-C(9)	121.73(19)
C(10)-C(11)-C(12)	120.07(18)
C(11)-C(12)-C(13)	119.2(2)
C(8)-C(13)-C(12)	120.95(18)
C(20)-C(15)-C(16)	121.21(15)
C(20)-C(15)-N(2)	117.33(15)
C(16)-C(15)-N(2)	121.44(15)
C(17)-C(16)-C(15)	117.81(15)
C(17)-C(16)-C(21)	119.32(16)
C(15)-C(16)-C(21)	122.77(15)
C(18)-C(17)-C(16)	121.20(16)
C(19)-C(18)-C(17)	120.20(16)
C(18)-C(19)-C(20)	119.61(17)
C(15)-C(20)-C(19)	119.96(16)
C(23)-C(22)-Ru(1)	118.53(13)
C(28)-C(23)-C(24)	118.66(17)
C(28)-C(23)-C(22)	118.41(16)
C(24)-C(23)-C(22)	122.92(17)
C(25)-C(24)-C(23)	120.48(19)
C(24)-C(25)-C(26)	119.27(19)
C(25)-C(26)-C(27)	121.83(19)
C(28)-C(27)-C(26)	118.38(19)
O(1)-C(28)-C(27)	125.80(17)
O(1)-C(28)-C(23)	112.83(16)
C(27)-C(28)-C(23)	121.36(17)
O(1)-C(29)-C(31)	105.52(17)
O(1)-C(29)-C(30)	109.35(18)
C(31)-C(29)-C(30)	113.5(2)

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for 20 (CCDC 651007). 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)	111(1)	137(1)	134(1)	-14(1)	-27(1)	-33(1)
Cl(1)	234(2)	201(2)	202(2)	-50(2)	-57(2)	-76(2)
Cl(2)	163(2)	243(2)	158(2)	-21(2)	-40(1)	-96(2)
O(1)	190(6)	165(6)	208(6)	11(5)	-51(5)	-11(5)
N(1)	124(6)	181(7)	161(6)	15(5)	-1(5)	-18(5)
N(2)	129(6)	165(7)	182(7)	20(5)	2(5)	-23(5)
C(1)	120(6)	189(8)	130(6)	-15(6)	-14(5)	-50(6)
C(2)	191(7)	193(8)	222(8)	29(7)	16(6)	-37(7)
C(3)	167(7)	216(9)	269(9)	23(7)	5(6)	-29(7)
C(4)	297(10)	282(10)	229(9)	62(8)	16(7)	-61(8)
C(5)	244(9)	258(10)	308(10)	-54(8)	42(7)	-112(8)
C(6)	213(9)	399(13)	322(11)	73(10)	-80(8)	-65(9)
C(7)	284(10)	200(9)	389(12)	-15(8)	18(9)	-61(8)
C(8)	149(7)	190(8)	142(7)	1(6)	6(5)	-29(6)
C(9)	255(8)	229(9)	190(8)	-11(7)	-22(7)	-84(7)
C(10)	368(11)	253(10)	207(9)	-58(8)	54(8)	-100(9)
C(11)	243(9)	227(10)	303(10)	-40(8)	82(8)	-14(8)
C(12)	162(7)	288(10)	286(10)	6(8)	18(7)	-8(7)
C(13)	159(7)	263(9)	171(8)	-13(7)	0(6)	-39(7)
C(14)	378(11)	357(12)	295(11)	-9(9)	-166(9)	-129(10)
C(15)	103(6)	162(7)	162(7)	-6(6)	-8(5)	-19(6)
C(16)	136(6)	181(8)	183(7)	-34(6)	-31(5)	-36(6)
C(17)	124(6)	270(9)	252(9)	-63(7)	-14(6)	-74(7)
C(18)	182(8)	344(11)	241(9)	-95(8)	60(7)	-116(8)
C(19)	221(8)	322(11)	221(9)	-96(8)	14(7)	-125(8)
C(20)	163(7)	226(9)	208(8)	-33(7)	-24(6)	-81(7)
C(21)	253(9)	364(12)	313(11)	-105(9)	-27(8)	-137(9)
C(22)	168(7)	160(7)	170(7)	9(6)	-49(6)	-61(6)
C(23)	191(7)	174(8)	163(7)	28(6)	-51(6)	-97(6)
C(24)	260(8)	243(9)	185(8)	12(7)	-27(6)	-140(7)
C(25)	382(11)	324(11)	167(8)	47(8)	-58(7)	-219(9)
C(26)	418(11)	286(10)	233(9)	100(8)	-163(8)	-200(9)
C(27)	295(9)	219(9)	273(10)	82(7)	-142(8)	-103(8)
C(28)	215(8)	182(8)	196(8)	26(6)	-83(6)	-82(7)
C(29)	248(9)	215(9)	325(11)	-17(8)	-99(8)	43(8)
C(30)	593(16)	185(10)	458(14)	-50(10)	-175(12)	-44(11)
C(31)	227(9)	391(13)	324(11)	-52(10)	-50(8)	85(9)

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- ⁱ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
- ⁱⁱ Jazzer, R.; Bourg, J.-B.; Dewhurst, R. D.; Donnadieu, B.; Bertrand, G. *J. Org. Chem.* **2007**, *72*, 3492-3499.
- ⁱⁱⁱ Türkmen, H.; Çetinkaya, B. *J. Organomet. Chem.* **2006**, *691*, 3749-3759.
- ^{iv} Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219-224.