SUPPLEMENTARY INFORMATION

Guest-Induced Formation of an Icosahedral Coordination Cage

Thomas Brasey, Rosario Scopelliti, and Kay Severin

Synthesis of complex 3: $[(cymene)RuCl_2]_2$ (30.6 mg, 0.05 mmol), and $AgNO_3$ (34.0 mg, 0.20 mmol) were dissolved in acetone (2 ml) and stirred for 1 h at room temperature. After separation of the AgCl precipitate, the solvent was removed in vacuum and the oily residue was immediately re-dissolved in H_2O (2 ml). Pyridine-3,5-dicarboxylic acid (16.7 mg, 0.10 mmol) was added and the mixture was stirred for 4 h at 60 °C. The yellow precipitate was collected by filtration, washed with H_2O, and dried (yield 20.4 mg, 48%). Elemental analysis (%) calc. for $C_{102}H_{102}N_6O_{24}Ru_6 \cdot 7H_2O$: C 48.45, H 4.62, N 3.32; found: C 48.07, H 4.71, N 3.76. MS-ESI: calc. for $[M+H]^+$ (*m/z*) 2403.4; found, 2403.2. Single crystals were grown by slow diffusion of diethyl ether in a solution of the product in methanol.

^{1}H NMR data for complex 3 (400 MHz, CD_3OD): δ (ppm) = 1.37 (d, ^3J = 7 Hz, 36 H, CH_3, cymene), 1.93 (s, 18 H, CH_3, cymene), 2.78 (sept, ^3J = 7 Hz, 6 H, CH, cymene), 5.86 (d, ^3J = 6 Hz, 12 H, CH, cymene), 6.16 (d, ^3J = 6 Hz, 12 H, CH, cymene), 8.40 (br, 6 H, CH, pyridine), 9.64 (br, 12 H, CH, pyridine).

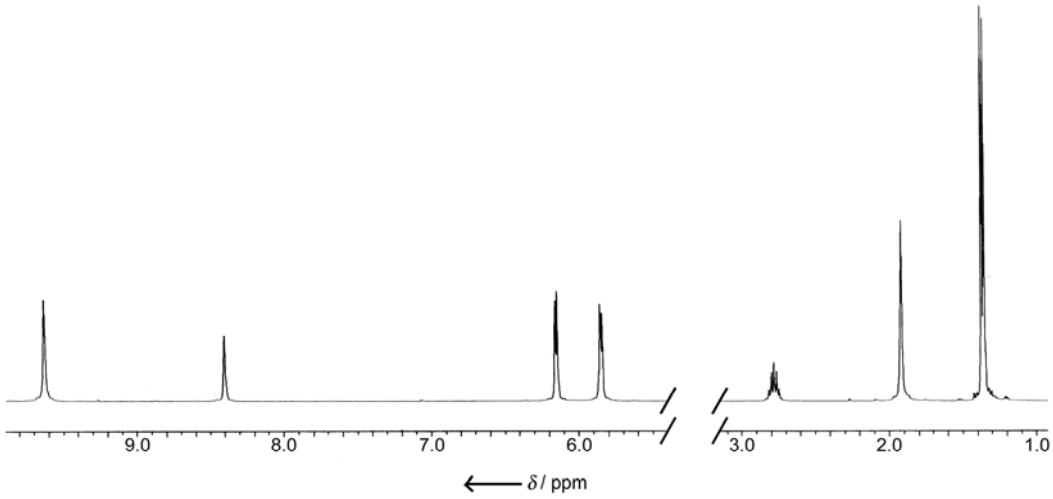

Figure S1. ^{1}H NMR spectrum of complex **3** in CD_3OD.

^{13}C NMR data for complex 3 (101 MHz, CD_3OD): δ (ppm) = 19.83 (CH_3, cymene), 24.68 (CH_3, cymene), 34.00 (CH, cymene), 81.68 (CH, cymene), 86.27 (CH, cymene), 100.76 (C, cymene), 104.87 (C, cymene), 136.36, 136.42, 141.40, 141.45 (C and CH, pyridine), 158.98 (CH, pyridine), 174.17 (COO).

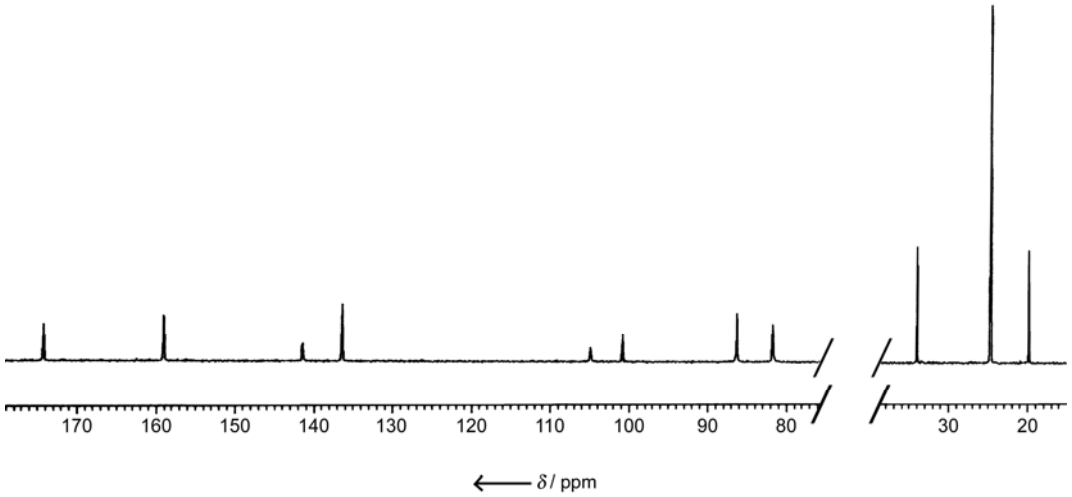

Figure S2. ^{13}C NMR spectrum of complex **3** in CD_3OD.

NMR experiments for the interaction of complex 3 with MOAc (M = Na, K, Cs): 234 µl of a stock solution of MOAc (320 mM) was added to a solution of complex **3** (18 mg, 7.5 µmol) in CD_3OD (366 µl). NMR spectra were recorded after an equilibration time of 30 minutes. Final concentrations: [**3**] = 12.5 mM, [salt] = 125 mM. Experiments with different MOAc concentrations were performed accordingly.

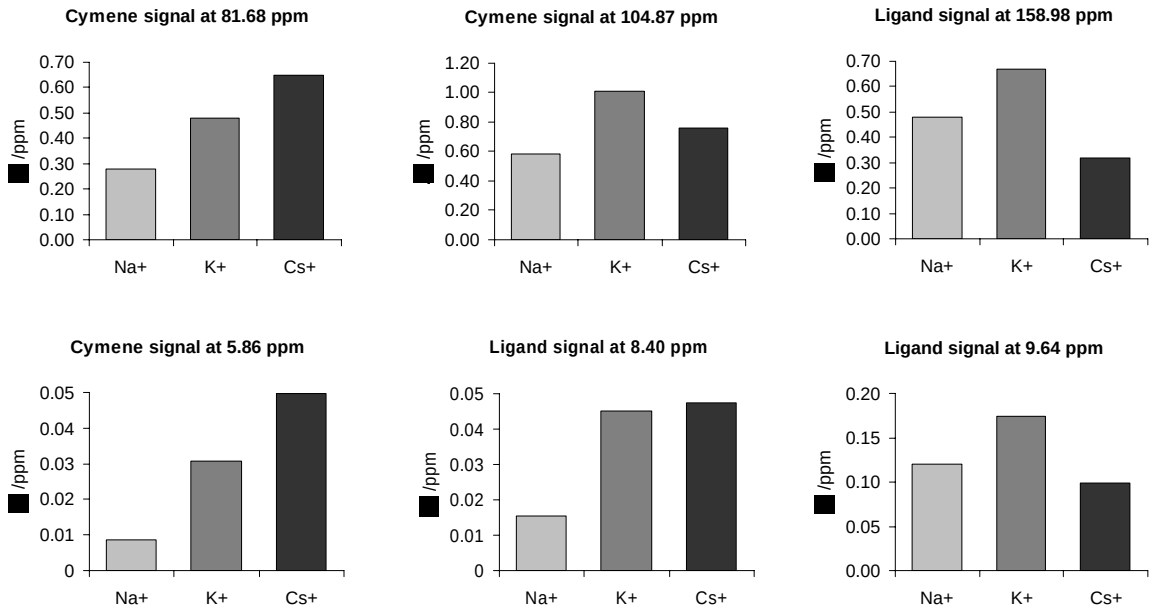

Figure S4. Differences of the chemical shifts of selected ^{13}C (top) and ^{1}H NMR signals (bottom) of complex **3** upon addition of 10 equivalents of MOAc.