Electronic Supplementary Information

Deprotonation of C-Alkyl groups of cationic N-heterocyclic ligands

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General Experimental Details: Solvents were dried over Na[Ph_2CO] (THF, diethyl ether, hydrocarbons) or CaH_2 (dichloromethane) and were distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy and by spot TLC on silica gel. All reagents were purchased from commercial sources. All reaction products were vacuum-dried for several hours prior to being weighted and analyzed. The instrumentation used was as follows:

IR: Perkin-Elmer FT Paragon 1000X.

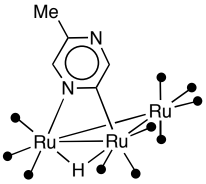
NMR: Bruker AV-400, AV-300, NAV-400, and DPX-300, room temperature, residual solvent as internal standard.

Microanalyses: Perkin-Elmer 2400B.

MS: VG Autospec double-focusing mass spectrometer operating in the FAB+ mode; ions were produced with a standard Cs^+ gun at about 30 kV; 3-nitrobenzyl alcohol was used as matrix.

X-Ray Diffraction: Crystals of **2c** and **4c** were analyzed by X-ray diffraction methods. Selected crystal, measurement, and refinement data are given in Table S1. Diffraction data were collected on an Oxford Diffraction Xcalibur Nova diffractometer, using Cu-Kα radiation. Empirical absorption corrections were applied using XABS2[1] (for **2c**) and the SCALE3 ABSPACK algorithm as implemented in the program CrysAlisPro RED[2] (for **4c**). Structures were solved by Patterson interpretation using the program DIRDIF.[3] Isotropic and full matrix anisotropic least square refinements were carried out using SHELXL.[4] All non-H atoms were refined anisotropically. The position of the hydride atom of **2c** was calculated with XHYDEX.[5] The hydride ligand and the hydrogen atoms bonded to C8 of **4c** were located in a Fourier map. The remaining hydrogen atoms were set in calculated positions and refined riding on their parent atoms. The molecular plots were made with the PLATON program package.[6] The WINGX program system[7] was used throughout the structure determinations. CCDC-832808 (**2c**) and CCDC-832809 (**4c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Theoretical Calculations: Density functional theory (DFT) calculations were carried out using the Becke's three-parameter hybrid exchange-correlation functional[8] and the B3LYP non-local gradient correction.[9] The LanL2DZ basis set, with relativistic effective core potentials, was used for the Ru atoms.[10] The basis set used for the remaining atoms was the 6-311+G**.[11] All optimized stationary points were confirmed as energy minima (all positive eigenvalues) or transition states (one imaginary eigenvalue) by analytical calculation of frequencies. IRC calculations were used to verify that the transition states found were correct saddle points connecting the proposed minima. All energies given in this contribution are potential energies calculated in gas phase. Molecular orbital data were obtained from the natural bond order (NBO) analysis of the data.[12] All calculations were carried out with the Gaussian03 package.[13] Cartesian coordinates for the atoms of all optimized structures are given in Tables S4-S14.



[Ru$_3$(μ-H)(μ-κ^2*N*^{1},*C*^{2}-5-MeC$_4$H$_2$N$_2$)(CO)$_{10}$] (1a): A solution of [Ru$_3$(CO)$_{12}$] (500 mg, 0.782 mmol) and 2-methylpyrazine (80 μL, 0.860 mmol) in THF (50 mL) was stirred at reflux temperature for 3 h. The color changed from orange to dark brown. The solvent was removed under reduced pressure, the residue was extracted into dichloromethane (3 mL), and this solution was placed onto a silica gel column (2 x 10 cm) packed in hexane. Hexane eluted a trace amount of [Ru$_3$(CO)$_{12}$]. Hexane-dichloromethane (2:3) eluted compound **1a**, which was isolated as an orange solid (300 mg, 57%).

Analysis (%), found for C$_{15}$H$_6$N$_2$O$_{10}$Ru$_3$ (calcd): C 26.66 (26.59); H 0.94 (0.89); N 4.10 (4.14).

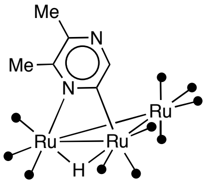
+FAB MS (MW, amu): 679 (677.43).

IR, (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2101 (w), 2064 (s), 2052 (vs), 2023 (m, sh), 2014 (m, br), 1998 (w, sh).

^{1}H NMR (CD$_2$Cl$_2$, r.t., ppm): δ 8.36 (s, br, 1 H, C*H*), 7.98 (s, br, 1 H, C*H*), 2.41 (s, 3 H, C*H*$_3$), –14.47 (s, 1 H, μ-*H*).

^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, r.t., ppm): δ 207.6, 205.6, 201.0, 200.4, 195.5, 195.0, 191.9, 190.8, 189.5, 185.9 (10 *C*Os), 170.2 (*C*), 155.9 (*C*H), 150.1 (*C*), 148.5 (*C*H), 20.3 (*C*H$_3$).

[Ru$_3$(μ-H)(μ-κ^2*N*^{1},*C*^{2}-5,6-Me$_2$C$_4$HN$_2$)(CO)$_{10}$] (2a): A solution of [Ru$_3$(CO)$_{12}$] (500 mg, 0.782 mmol) and 2,3-dimethylpyrazine (91 μL, 0.860 mmol) in THF (50 mL) was stirred at reflux temperature for 7 h. The color changed from orange to dark garnet. The solvent was removed under reduced pressure, the residue was extracted into dichloromethane (3 mL), and this solution was placed onto a silica gel column (2 x 10 cm) packed in hexane. Hexane-dichloromethane (4:1) eluted a trace amount of [Ru$_3$(CO)$_{12}$]. Dichloromethane eluted compound **2a**, which was isolated as a yellow-orange solid (300 mg, 55%).



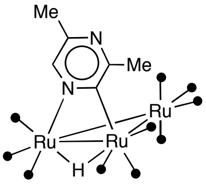
Analysis (%), found for $C_{16}H_8N_2O_{10}Ru_3$ (calcd): C 27.86 (27.79); H 1.22 (1.17); N 3.96 (4.05).

+FAB MS (MW, amu): 693 (691.45).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2100 (w), 2061 (s), 2051 (vs), 2023 (m, sh), 2014 (m, br), 1997 (w, sh).

^{1}H NMR (CD_2Cl_2, r.t., ppm): δ 8.10 (s, 1 H, C*H*), 2.56 (s, 3 H, C*H*$_3$), 2.47 (s, 3 H, C*H*$_3$), –14.18 (s, 1 H, μ-*H*).

^{13}C{^{1}H} NMR (CD_2Cl_2, r.t., ppm): δ 207.5, 205.1, 200.9, 200.6, 195.6, 195.5, 192.0, 190.6, 189.9, 187.7 (10 *C*Os), 169.3 (*C*), 152.9 (*C*H), 152.5 (*C*), 149.3 (*C*), 22.0 (*C*H$_3$), 21.8 (*C*H$_3$).



[Ru$_3$(μ-H)(μ-κ^2*N*^{1},*C*^{2}-3,5-Me$_2$C$_4$HN$_2$)(CO)$_{10}$] (3a): A solution of [$Ru_3(CO)_{12}$] (500 mg, 0.782 mmol) and 2,6-dimethylpyrazine (80 μL, 0.860 mmol) in THF (50 mL) was stirred at reflux temperature for 2 h. The color changed from orange to dark brown. The solvent was removed under reduced pressure, the residue was extracted into dichloromethane (3 mL), and this solution was placed onto a silica gel column (2 x 10 cm) packed in hexane. Hexane eluted a trace amount of [$Ru_3(CO)_{12}$]. Dichloromethane eluted compound **3a**, which was isolated as an orange solid (390 mg, 72%).

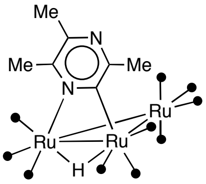
Analysis (%), found for $C_{16}H_8N_2O_{10}Ru_3$ (calcd): C 27.84 (27.79); H 1.23 (1.17); N 3.98 (4.05).

+FAB MS (MW, amu): 693 (691.45).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2100 (w), 2062 (s), 2049 (vs), 2012 (m, sh), 1998 (m, sh).

^{1}H NMR (CD_2Cl_2, r.t., ppm): δ 7.82 (s, 1 H, C*H*), 2.69 (s, 3 H, C*H*$_3$), 2.38 (s, 3 H, C*H*$_3$), –14.33 (s, 1 H, μ-*H*).

^{13}C{^{1}H} NMR (CD_2Cl_2, r.t., ppm): δ 207.5, 205.1, 200.9, 200.6, 195.6, 195.5, 192.0, 190.6, 189.9, 187.7 (10 *C*Os), 169.3 (*C*), 152.9 (*C*H), 152.5 (*C*), 149.3 (*C*), 22.0 (*C*H$_3$), 21.8 (*C*H$_3$).



[Ru$_3$(μ-H)(μ-κ^2*N*^{1},*C*^{2}-3,5,6-Me$_3$C$_4$N$_2$)(CO)$_{10}$] (4a): A solution of [$Ru_3(CO)_{12}$] (500 mg, 0.782 mmol) and 2,3,5-trimethylpyrazine (105 μL, 0.860 mmol) in THF (50 mL) was stirred at reflux temperature for 6 h. The color changed from orange to dark brown. The solution was concentrated to ca. 3 mL and was supported onto preparative silica gel TLC plates. Hexane-dichloromethane (1:1) eluted a trace amount of [$Ru_3(CO)_{12}$] followed by compound **4a**, which was isolated as a yellow solid (280 mg, 51%).

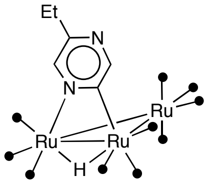
Analysis (%), found for $C_{17}H_{10}N_2O_{10}Ru_3$ (calcd): C 29.00 (28.94); H 1.49 (1.43); N 3.90 (3.97).

+FAB MS (MW, amu): 707 (705.48).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2099 (w), 2059 (s), 2049 (vs), 2014 (m, sh), 1996 (m, sh).

^{1}H NMR (CD_2Cl_2, r.t., ppm): δ 2.66 (s, 3 H, C*H*$_3$), 2.56 (s, 3 H, C*H*$_3$), 2.44 (s, 3 H, C*H*$_3$), –13.99 (s, 1 H, μ-*H*).

^{13}C{^{1}H} NMR (CD_2Cl_2, r.t., ppm): δ 207.4, 204.7, 201.0, 200.5, 196.0, 195.4, 191.9, 190.8, 190.5, 187.0 (10 *C*Os), 170.1 (*C*), 157.3 (*C*), 148.3 (*C*), 147.8 (*C*), 25.8 (*C*H$_3$), 22.1 (*C*H$_3$), 21.9 (*C*H$_3$).



[Ru_3(μ-H)(μ-κ^2N^1,C^2-5-Et$C_4H_2N_2$)$(CO)_{10}$] (5a): A solution of [$Ru_3(CO)_{12}$] (500 mg, 0.782 mmol) and 2-ethylpyrazine (94 μL, 0.860 mmol) in THF (50 mL) was stirred at reflux temperature for 4.5 h. The color changed from orange to dark brown. The solvent was removed under reduced pressure, the residue was extracted into dichloromethane (3 mL), and this solution was placed onto a silica gel column (2 x 10 cm) packed in hexane. Hexane eluted a trace amount of [$Ru_3(CO)_{12}$]. Hexane-dichloromethane (4:1) eluted compound **5a**, which was isolated as an orange solid (400 mg, 74%).

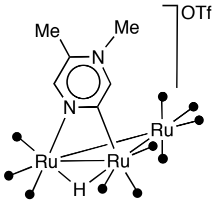
Analysis (%), found for $C_{16}H_8N_2O_{10}Ru_3$ (calcd): C 27.83 (27.79); H 1.21 (1.17); N 3.97 (4.05).

+FAB MS (MW, amu): 693 (691.45).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2101 (w), 2063 (s), 2052 (vs), 2023 (m, sh), 2014 (m, br), 1998 (m, sh), 1982 (vw, sh).

^{1}H NMR (CD_2Cl_2, r.t., ppm): δ 8.38 (s, 1 H, C*H*), 7.96 (s, 1 H, C*H*), 2.69 (q, *J* = 7.5 Hz, 2 H, CH_2), 1.27 (t, *J* = 7.5 Hz, 3 H, CH_3), –14.45 (s, 1 H, μ-*H*).

^{13}C{^{1}H} NMR (CD_2Cl_2, r.t., ppm): δ 207.6, 205.4, 201.0, 200.4, 195.6, 195.1, 191.8, 190.8, 189.5, 185.9 (10 *C*Os), 70.5 (*C*), 156.0 (*C*H), 155.3 (*C*), 147.8 (*C*H), 27.6 (*C*H_2), 13.3 (*C*H_3).



[Ru_3(μ-H)(μ-κ^2N^1,C^2-4,5-$Me_2C_4H_2N_2$)$(CO)_{10}$]OTf (1b): A solution of **1a** (150 mg, 0.221 mmol) and methyl triflate (125 μL, 1.107 mmol) in dichloromethane (30 mL) was stirred at room temperature for 15 h. A red-orange solid precipitated. The solvent was removed under reduced pressure to give an oily residue that was stirred in diethyl ether (2 x 5 mL). Compound **1b** was isolated as a red-orange solid (170 mg, 91%).

Analysis (%), found for $C_{17}H_9F_3N_2O_{13}Ru_3S$ (calcd): C 24.33 (24.26); H 1.14 (1.08); N 3.26 (3.33).

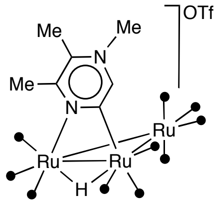
+FAB MS (MW, amu): 693 [M – CF_3SO_3] (841.53).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2107 (w), 2074 (s), 2062 (vs), 2039 (w), 2025 (w, sh), 2014 (m, br), 1999 (w, sh).

^{1}H NMR (Me_2CO-d_6, r.t., ppm): δ 9.59 (s, 1 H, C*H*), 9.04 (s, 1 H, C*H*), 4.44 (s, 3 H, NCH_3), 2.83 (s, 3 H, CH_3), –14.46 (s, 1 H, μ-*H*).

^{13}C{^{1}H} NMR (Me_2CO-d_6, r.t., ppm): δ 207.1, 200.6, 200.4, 194.3, 192.9, 191.2, 190.2, 188.4, 185.0 (9 *C*Os; a CO seems to be hidden by the solvent peak), 183.3 (*C*), 155.7 (*C*H), 145.3 (*C*H), 144.3 (*C*), 45.4 (N*C*H_3), 16.0 (*C*H_3).

[Ru_3(μ-H)(μ-κ^2N^1,C^2-4,5,6-$Me_3C_4HN_2$)$(CO)_{10}$]OTf (2b): A solution of **2a** (300 mg, 0.434 mmol) and methyl triflate (245 μL, 2.164 mmol) in dichloromethane (40 mL) was stirred at room temperature for 14 h. A red-orange solid precipitated from a dark garnet solution. The solvent was removed under reduced pressure to give an oily residue that was stirred in diethyl ether (2 x 10 mL). Compound **2b** was isolated as an orange solid (350 mg, 94%).



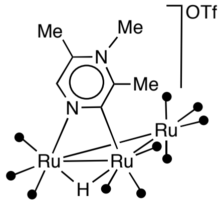
Analysis (%), found for $C_{18}H_{11}F_3N_2O_{13}Ru_3S$ (calcd): C 25.34 (25.27); H 1.34 (1.30); N 3.21 (3.27).

+FAB MS (MW, amu): 708 [M – CF_3SO_3] (855.56).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2107 (w), 2073 (s), 2061 (vs), 2036 (w), 2012 (m, br), 1993 (w, sh).

^1H NMR (Me_2CO-*d*$_6$, r.t., ppm): δ 8.82 (s, 1 H, C*H*), 4.46 (s, 3 H, NC*H*$_3$), 3.06 (s, 3 H, C*H*$_3$), 2.89 (s, 3 H, C*H*$_3$), –14.09 (s, 1 H, μ-*H*).

$^{13}C\{^1H\}$ NMR (Me_2CO-*d*$_6$, r.t., ppm): δ 207.2, 206.8, 200.9, 200.7, 194.7, 194.2, 191.5, 190.3, 189.0, 186.1 (10 *C*Os), 182.5 (*C*), 161.5 (*C*H), 144.4 (*C*), 142.8 (*C*), 46.8 (N*C*H$_3$), 23.7 (*C*H$_3$), 16.6 (*C*H$_3$).



[Ru$_3$(μ-H)(μ-κ^2*N*^{1},*C*^{2}-3,4,5-Me$_3$C$_4$HN$_2$)(CO)$_{10}$]OTf (3b): A solution of **3a** (350 mg, 0.506 mmol) and methyl triflate (286 μL, 2.531 mmol) in dichloromethane (40 mL) was stirred at room temperature for 18 h. A red-orange solid precipitated from a dark garnet solution. The solution was decanted off and the solid was washed with dichloromethane (5 mL) and diethyl ether (2 x 10 mL). Compound **3b** was isolated as an orange solid (350 mg, 94%).

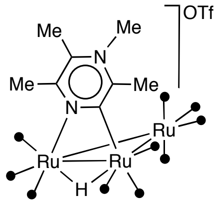
Analysis (%), found for $C_{18}H_{11}F_3N_2O_{13}Ru_3S$ (calcd): C 25.32 (25.27); H 1.37 (1.30); N 3.20 (3.27).

+FAB MS (MW, amu): 708 [M – CF_3SO_3] (855.56).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2107 (w), 2072 (s), 2061 (vs), 2037 (w), 2018 (m, br), 1995 (vw, sh).

^1H NMR (Me_2CO-*d*$_6$, r.t., ppm): δ 9.41 (s, 1 H, C*H*), 4.39 (s, 3 H, NC*H*$_3$), 3.27 (s, 3 H, C*H*$_3$), 2.86 (s, 3 H, C*H*$_3$), –14.28 (s, 1 H, μ-*H*).

$^{13}C\{^1H\}$ NMR (Me_2CO-*d*$_6$, r.t., ppm): δ 207.2, 207.0, 201.2, 200.7, 195.8, 193.0, 191.3, 190.5, 189.5, 186.7 (10 *C*Os), 185.6 (*C*), 155.2 (*C*), 153.1 (*C*H), 144.3 (*C*), 42.5 (N*C*H$_3$), 23.0 (*C*H$_3$), 17.7 (*C*H$_3$).



[Ru$_3$(μ-H)(μ-κ^2*N*^{1},*C*^{2}-3,4,5,6-Me$_4$C$_4$N$_2$)(CO)$_{10}$]OTf (4b): A solution of **4a** (260 mg, 0.369 mmol) and methyl triflate (210 μL, 1.855 mmol) in dichloromethane (40 mL) was stirred at room temperature for 72 h. An orange solid precipitated from a dark garnet solution. The solvent was removed under reduced pressure to give an oily residue that was stirred in diethyl ether (2 x 10 mL). Compound **4b** was isolated as an orange solid (240 mg, 75%).

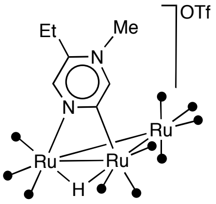
Analysis (%), found for $C_{19}H_{13}F_3N_2O_{13}Ru_3S$ (calcd): C 26.31 (26.24); H 1.56 (1.51); N 3.16 (3.22).

+FAB MS (MW, amu): 722 [M – CF_3SO_3] (869.58).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2106 (w), 2070 (s), 2060 (vs), 2035 (m), 2015 (s, br), 1990 (w, sh).

^{1}H NMR (Me_2CO-d_6, r.t., ppm): δ 4.37 (s, 3 H, NC*H_3*), 3.23 (s, 3 H, C*H_3*), 3.05 (s, 3 H, C*H_3*), 2.90 (s, 3 H, C*H_3*), –13.86 (s, 1 H, μ-*H*).

^{13}C{^{1}H} NMR (Me_2CO-d_6, r.t., ppm): δ 206.8, 200.9, 200.7, 195.6, 193.9, 191.2, 190.1, 189.8, 186.3 (9 *C*Os; a CO seems to be hidden by the solvent peak), 186.0 (*C*), 157.1 (*C*), 150.8 (*C*), 144.1 (*C*), 43.6 (N*C*H_3), 24.6 (*C*H_3), 23.7 (*C*H_3), 18.0 (*C*H_3).



[Ru_3(μ-H)(μ-κ^2*N*^{1},*C*^{2}-4-Me-5-Et-$C_4H_2N_2$)$(CO)_{10}$]OTf (5b): A solution of **5a** (400 mg, 0.578 mmol) and methyl triflate (330 μL, 2.916 mmol) in dichloromethane (50 mL) was stirred at room temperature for 17 h. The color changed from orange to garnet. The solvent was removed under reduced pressure to give an oily residue that was stirred in diethyl ether (2 x 15 mL). Compound **5b** was isolated as a red solid (450 mg, 91%).

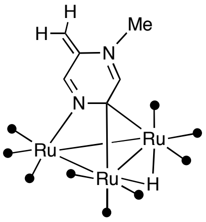
Analysis (%), found for $C_{18}H_{11}F_3N_2O_{13}Ru_3S$ (calcd): C 25.31 (25.27); H 1.36 (1.30); N 3.23 (3.27).

+FAB MS (MW, amu): 708 [M – CF_3SO_3] (855.56).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2108 (w), 2073 (s), 2075 (s), 2062 (vs), 2038 (w), 2015 (m, br), 1993 (w, sh).

^{1}H NMR (Me_2CO-d_6, r.t., ppm): δ 9.53 (s, 1 H, C*H*), 8.98 (s, 1 H, C*H*), 4.43 (s, 3 H, NC*H_3*), 3.18 (q, *J* = 7.5 Hz, 2 H, C*H_2*), 1.41 (t, *J* = 7.5 Hz, 3 H, C*H_3*), –14.48 (s, 1 H, μ-*H*).

^{13}C{^{1}H} NMR (Me_2CO-d_6, r.t., ppm): δ 207.2, 207.0, 200.8, 200.5, 194.2, 192.7, 191.2, 190.3, 188.3, 185.0 (10 *C*Os), 183.3 (*C*), 154.6 (*C*H), 148.3 (*C*), 145.5 (*C*H), 45.1 (N*C*H_3), 23.1 (*C*H_2), 10.7 (*C*H_3).

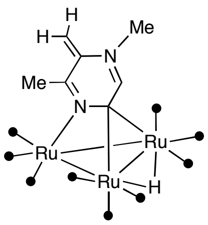


[Ru_3(μ-H)($μ_3$-κ^2*N*^{1},*C*^{2}-4-Me-5-CH_2-$C_4H_2N_2$)$(CO)_9$] (1c): A toluene solution of K[N$(SiMe_3)_2$] (355 μL, 0.5 M, 0.178 mmol) was dropwise added to a suspension of compound **1b** (150 mg, 0.178 mmol) in THF (30 mL) at –80 °C. The color changed from red to brown. The system was warmed up to room temperature and the solid was filtered off. An aliquot of the resulting solution was analyzed by ^{1}H NMR. The spectrum showed the presence of a mixture that comprised **1a** (17%), **1c** (48%), and smaller amounts of unidentified hydride-containing products. All attempts to obtain pure **1c** by chromatographic methods (TLC and silica or alumina columns) were unsuccessful.

^{1}H NMR (CD_2Cl_2, r.t., ppm): δ 7.52 (s, 1 H, C*H*), 6.49 (s, 1 H, C*H*), 4.53 (d, *J* = 3.2 Hz, 1 H, C*H_2*), 4.45 (d, *J* = 3.2 Hz, 1 H, C*H_2*), 3.08 (s, 3 H, NC*H_3*), –14.56 (s, 1 H, μ-*H*).

^{13}C{^{1}H} NMR (CD_2Cl_2, r.t., ppm): δ 199.3, 195.9 (*C*Os), 166.6 (*C*H), 151.7 (*C*H), 137.0 (*C*), 101.7 (*C*), 96.2 (*C*H_2), 40.8 (N*C*H_3).

[Ru_3(μ-H)($μ_3$-κ^2*N*^{1},*C*^{2}-4,6-Me_2-5-CH_2-C_4HN_2)$(CO)_9$] (2c): A toluene solution of K[N$(SiMe_3)_2$] (175 μL, 0.5 M, 0.088 mmol) was dropwise added to a suspension of compound **2b** (75 mg, 0.088 mmol) in



THF (30 mL) at –80 °C. The color changed from orange to brown. The system was warmed up to room temperature, the solid was filtered off, the solvent was removed under reduced pressure, the residue was extracted into dichloromethane (1.5 mL), and this solution was placed onto an alumina column (2 x 10 cm, activity IV) packed in hexane. Hexane eluted a trace amount of $[Ru_3(CO)_{12}]$. Hexane-dichloromethane (4:1) eluted compound **2c**, which was isolated as an orange solid (50 mg, 84%).

Analysis (%), found for $C_{16}H_{10}N_2O_9Ru_3$ (calcd): C 28.41 (28.37); H 1.58 (1.49); N 4.05 (4.14).

+*FAB MS* (MW, amu): 679 (677.47).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2069 (w), 2038 (vs), 2018 (m), 1989 (m, br), 1973 (w, sh).

^{1}H NMR (CD_2Cl_2, r.t., ppm): δ 6.54 (s, 1 H, C*H*), 4.77 (d, *J* = 4.0 Hz, 1 H, C*H*$_2$), 4.53 (d, *J* = 4.0 Hz, 1 H, C*H*$_2$), 3.15 (s, 3 H, NC*H*$_3$), 2.19 (s, 3 H, C*H*$_3$), –14.70 (s, 1 H, μ-*H*).

^{13}C{^{1}H} NMR (CD_2Cl_2, r.t., ppm): δ 205.4, 196.3 (*C*Os), 166.7 (*C*H), 154.1 (*C*), 137.2 (*C*), 101.5 (*C*), 95.2 (*C*H$_2$), 41.9 (N*C*H$_3$), 20.9 (*C*H$_3$).

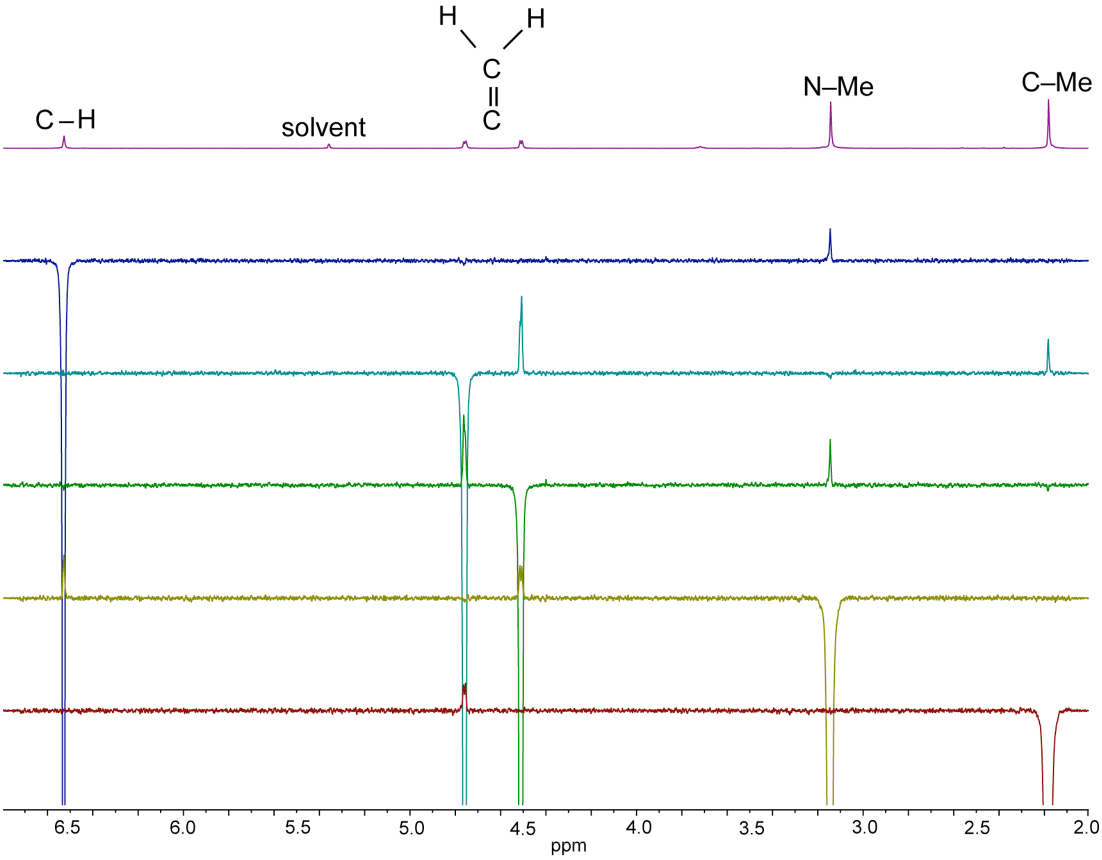
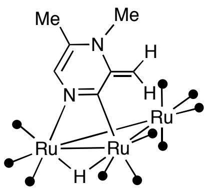


Figure S1. ^{1}H NMR in CD_2Cl_2 of compound **2c** in the 6.8–2.0 ppm region (top) and selected 1D NOE difference spectra after saturation at the frequencies of the inverted signals.

$[Ru_3(\mu\text{-}H)(\mu\text{-}\kappa^2N^1,C^2\text{-}3\text{-}CH_2\text{-}4,5\text{-}Me_2\text{-}C_4HN_2)(CO)_{10}]$ (3c): A toluene solution of $K[N(SiMe_3)_2]$ (175 μL, 0.5 M, 0.082 mmol) was dropwise added to a suspension of compound **3b** (70 mg, 0.082 mmol) in THF (30 mL) at –80 °C. The color changed from orange to brown. The system was warmed up to room temperature, the solid was filtered off, and the solvent was removed under reduced pressure. The



resulting oily solid was washed with hexane (5 mL) to give compound **3c** as an orange solid (40 mg, 69%).

Analysis (%), found for $C_{17}H_{10}N_2O_{10}Ru_3$ (calcd): C 29.0 (28.94); H 1.48 (1.43); N 3.91 (3.97).

+*FAB MS* (MW, amu): 707 (705.48).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2098 (w), 2059 (s), 2046 (vs), 2012 (m, br), 1993 (m, sh), 1976 (w, sh).

^{1}*H NMR* (CD_2Cl_2, r.t., ppm): δ 5.78 (s, 1 H, C*H*), 4.38 (d, *J* = 2.4 Hz, 1 H, C*H*$_2$), 4.11 (d, *J* = 2.4 Hz, 1 H, C*H*$_2$), 2.90 (s, 3 H, NC*H*$_3$), 1.96 (s, 3 H, C*H*$_3$), –14.66 (s, 1 H, μ-*H*).

$^{13}C\{^1H\}$ *NMR* (CD_2Cl_2, r.t., ppm): δ 208.3, 205.6, 201.8, 201.4, 196.7, 195.7, 192.2, 191.4, 191.0, 186.8 (10 *C*Os), 185.8 (*C*), 148.3 (*C*), 134.8 (*C*), 120.0 (*C*H), 89.1 (*C*H$_2$), 34.2 (N*C*H$_3$), 16.8 (*C*H$_3$).

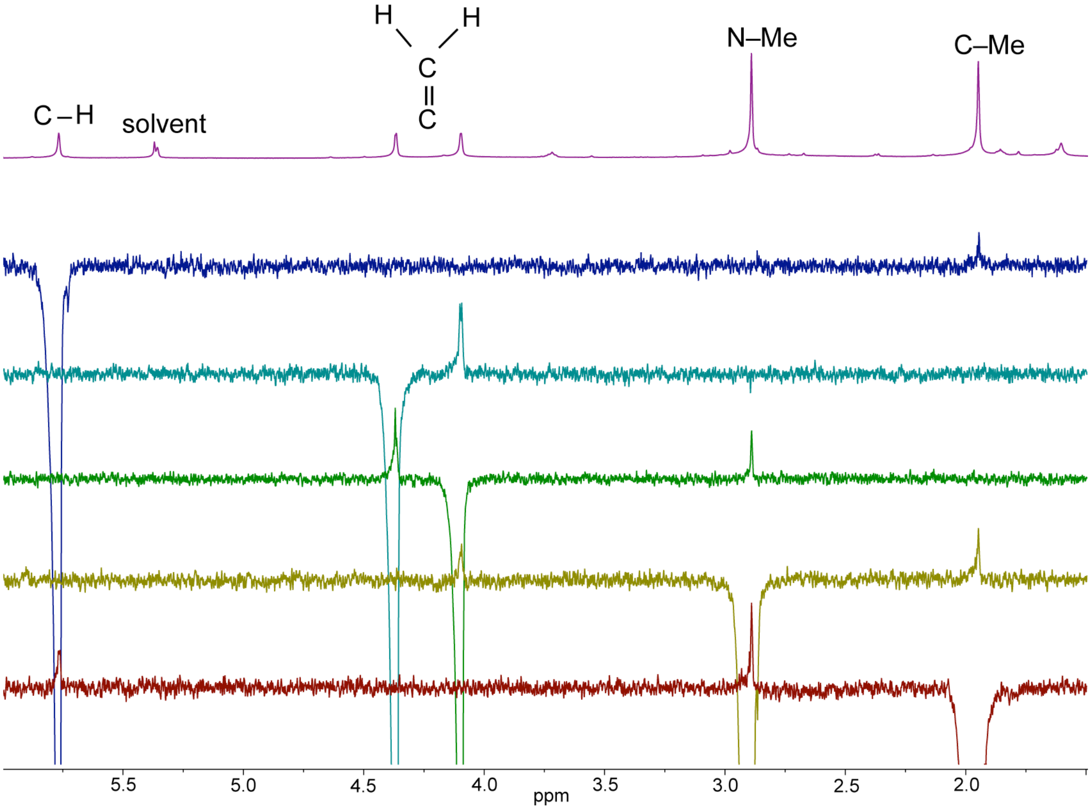
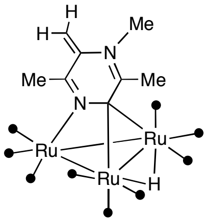


Figure S2. ^{1}H NMR in CD_2Cl_2 of compound **3c** in the 6.0–1.5 ppm region (top) and selected 1D NOE difference spectra after saturation at the frequencies of the inverted signals.



[Ru$_3$(μ-H)(μ$_3$-κ^2*N*^{1},*C*^{2}-3,4,6-Me$_3$-5-CH$_2$-C$_4$N$_2$)(CO)$_9$] (4c): A toluene solution of K[N(SiMe$_3$)$_2$] (195 μL, 0.5 M, 0.098 mmol) was dropwise added to a suspension of compound **4b** (85 mg, 0.098 mmol) in THF (30 mL) at –80 °C. The color changed from red to brown. The system was warmed up to room temperature, the solvent was removed under reduced pressure, the residue was extracted into dichloromethane (2 mL), and this solution was placed onto an alumina column (2 x 10 cm, activity IV) packed in hexane. Hexane eluted a trace amount of [Ru$_3$(CO)$_{12}$]. Hexane-dichloromethane (4:1) eluted compound **4c**, which was isolated as an orange solid (35 mg, 52%).

Analysis (%), found for $C_{17}H_{12}N_2O_9Ru_3$ (calcd): C 29.60 (29.53); H 1.80 (1.75); N 3.99 (4.05).

+FAB MS (MW, amu): 693 (691.50).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2069 (w), 2038 (vs), 2018 (m), 1989 (m, br), 1973 (w, sh).

^1H NMR (CD_2Cl_2, r.t., ppm): δ 4.76 (d, *J* = 3.7 Hz, 1 H, CH_2), 4.61 (d, *J* = 3.7 Hz, 1 H, CH_2), 3.17 (s, 3 H, NCH_3), 2.43 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3), –14.04 (s, 1 H, μ-*H*).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, r.t., ppm): δ 206.4, 196.0 (*C*Os), 180.7 (*C*), 152.0 (*C*), 137.3 (*C*), 106.8 (*C*), 95.2 (CH_2), 37.7 (NCH_3), 24.6 (CH_3), 21.4 (CH_3).

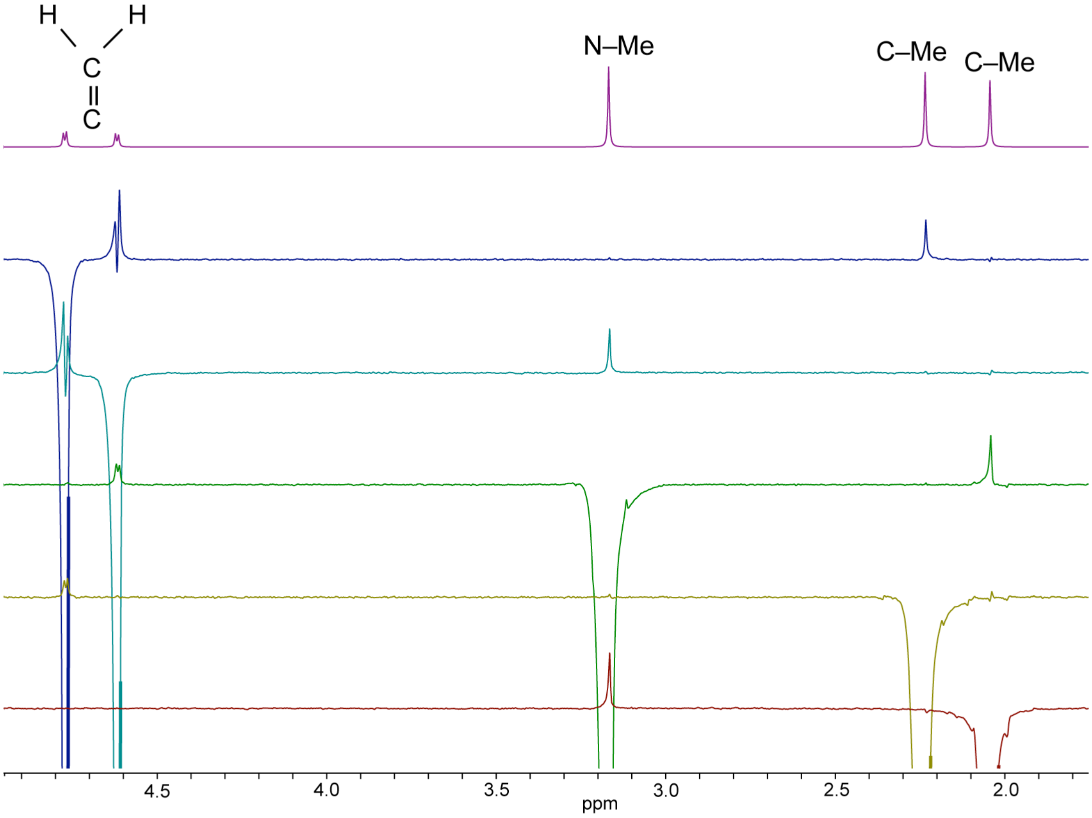
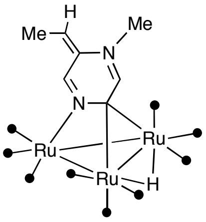


Figure S3. ^1H NMR in CD_2Cl_2 of compound **4c** in the 5.0–1.8 ppm region (top) and selected 1D NOE difference spectra after saturation at the frequencies of the inverted signals.

[Ru_3(μ-H)($μ_3$-$κ^2$*N^1*,*C^2*-4-Me-5-CHMe-$C_4H_2N_2$)$(CO)_9$] (5c): A toluene solution of K[N($SiMe_3$)$_2$] (230 μL, 0.5 M, 0.117 mmol) was dropwise added to a suspension of compound **5b** (100 mg, 0.117 mmol) in THF (30 mL) at –80 °C. The color changed from red to dark brown. The system was warmed up to room temperature. The solvent was removed under reduced pressure, the residue was extracted into dichloromethane (1.5 mL), and this solution was placed onto a silica gel column (2 x 10 cm) packed in hexane. Hexane eluted a red band containing a mixture of unidentified compounds. Hexane-dichloromethane (3:1) eluted an orange band that also contained a mixture of unidentified compounds. Further elution with the same solvent mixture eluted a yellow-orange band that contained compounds **5a** and **5c**. This solution was evaporated to dryness and the solid residue was washed with hexane (2 x 4 mL) to give compound **5c** as an orange solid (20 mg, 25%).



Analysis (%), found for $C_{16}H_{10}N_2O_9Ru_3$ (calcd): C 28.43 (28.37); H 1.55 (1.49); N 4.07 (4.14).

+FAB MS (MW, amu): 679 (677.47).

IR, (CH_2Cl_2, cm^{-1}): ν(CO) 2070 (w), 2039 (vs), 2020 (s), 1990 (m, br), 1975 (w, sh), 1948 (vw, sh).

^{1}H NMR (CD_2Cl_2, r.t., ppm): δ 7.70 (s, 1 H, C*H*), 6.43 (s, 1 H, C*H*), 4.95 (q, *J* = 7.5 Hz, 1 H, C*H*), 3.02 (s, 3 H, NCH_3), 1.83 (d, *J* = 7.5 Hz, 3 H, CH_3), –14.53 (s, 1 H, μ-*H*).

^{13}C{^{1}H} NMR (CD_2Cl_2, r.t., ppm): δ 205.0, 196.4 (*C*Os), 167.8 (*C*H), 147.4 (*C*H), 130.8 (*C*), 108.1 (*C*HCH$_3$), 100.5 (*C*), 41.1 (N*C*H$_3$), 11.0 (CH*C*H$_3$).

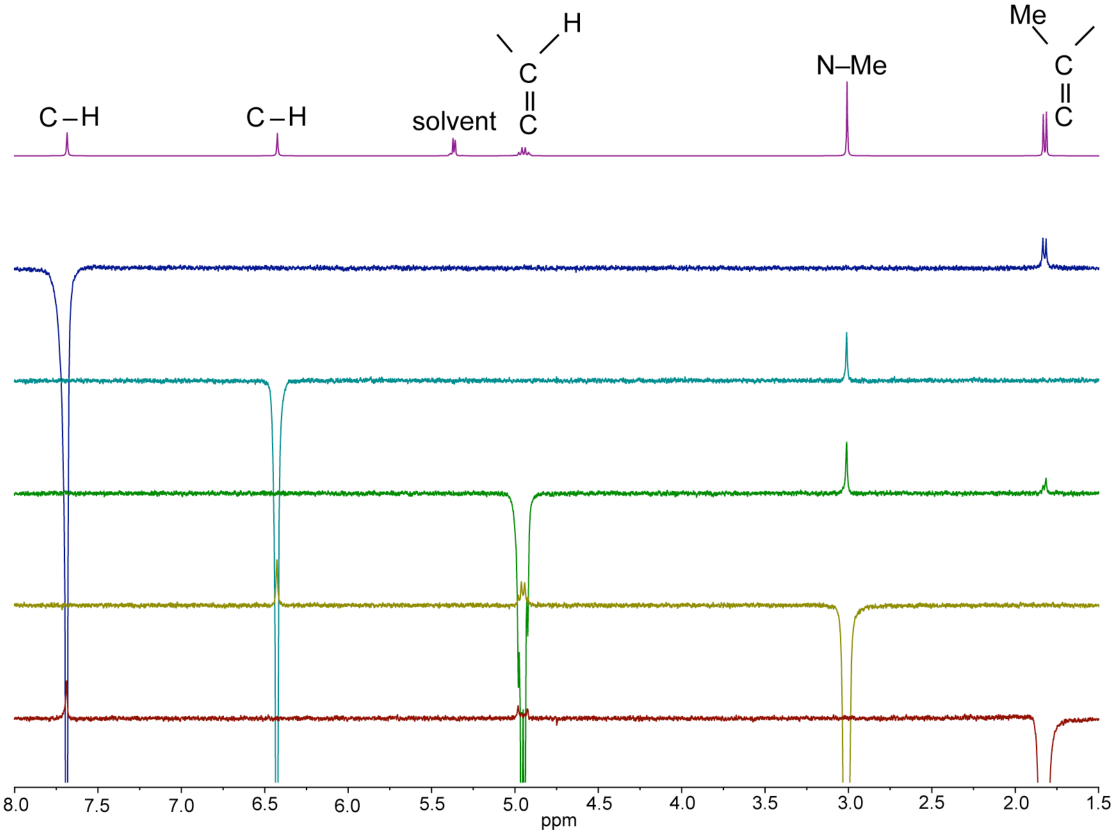


Figure S4. ^{1}H NMR in CD_2Cl_2 of compound **5c** in the 8.0–1.5 ppm region (top) and selected 1D NOE difference spectra after saturation at the frequencies of the inverted signals.

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Table S1. Crystal, measurement, and refinement data for compounds **2c** and **4c**

	2c	**4c**
formula	$C_{16}H_{10}N_2O_9Ru_3$	$C_{17}H_{12}N_2O_9Ru_3$
fw	677.47	691.50
cryst syst	orthorhombic	triclinic
space group	*P*bca	*P*–1
a, Å	9.8069(1)	9.8219(2)
b, Å	16.2228(2)	10.5531(2)
c, Å	27.3337(3)	12.9125(3)
α, β, γ, deg	90, 90, 90	67.189(2), 78.126(2), 66.617(2)
V, Å^3	4348.67(1)	1130.27(4)
Z	8	2
$F(000)$	2592	664
D_{calcd}, g cm^{-3}	2.070	2.032
μ(Cu Kα), mm^{-1}	17.114	16.477
cryst size, mm	0.26 x 0.19 x 0.12	0.20 x 0.11 x 0.05
T, K	293(2)	293(2)
θ range, deg	3.23 to 70.00	3.72 to 74.06
min./max. h, k, l	0/11, 0/19, 0/33	–12/12, –13/13, –16/16
no. collected reflns	4086	33320
no. unique reflns	4086	4575
no. reflns with $I > 2\sigma(I)$	3737	4471
no. params/restraints	275/0	295/0
GOF on F^2	1.053	1.076
R_1 (on F, $I > 2\sigma(I)$)	0.0326	0.0285
wR_2 (on F^2, all data)	0.0884	0.0759
min./max. $\Delta\rho$, e Å^{-3}	–0.639/0.650	–1.167/0.652

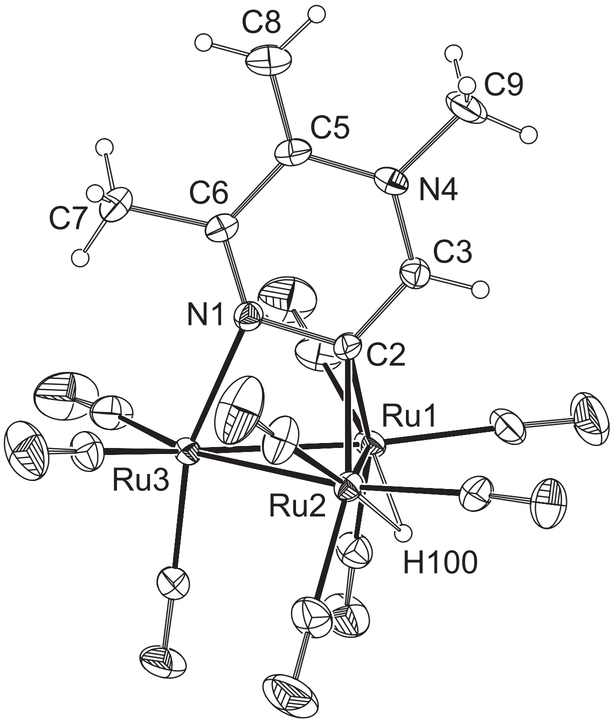

Table S2. Selected interatomic distances (Å) in compound **2c**

Ru1–Ru2	2.7695(4)	C5–C8	1.338(6)
Ru1–Ru3	2.7636(4)	C5–N4	1.410(5)
Ru2–Ru3	2.7550(4)	C6–C7	1.494(5)
C2–C3	1.387(5)	C6–N1	1.294(5)
C2–N1	1.429(5)	C9–N4	1.462(5)
C2–Ru1	2.183(3)	N1–Ru3	2.109(3)
C2–Ru2	2.175(4)	C–O (av.)	1.13(1)
C3–N4	1.324(5)	$C_{(CO)}$–Ru (av.)	1.91(2)
C5–C6	1.457(6)		

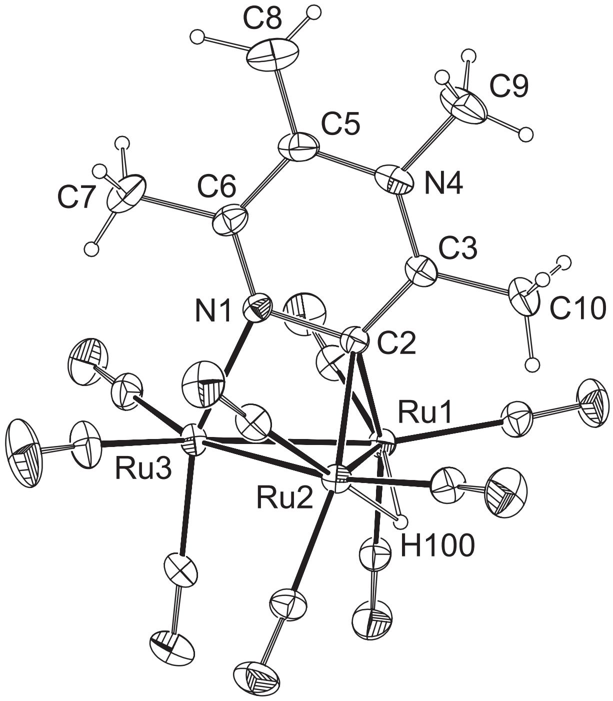

Table S3. Selected interatomic distances (Å) in compound **4c**

Ru1–Ru2	2.7816(3)	C5–C6	1.454(6)
Ru1–Ru3	2.7471(3)	C5–C8	1.339(7)
Ru2–Ru3	2.7493(3)	C5–N4	1.416(6)
C2–C3	1.406(4)	C6–C7	1.498(5)
C2–N1	1.432(4)	C6–N1	1.293(4)
C2–Ru1	2.190(3)	C9–N4	1.479(5)
C2–Ru2	2.199(3)	N1–Ru3	2.117(3)
C3–C10	1.487(5)	C–O (av.)	1.133(8)
C3–N4	1.337(4)	$C_{(CO)}$–Ru (av.)	1.92(2)

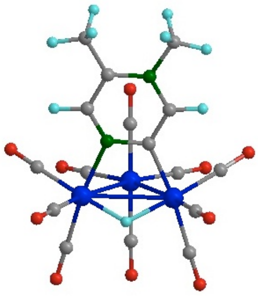

Table S4. DFT-Optimized coordinates for the cation of **1b**

N	1.79090900	0.70955800	0.07484300
C	2.90731400	-1.29561000	-0.39037200
C	4.00491900	0.74018800	-0.84720200
C	2.86921300	1.37260100	-0.35993200
C	0.92068900	2.34624300	2.36473300
C	-0.09446600	3.01136100	-0.34498100
C	-1.75545100	1.96842600	1.62914400
C	1.05648000	-2.27172000	2.31295200
C	0.06677400	-2.98974500	-0.33888600
C	-1.70599500	-2.07258900	1.71179000
C	-2.25028900	-1.50938900	-2.18016500
C	-2.37272900	1.42958700	-2.18115300
C	5.19193100	1.49428500	-1.35562100
C	-3.10644700	-0.09692000	0.08099800
C	1.75960400	-0.65190900	0.08071400
N	3.98669100	-0.62352800	-0.84887000
O	1.44508400	2.86551700	3.22938900
O	-0.09771800	3.90377300	-1.05398500
O	-2.72346000	2.28054100	2.13793700
O	1.68177600	-2.74473500	3.13898100
O	0.14513000	-3.87526900	-1.05500300
O	-2.63276500	-2.44234700	2.25310300
O	-2.65059300	-2.37665600	-2.79801700
O	-2.84768600	2.25747200	-2.79961700
O	-4.06891400	-0.14465100	0.68432600
Ru	-0.04154900	1.50182000	0.87048700
Ru	0.00633600	-1.49192600	0.87269900
Ru	-1.55015200	-0.01397900	-1.14678700
C	5.14906800	-1.38359900	-1.36207100
C	0.11100300	0.03600600	-2.17498600
O	1.03529000	0.06916500	-2.84918600
H	2.97752600	-2.37373100	-0.42156600
H	2.83711900	2.45445400	-0.33620500
H	6.09374100	1.26706000	-0.77976200
H	5.00753300	2.56495200	-1.27896000
H	5.39728000	1.26385900	-2.40489400
H	-0.08807600	0.00892100	1.88461700
H	5.30338300	-1.14632700	-2.41443800
H	4.94647800	-2.44550800	-1.25462600
H	6.03900300	-1.12193500	-0.79074800

Total electronic energy = –1759.01012034 hartree

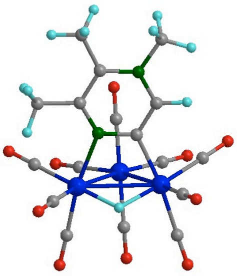

Table S5. DFT-Optimized coordinates for the cation of **2b**

N	-1.83832100	-0.50793600	0.13056600
C	-2.66949700	1.64201300	-0.31841400
C	-4.02931300	-0.22024100	-0.79931200
C	-3.00816000	-1.03981300	-0.28412800
C	-0.92823100	-2.21607800	2.43660700
C	-0.00276000	-2.96691100	-0.32549900
C	1.70931200	-1.99022000	1.58937200
C	-0.73828600	2.37553800	2.35201600
C	0.27168900	3.01688500	-0.30762600
C	1.98269300	1.92856700	1.71674900
C	2.33543000	1.37655500	-2.25189900
C	2.26142200	-1.56156800	-2.24737900
C	-5.31548900	-0.75472500	-1.35528300
C	3.18789200	-0.08343600	-0.02740800
C	-1.62516000	0.83817600	0.13373700
N	-3.82266900	1.12367300	-0.78726800
O	-1.40736500	-2.68378500	3.35606800
O	-0.00348100	-3.87179700	-1.01925400
O	2.67413200	-2.34583800	2.07709300
O	-1.30559000	2.90139000	3.18830800
O	0.26331100	3.91393000	-1.01397000
O	2.94391200	2.20593400	2.25349800
O	2.76888600	2.20907300	-2.89508300
O	2.65976600	-2.41552800	-2.88440900
O	4.17885700	-0.09799600	0.52981100
Ru	0.00655300	-1.45130500	0.88429600
Ru	0.21324200	1.50982500	0.89519300
Ru	1.57720200	-0.06548800	-1.18610700
C	-4.85964500	2.05228400	-1.29655800
C	-0.11895100	-0.00905200	-2.15401000
O	-1.06340600	0.01611000	-2.80051300
C	-3.21732000	-2.52445600	-0.20884800
H	-2.50667700	-2.97477900	0.47673800
H	-3.08153700	-2.99209600	-1.18960200
H	-4.22222800	-2.76612900	0.13893300
H	-6.14067500	-0.63067300	-0.64478200
H	-5.23043400	-1.81392300	-1.58031600
H	-5.59411400	-0.24694700	-2.27982700
H	0.16751500	0.02122400	1.91094500
H	-4.95287900	1.94065400	-2.37687400
H	-4.55662700	3.06897100	-1.06268300
H	-5.81346000	1.83763000	-0.81816400
H	-2.59575500	2.71942000	-0.33135100

Total electronic energy = –1798.33667314 hartree

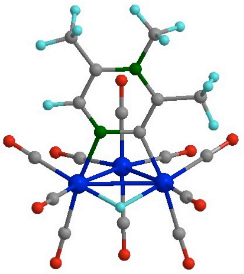

Table S6. DFT-Optimized coordinates for the cation of **3b**

N	1.63770100	0.90612400	0.10018300
C	3.04723300	-0.94605700	-0.31259300
C	3.81484000	1.25827200	-0.81136000
C	2.61147700	1.72294500	-0.32368100
C	0.60155600	2.46403600	2.36068200
C	-0.45209300	3.01768100	-0.35654100
C	-2.02387500	1.84040100	1.62143400
C	1.12232300	-2.11096700	2.37579200
C	0.17890400	-2.92009500	-0.32317400
C	-1.60779400	-2.10400100	1.71244900
C	-2.18429300	-1.66233400	-2.20962400
C	-2.50053300	1.25726000	-2.21619300
C	4.86702200	2.19895300	-1.31513500
C	-3.17907700	-0.31159700	0.03000600
C	1.79530000	-0.43881400	0.12589300
N	3.99720900	-0.09840600	-0.80828600
O	1.07416700	3.03247600	3.22469700
O	-0.52873200	3.90385700	-1.06951000
O	-3.01753700	2.06585800	2.12684600
O	1.73126100	-2.52596300	3.24526500
O	0.25366000	-3.81179700	-1.03297700
O	-2.51498300	-2.52333800	2.25218700
O	-2.51941500	-2.54961600	-2.83772100
O	-3.01587000	2.04839900	-2.85073600
O	-4.14959200	-0.42894000	0.61050300
Ru	-0.27087800	1.52596100	0.87002300
Ru	0.06634900	-1.42846400	0.89332900
Ru	-1.60375800	-0.12303500	-1.16242100
C	5.26309200	-0.65643100	-1.34520600
C	0.07247800	0.02941800	-2.15484800
O	1.00568500	0.11477200	-2.81222800
H	2.42407900	2.78783400	-0.29215000
H	5.82247700	2.05788500	-0.80391800
H	4.54359500	3.22429300	-1.13991900
H	5.03365000	2.08714000	-2.39067900
H	-0.16928100	0.05651100	1.89977200
H	5.04921500	-1.55234400	-1.92052100
H	5.93696300	-0.89991800	-0.52199500
H	5.73426600	0.07157900	-1.99436000
C	3.37754300	-2.40526300	-0.26195800
H	3.32480700	-2.86543100	-1.25521500
H	2.66756300	-2.92117100	0.37425700
H	4.37918100	-2.58285200	0.13421000

Total electronic energy = –1798.33611057 hartree

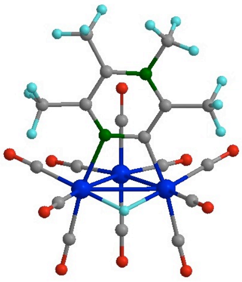

Table S7. DFT-Optimized coordinates for the cation of **4b**

N	1.70189600	0.73815900	0.15973400
C	2.90968100	-1.26759500	-0.23352300
C	3.88023200	0.83750000	-0.79933600
C	2.75417400	1.47107700	-0.26957200
C	0.62488500	2.26595500	2.50412500
C	-0.44103600	2.98856700	-0.20972300
C	-1.97611800	1.74630900	1.69711200
C	0.85552500	-2.32672700	2.31957700
C	-0.13881700	-2.94280500	-0.41325100
C	-1.85224200	-2.03949200	1.64169000
C	-2.25155100	-1.47201200	-2.33571400
C	-2.39455700	1.45125000	-2.24511600
C	4.98979200	1.59418600	-1.47281400
C	-3.25655200	-0.15347700	-0.09175300
C	1.71273700	-0.62156300	0.16176400
N	3.94568200	-0.52311400	-0.71605600
O	1.06497900	2.75872900	3.43039600
O	-0.57807200	3.91732200	-0.85729500
O	-2.96571500	1.95917700	2.21737200
O	1.41428500	-2.83055000	3.17607800
O	-0.14966000	-3.81700100	-1.14851600
O	-2.79909900	-2.38824400	2.16376500
O	-2.61635800	-2.30758200	-3.01619700
O	-2.84107700	2.28574900	-2.87632600
O	-4.26021600	-0.23591700	0.43593200
Ru	-0.23527200	1.44184000	0.94288200
Ru	-0.11428600	-1.49105300	0.86047700
Ru	-1.62070400	-0.01400400	-1.20744100
C	5.18046800	-1.20114600	-1.18822000
C	0.09493200	0.06943000	-2.13831700
O	1.04939500	0.11829300	-2.76848300
C	2.71069700	2.97072000	-0.19553600
H	2.03697300	3.29479800	0.59154400
H	2.35996300	3.40671200	-1.13661200
H	3.69514500	3.38579600	0.01795600
H	5.86436500	1.71035400	-0.82307000
H	4.65415000	2.58889200	-1.75198800
H	5.31282400	1.09591200	-2.38781200
H	-0.17835400	-0.05346300	1.94037500
H	5.07614900	-1.45590600	-2.24464800
H	5.34366200	-2.10449500	-0.61345200
H	6.03263100	-0.54537800	-1.05081000
C	3.09573700	-2.75312200	-0.15490000
H	3.32459600	-3.19087900	-1.13046600
H	2.19461400	-3.22005800	0.21851900
H	3.90612700	-3.01823000	0.53155500

Total electronic energy = –1837.65963846 hartree

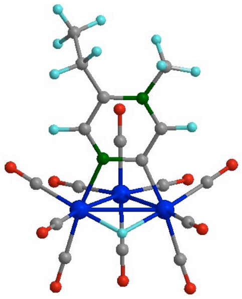

Table S8. DFT-Optimized coordinates for the cation of **5b**

N	-1.70019900	-0.41758500	0.43638300
C	-2.64674500	1.63657500	-0.16440100
C	-4.01357800	-0.28420000	-0.19370800
C	-2.89386000	-0.98642100	0.23597700
C	-0.71993500	-1.81967400	2.83142300
C	-0.16187200	-2.98277300	0.15558800
C	1.85796100	-1.90948400	1.74095900
C	-0.33142300	2.71556100	2.10514500
C	0.33668000	2.93606700	-0.73071400
C	2.27726500	2.08773100	1.19734300
C	2.22996900	0.93437300	-2.57605600
C	2.01717500	-1.97228800	-2.15376000
C	-5.31811400	-0.97639500	-0.47395500
C	3.21952300	-0.26959100	-0.25008600
C	-1.51974800	0.91783000	0.24086100
N	-3.84848500	1.05543400	-0.38493300
O	-1.17963200	-2.13818600	3.82120500
O	-0.35695200	-3.95618400	-0.40468600
O	2.84267900	-2.27552800	2.17662200
O	-0.77390100	3.37063600	2.92504900
O	0.24780000	3.71713200	-1.55854700
O	3.30637700	2.40731400	1.55467200
O	2.63940500	1.65263100	-3.35762300
O	2.30576700	-2.93144000	-2.69276200
O	4.25426100	-0.27102300	0.22112900
Ru	0.12314900	-1.32747500	1.12323200
Ru	0.41046500	1.62202200	0.67672600
Ru	1.51117300	-0.30700100	-1.25867600
C	-4.98602900	1.90888000	-0.80452100
C	-0.26879200	-0.27737900	-2.06445600
O	-1.27353100	-0.28193600	-2.61271800
H	-2.97874900	-2.05128600	0.41396500
C	-5.46286200	-1.43857700	-1.94013700
H	-6.15719800	-0.33566000	-0.19517700
H	-5.37203400	-1.84803200	0.18234200
H	-4.66570300	-2.13268600	-2.21289700
H	-5.43427400	-0.60391200	-2.64399400
H	-6.41784600	-1.95095300	-2.06718800
H	0.48332000	0.27015800	1.88094400
H	-5.43077800	1.51034400	-1.71363700
H	-4.61384700	2.91191000	-0.99369500
H	-5.72982500	1.94075100	-0.00848000
H	-2.60477200	2.70367900	-0.33050800

Total electronic energy = –1798.33381927 hartree