Supporting Information for

16-Electron Pentadienyl- and Cyclopentadienyl-Ruthenium Half-Sandwich Complexes with Bis(imidazol-2-imine) Ligands and Their Use in Catalytic Transfer Hydrogenation

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Contents:

1. NMR Data

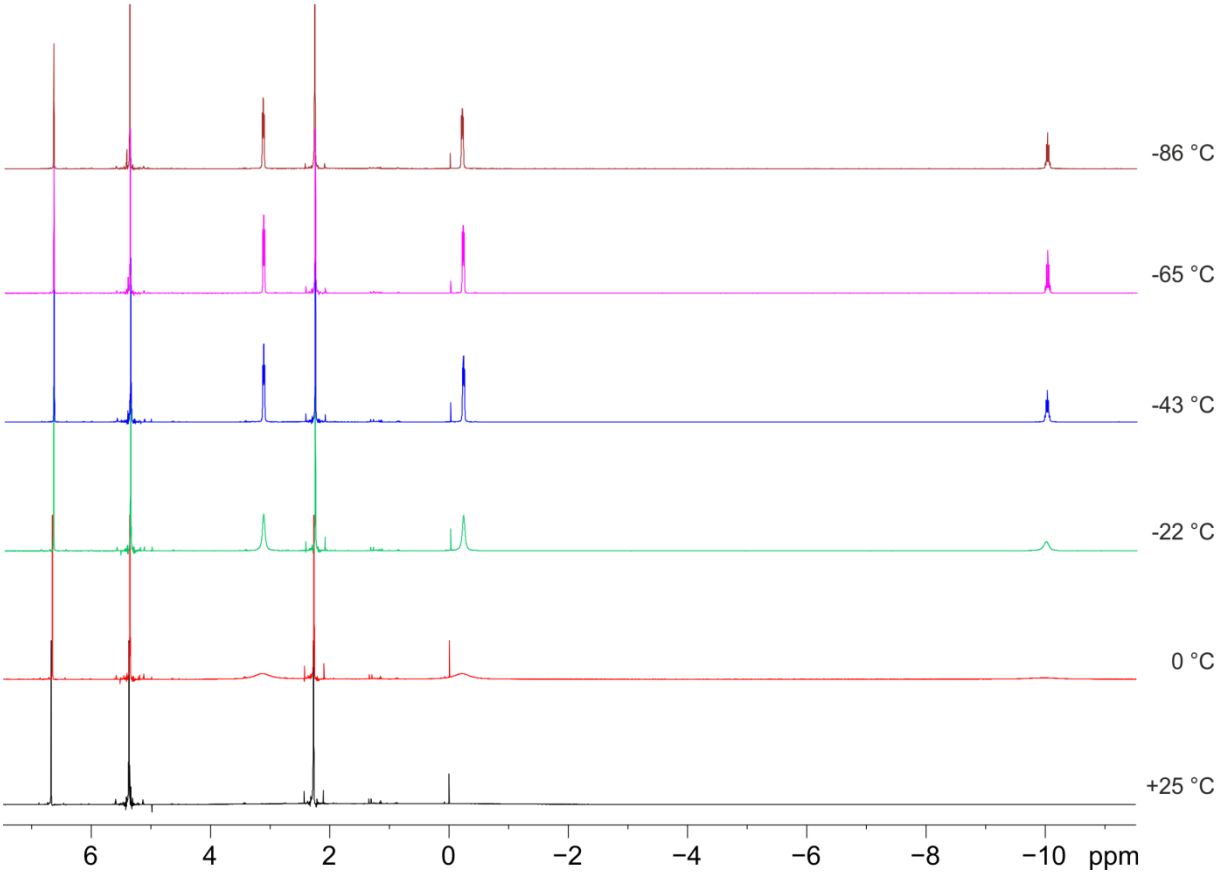

Figure 1: Variable temperature ^{1}H NMR spectrum of $[(\eta^5\text{-Cp})RuH(\eta^5\text{-}C_7H_{11})]BF_4$ (**3**) (CD_2Cl_2, 400 MHz).

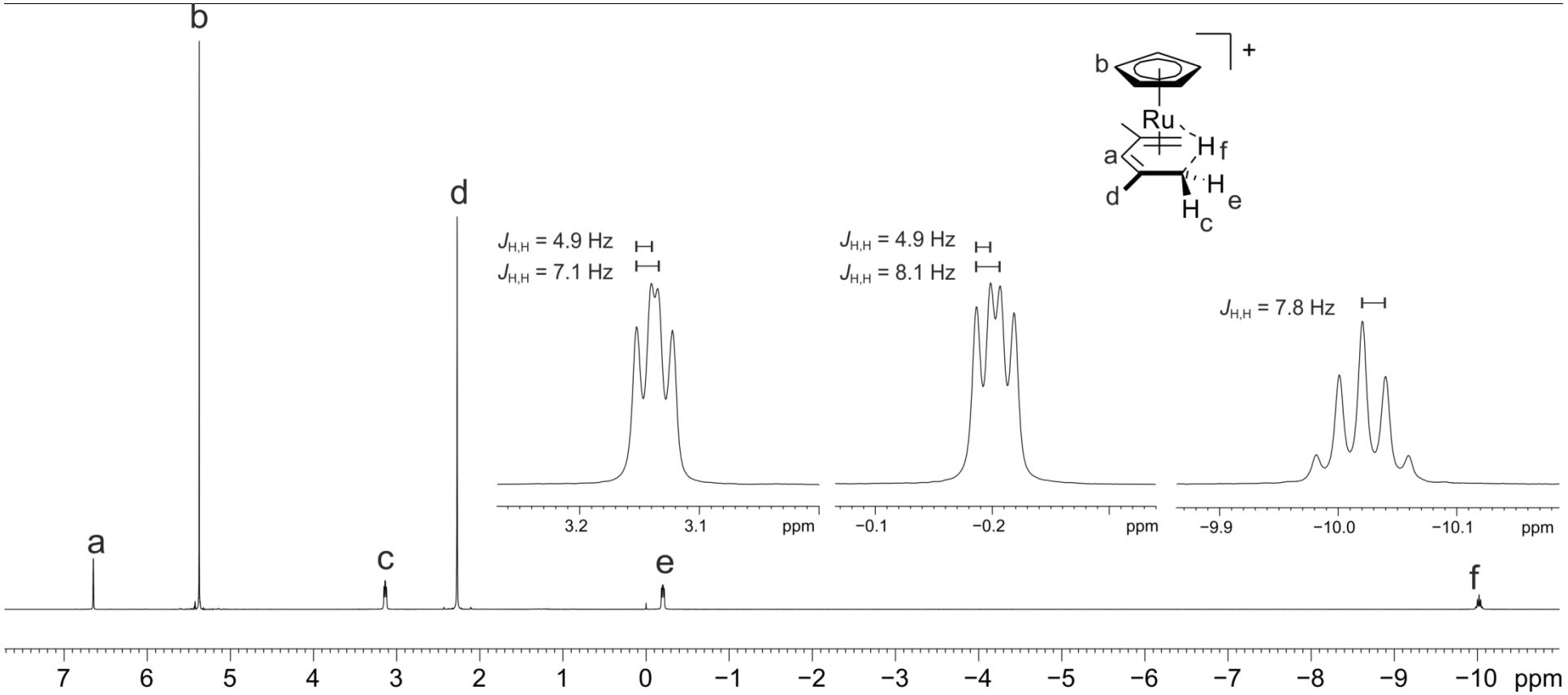

Figure 2: ^{1}H NMR spectrum of [(η^5-Cp)RuH(η^5-C_7H_{11})]BF_4 (**3**) at -86 °C (CD_2Cl_2, 400 MHz). Chemical shifts and assignment: δ [ppm] = 6.65 (s, 1 H, C_7H_{11}-C*H*), 5.37 (s, 5 H, C_5H_5), 3.14 (dd, 2 H, $J_{H,H}$ = 7.1 Hz, $J_{H,H}$ = 4.9 Hz, CH_2-exo), 2.27 (s, 6 H, CH_3), -0.20 (dd, 2 H, $J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 4.9 Hz, CH_2-endo), -10.02 (quin, 1 H, $J_{H,H}$ = 7.8 Hz, Ru-*H*).

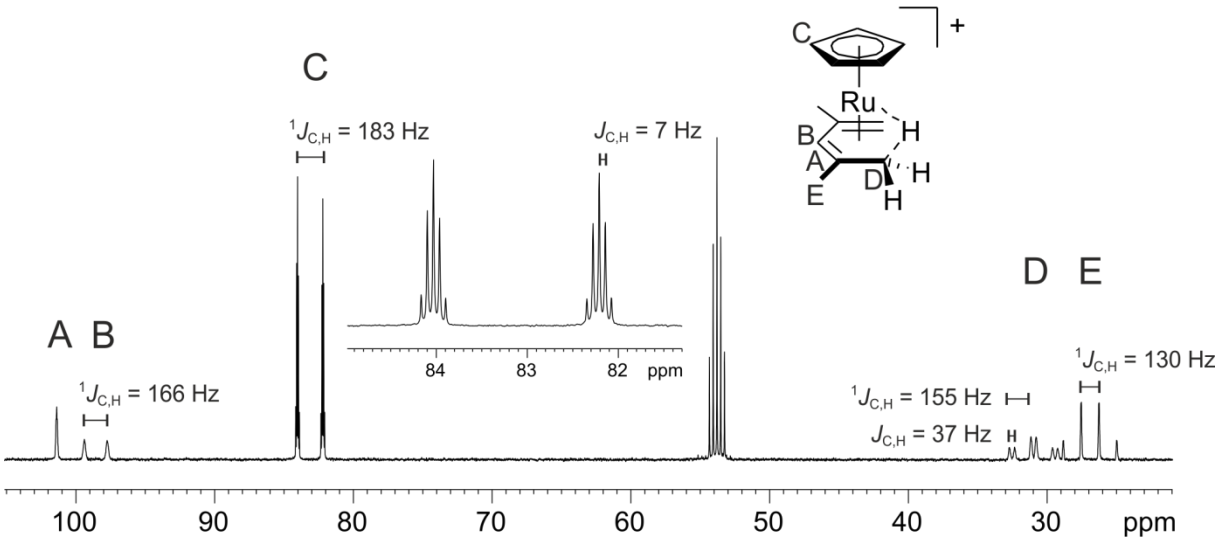

Figure 3: ^{13}C NMR spectrum (gated decoupling method) of [(η^5-Cp)RuH(η^5-C_7H_{11})]BF_4 (**3**) at -75 °C (CD_2Cl_2, 100 MHz). Chemical shifts and assignment: δ [ppm] = 101.4 (s, 2 C, *C*CH_3), 98.6 (d, 1 C, $^1J_{C,H}$ = 166 Hz, C_7H_{11}-*C*H), 83.1 (dquin, 5 C, $^1J_{C,H}$ = 183 Hz, $J_{C,H}$ = 7 Hz, *C*$_5H_5$), 31.0 (td, 2 C, $^1J_{C,H}$ = 155 Hz, $J_{C,H}$ = 37 Hz, *C*H_2), 26.9 (q, 2 C, $^1J_{C,H}$ = 130 Hz, C*C*H_3).

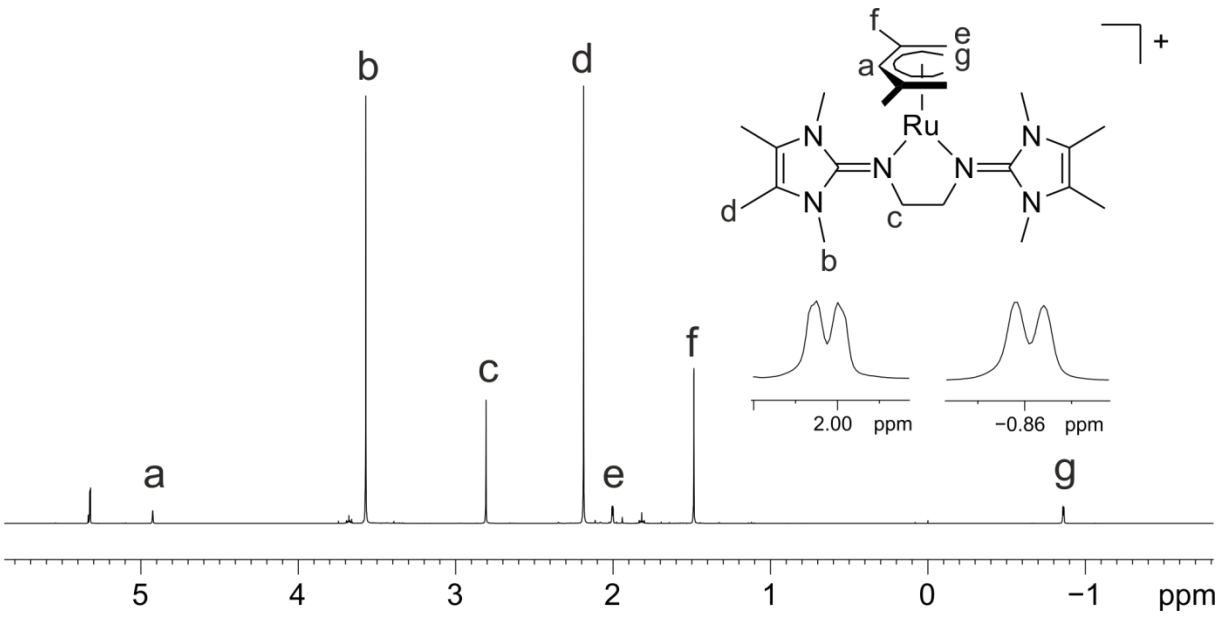

Figure 4: ^{1}H NMR spectrum of **4a** (400 MHz, CD_2Cl_2, 25 °C). For chemical shifts see full text.

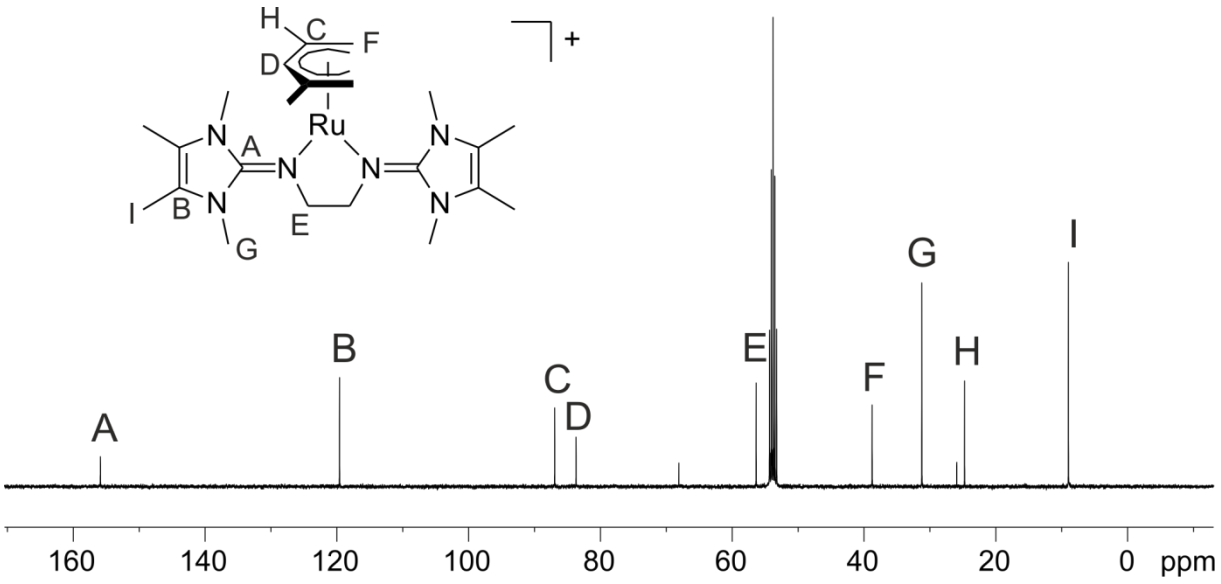

Figure 5: ^{13}C{^{1}H} NMR spectrum of **4a** (100 MHz, CD_2Cl_2, 25 °C). For chemical shifts see full text.

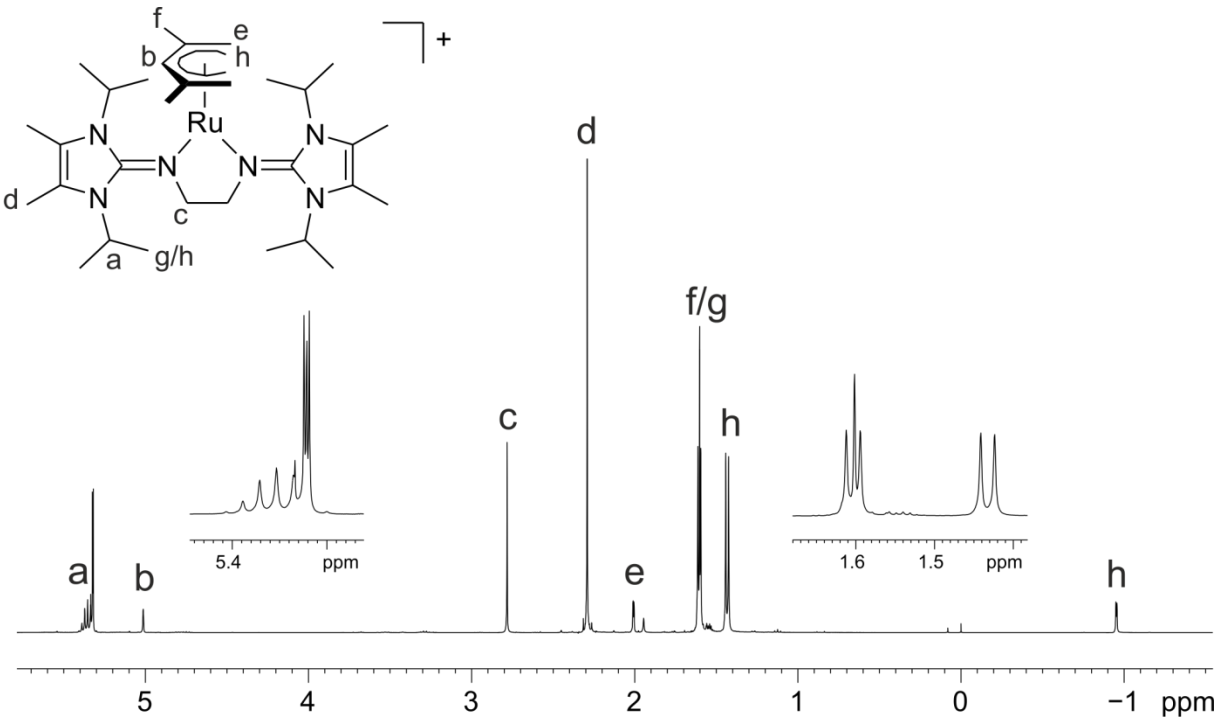

Figure 6: ^{1}H NMR spectrum of **4b** (400 MHz, CD_2Cl_2, 25 °C). For chemical shifts see full text.

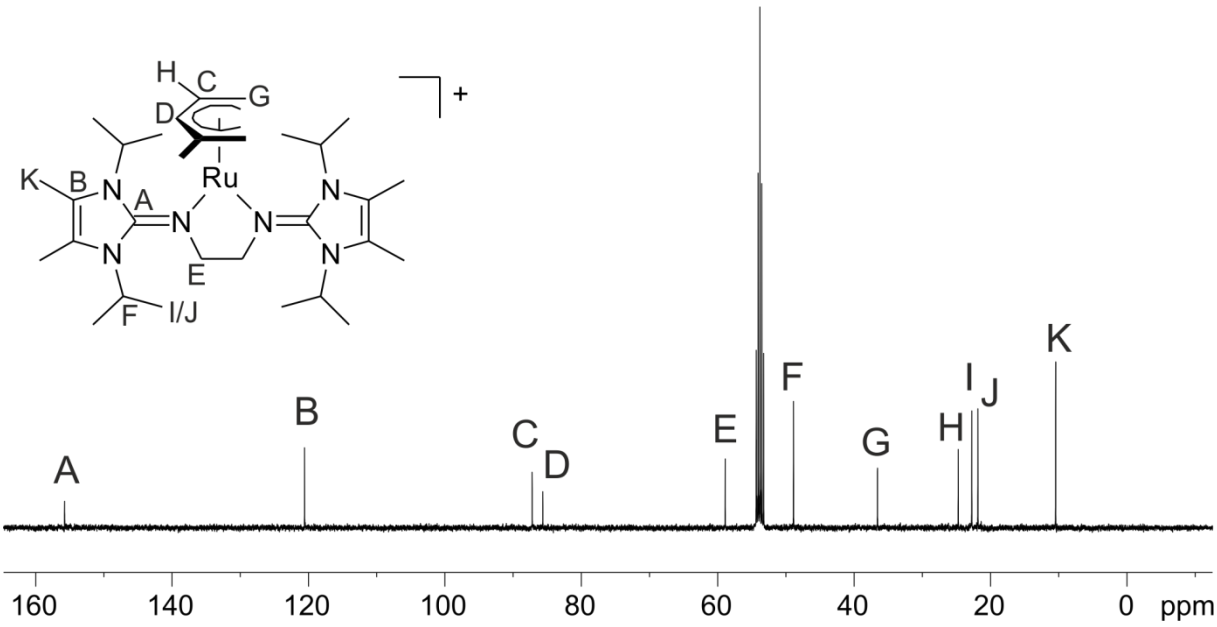

Figure 7: $^{13}C\{^{1}H\}$ NMR spectrum of **4b** (100 MHz, CD_2Cl_2, 25 °C). For chemical shifts see full text.

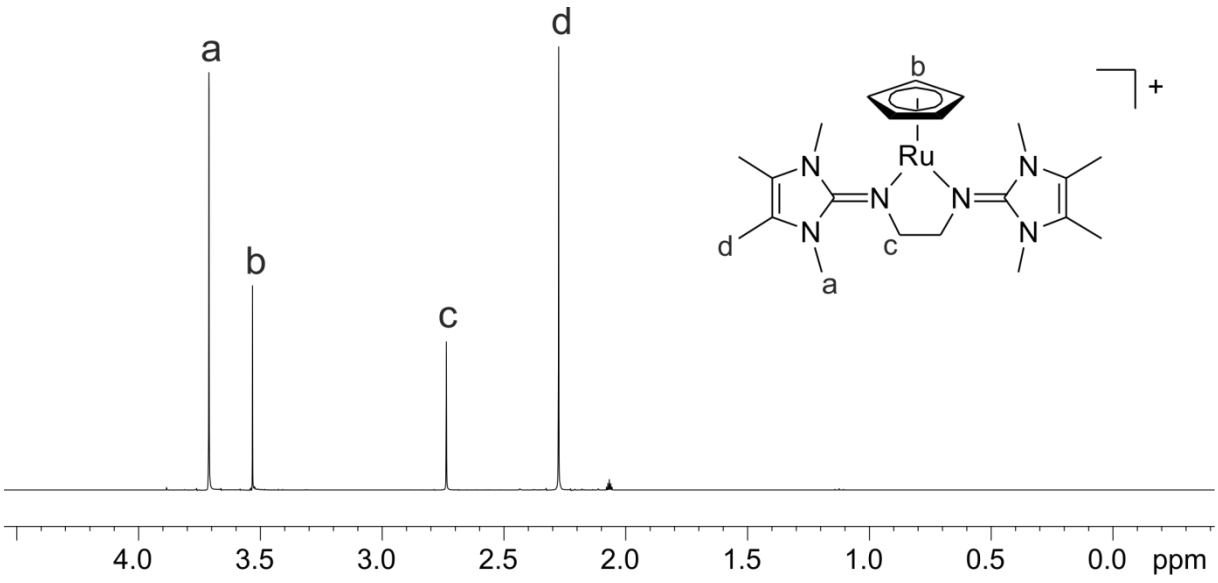

Figure 8: ^{1}H NMR spectrum of **5a** (400 MHz, acetone-d_6, 25 °C). For chemical shifts see full text.

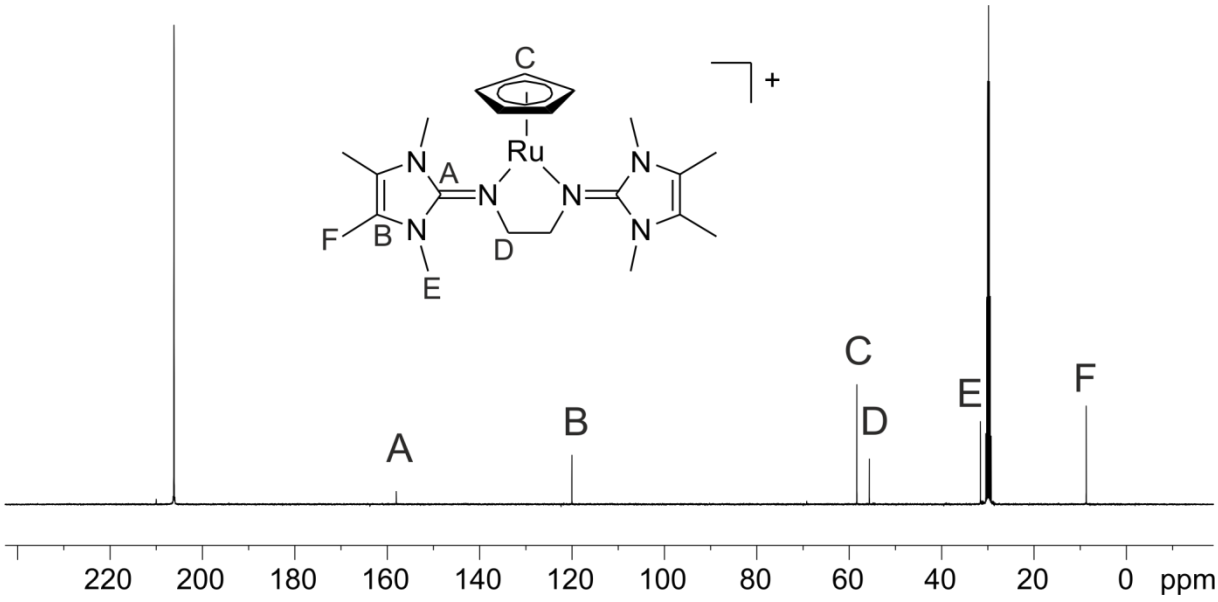

Figure 9: ^{13}C{^{1}H} NMR spectrum of **5a** (100 MHz, acetone-d_6, 25 °C). For chemical shifts see full text.

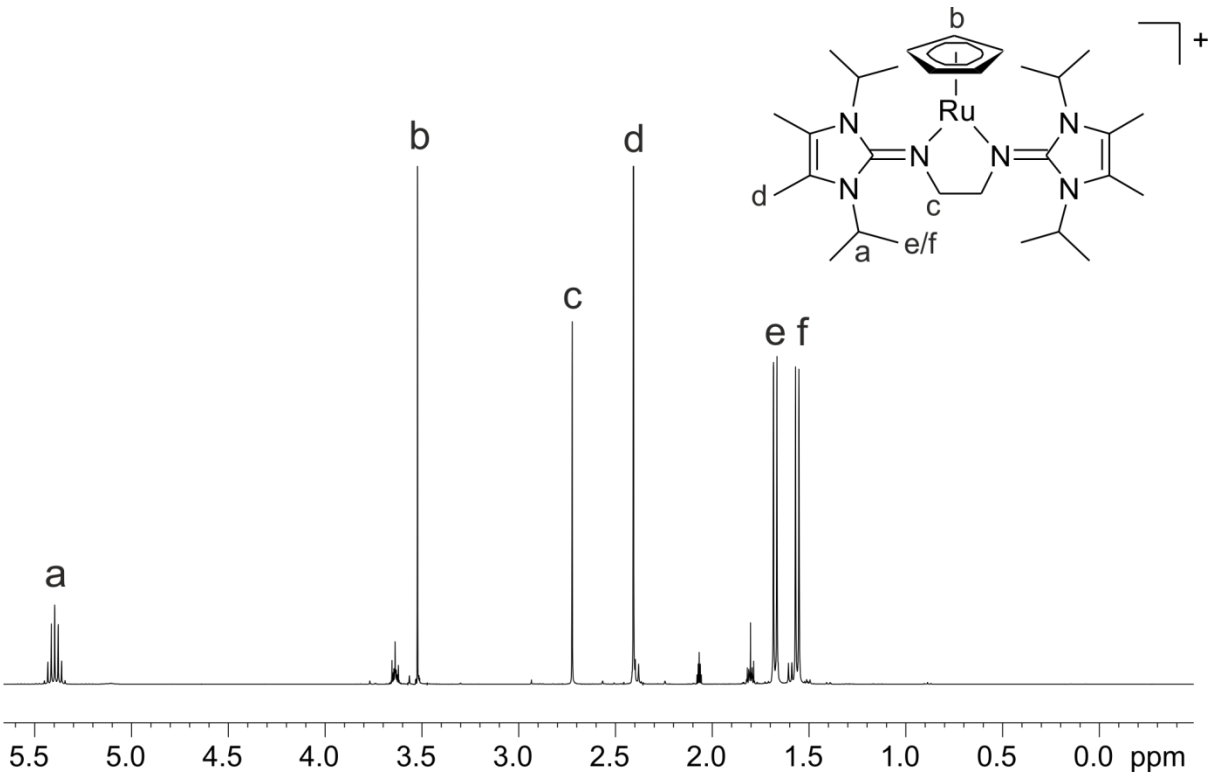

Figure 10: ^{1}H NMR spectrum of **5b** (400 MHz, acetone-d_6, 25 °C). For chemical shifts see full text.

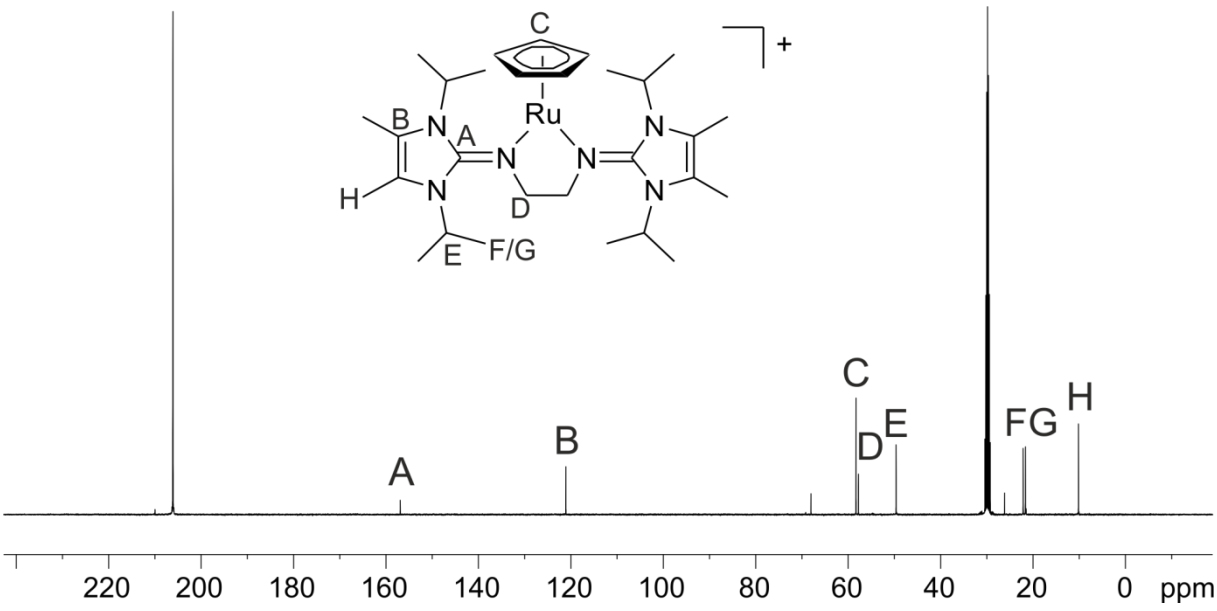

Figure 11: ^{13}C{^{1}H} NMR spectrum of **5b** (100 MHz, acetone-d_6, 25 °C). For chemical shifts see full text.

2. Computational Details

All computations were performed using the density functional method B3LYP as implemented in the Gaussian09 program.[1] For all main group elements (C and H) the all-electron triple-ζ basis set (6-311G**) was used,[2] whereas for the 4d transition metal ruthenium the Stuttgart Dresden ECP was applied.[3]

Energies for all optimized structures

Compounds	E(0 K)[a] / [Ha]	H(298 K)[b] / [Ha]	G(298 K)[b] / [Ha]
3 (A)	-562.087946	-562.073789	-562.127015
3 (TS)	-562.079948	-562.065957	-562.118948
3 (B)	-562.081279	-562.066971	-562.121102

[a] DFT energy incl. ZPE.
[b] standard conditions T = 298.15 K and p = 1 atm.

[1] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[2] X. Cao and M. Dolg, *J. Chem. Phys.*, 2001, **115**, 7348.

[3] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.2.2 [https://bse.pnl.gov/bse/portal]. a) The Role of Databases in Support of Computational Chemistry Calculations, D. Feller, *J. Comp. Chem.*, 1996, **17**, 1571-1586. b) Basis Set Exchange: A Community Database for Computational Sciences, K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li and T. L. Windus, *J. Chem. Inf. Model.*, 2007, **47**, 1045-1052.