

## Supporting Information

# Reactions of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with Nitron and with the “Enders Carbene”: Access to Ruthenium(III) NHC Complexes

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## 1. Experimental Section

### 1.1 General

All reactions were performed in an inert atmosphere (dinitrogen) by using standard Schlenk techniques or a conventional glovebox. **1** and its precursor MeO-**1**-H were synthesised according to the published procedures.<sup>S1</sup> [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] was procured commercially or synthesized according to the published procedure.<sup>S2</sup> NMR spectra were recorded with Varian Unity INOVA 500 and Varian MR-400 spectrometers operating at 500.1 and 400.1 MHz, respectively, for <sup>1</sup>H. High-resolution ESI mass spectra were obtained with a micrOTOF time-of-flight mass spectrometer (Bruker Daltonics, Bremen, Germany) using an Apollo™ “ion funnel” ESI source. Mass calibration was performed immediately prior to the measurement with ESI Tune Mix Standard (Agilent, Waldbronn, Germany). Elemental analyses were carried out at the Institute of Chemistry, University of Kassel, Germany.

### 1.2 Compound Synthesis and Characterization

**[RuCl(3)(PPh<sub>3</sub>)<sub>2</sub>]**. A solution of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (373 mg, 0.39 mmol), MeO-**1**-H (128 mg, 0.39 mmol) and triethylamine (73 mg, 0.72 mmol) in dichloromethane (6 mL) was stirred for 14 h. Volatile components were removed in vacuo. The residue was extracted with toluene (4 mL), leaving triethylammonium chloride (51 mg, 0.37 mmol) as a colorless solid. Storage of the extract at room temperature gave the product as dark red crystals, which contained toluene. Single crystals were found to contain one toluene molecule per formula unit. Yield 316 mg (85%). An analytically pure sample was obtained by recrystallization from dichloromethane. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 6.48 (t, *J* = 7.6 Hz, 1 H), 6.72 (m, 3H), 6.88 (d, *J* = 7.6 Hz, 1 H), 6.99 (d, *J* = 7.2 Hz, 2 H), 7.05 – 7.43 (m, 36 H), 7.76 (d, *J* = 7.7 Hz, 1 H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 111.7, 119.9, 121.7, 126.7, 127.2, 128.1 (t, *J* = 4.5 Hz), 128.7, 128.9, 128.95, 129.4, 129.6 (br.), 130.1, 134.4 (br.), 136.7, 142.0, 146.9, 150.9, 151.3 (t, <sup>2</sup>*J*<sub>PC</sub> = 11.5 Hz, Ru-C<sub>aryl</sub>), 197.7 (t, <sup>2</sup>*J*<sub>PC</sub> = 11.1 Hz, C<sub>carbene</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 32.7. HRMS/ESI(+): *m/z* 922.203668 [M – Cl]<sup>+</sup>, 922.204847 calcd for [C<sub>56</sub>H<sub>44</sub>N<sub>3</sub>P<sub>2</sub>Ru]<sup>+</sup>. Anal. Calcd for C<sub>56</sub>H<sub>44</sub>N<sub>3</sub>ClP<sub>2</sub>Ru·CH<sub>2</sub>Cl<sub>2</sub>: C, 65.68; H, 4.45; N, 4.03. Found: C, 64.85; H, 4.23; N, 3.75. Although the result for carbon is outside the range viewed as establishing analytical purity, these data are provided to illustrate the best values obtained to date.

**[RuCl(4)(PPh<sub>3</sub>)<sub>2</sub>]**. A solution of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (675 mg, 0.70 mmol) and Nitron (440 mg, 1.41 mmol) in dichloromethane (15 mL) was stirred for 14 h. Volatile components were removed in vacuo. The residue was extracted with toluene (8 mL), leaving [**2**-H]Cl (240 mg, 0.69 mmol) as a colorless solid. Storage of the extract at room temperature gave the product as dark red crystals, which contained toluene. Yield 480 mg (70%). An analytically pure

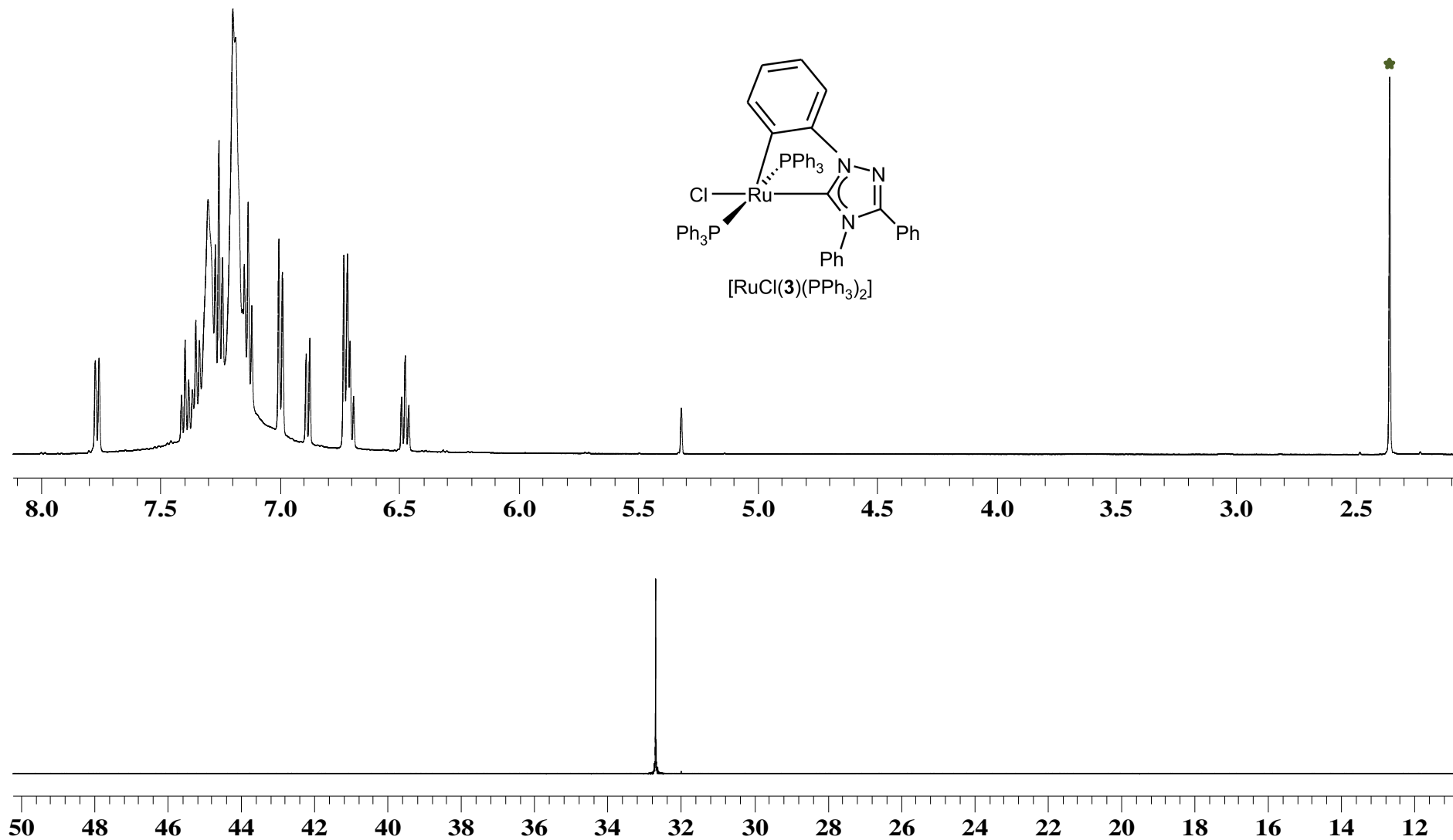
sample was obtained by recrystallization from dichloromethane.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  5.64 (s, 1 H, NH), 6.45 (t,  $J = 7.4$  Hz, 1 H), 6.68 (t,  $J = 7.4$  Hz, 1 H), 6.79 (d,  $J = 7.5$  Hz, 1 H), 6.84 (d,  $J = 7.6$  Hz, 2 H), 7.03 (t,  $J = 7.2$  Hz, 1 H), 7.06 – 7.44 (m, 36 H), 7.52 (t,  $J = 7.5$  Hz, 1 H), 7.73 (d,  $J = 7.7$  Hz, 1 H).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  111.1, 117.6, 119.8, 120.9, 122.6, 127.2, 128.1 (t,  $J = 4.5$  Hz), 129.4, 129.6 (br.), 129.7, 130.5, 134.4 (br.), 134.5, 138.9, 141.4, 147.5, 147.6, 151.0 (t,  $^2J_{\text{PC}} = 11.5$  Hz, Ru–C<sub>aryl</sub>), 194.0 (t,  $^2J_{\text{PC}} = 11.8$  Hz, C<sub>carbene</sub>).  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  33.4. HRMS/ESI(+):  $m/z$  937.214535 [M – Cl]<sup>+</sup>, 937.215746 calcd for [C<sub>56</sub>H<sub>45</sub>N<sub>4</sub>P<sub>2</sub>Ru]<sup>+</sup>. Anal. Calcd for C<sub>56</sub>H<sub>45</sub>N<sub>4</sub>ClP<sub>2</sub>Ru·CH<sub>2</sub>Cl<sub>2</sub>: C, 64.75; H, 4.48; N, 5.30. Found: C, 64.49; H, 4.66; N, 5.26.

**[RuCl<sub>2</sub>(3)(PPh<sub>3</sub>)<sub>2</sub>].** A solution of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (648 mg, 0.68 mmol) and **1** (201 mg, 0.68 mmol) in dichloromethane (15 mL) was stirred for 14 h in a flask equipped with a drying tube to allow the presence of dry air. Insoluble material was filtered off and the volume of the filtrate reduced in vacuo until first signs of crystallization were observed. Storage of the solution at room temperature gave the product as brownish orange crystals. Yield 235 mg (35%). HRMS/ESI(+):  $m/z$  922.206273 [M – 2 Cl]<sup>+</sup>, 922.204847 calcd for [C<sub>56</sub>H<sub>44</sub>N<sub>3</sub>P<sub>2</sub>Ru]<sup>+</sup>. Anal. Calcd for C<sub>56</sub>H<sub>44</sub>N<sub>3</sub>Cl<sub>2</sub>P<sub>2</sub>Ru·CH<sub>2</sub>Cl<sub>2</sub>: C, 63.52; H, 4.30; N, 3.90. Found: C, 63.36; H, 4.36; N, 4.12.

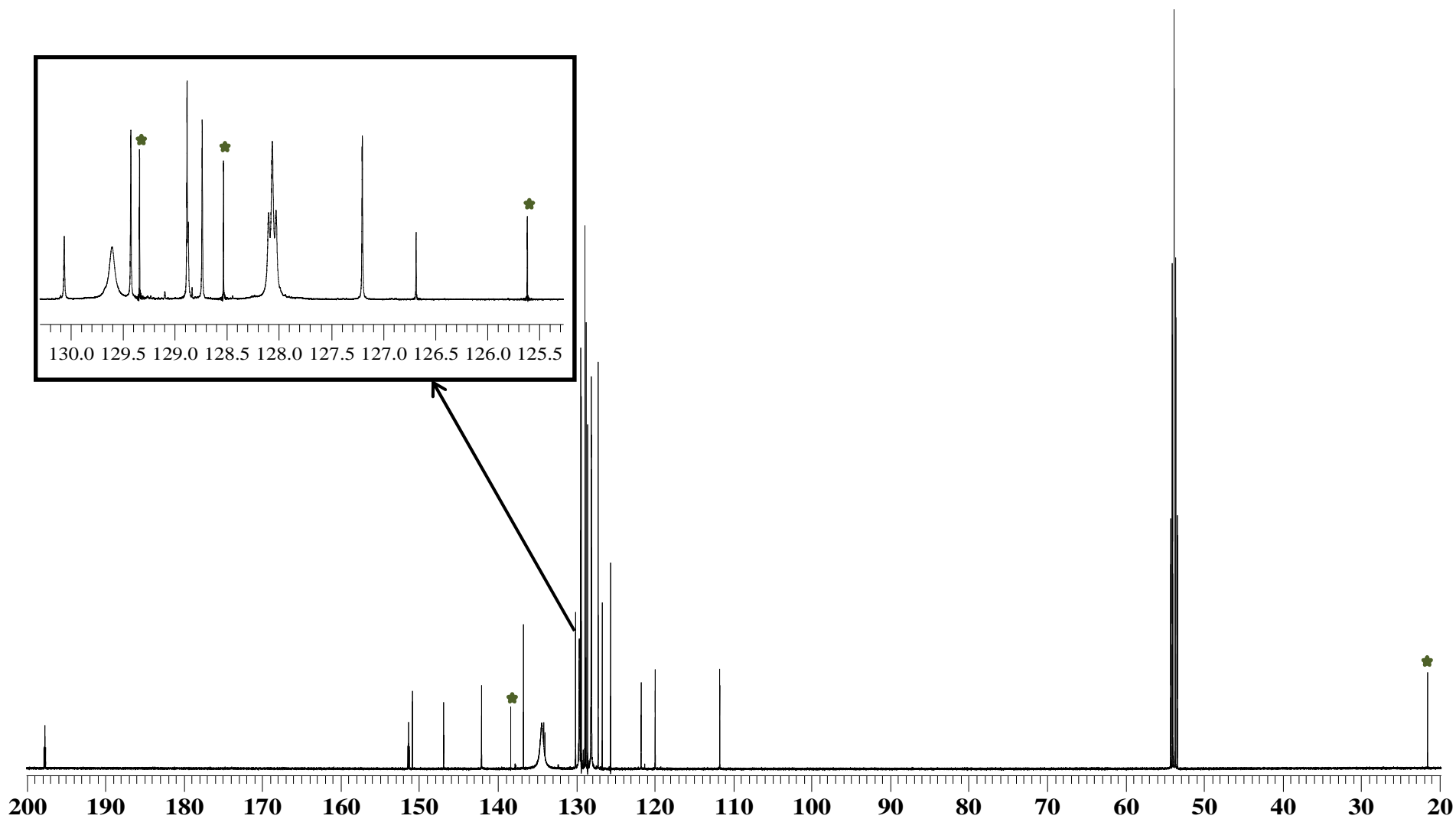
**[RuCl<sub>2</sub>(4)(PPh<sub>3</sub>)<sub>2</sub>].** A solution of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (675 mg, 0.70 mmol) and **2** (220 mg, 0.70 mmol) in dichloromethane (15 mL) was stirred for 14 h in a flask equipped with a drying tube to allow the presence of dry air. Insoluble material was filtered off and the volume of the filtrate reduced in vacuo until first signs of crystallization were observed. Storage of the solution at room temperature gave the product as brownish orange crystals. Yield 156 mg (22%). HRMS/ESI(+):  $m/z$  937.217268 [M – 2 Cl]<sup>+</sup>, 937.215746 calcd for [C<sub>56</sub>H<sub>45</sub>N<sub>4</sub>P<sub>2</sub>Ru]<sup>+</sup>. Anal. Calcd for C<sub>56</sub>H<sub>45</sub>N<sub>4</sub>Cl<sub>2</sub>P<sub>2</sub>Ru·CH<sub>2</sub>Cl<sub>2</sub>: C, 62.64; H, 4.34; N, 5.13. Found: C, 63.17; H, 3.78; N, 5.01.

## 1.3 NMR spectra

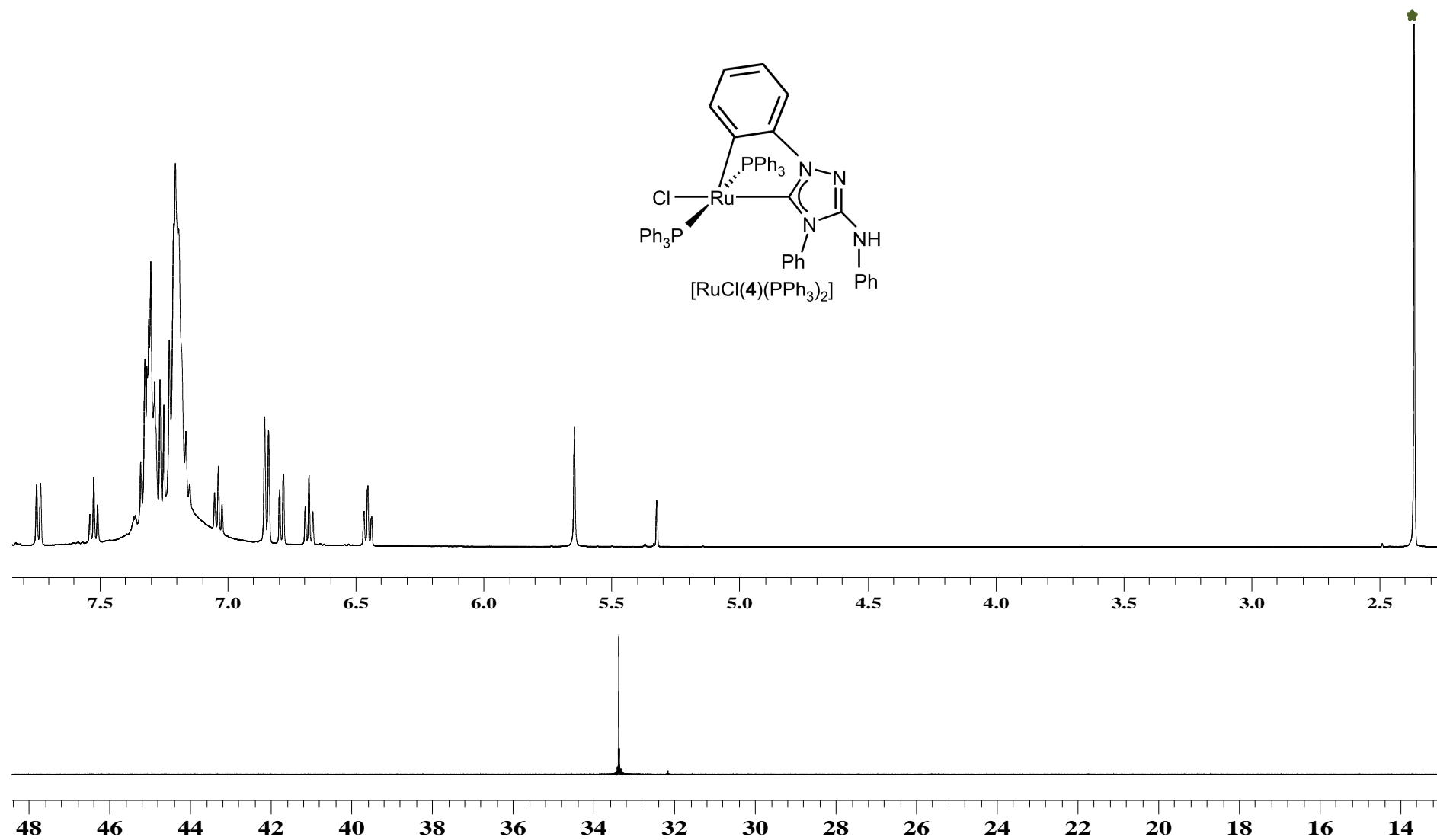
**Figure S1:** Top:  $^1\text{H}$  NMR spectrum of  $[\text{RuCl}(\mathbf{3})(\text{PPh}_3)_2]$  in  $\text{CD}_2\text{Cl}_2$ , the asterisk indicates the signal due to the methyl group of toluene ( $\delta = 2.36$  ppm). Bottom:  $^{31}\text{P}$  NMR spectrum of  $[\text{RuCl}(\mathbf{3})(\text{PPh}_3)_2]$  in  $\text{CD}_2\text{Cl}_2$ .



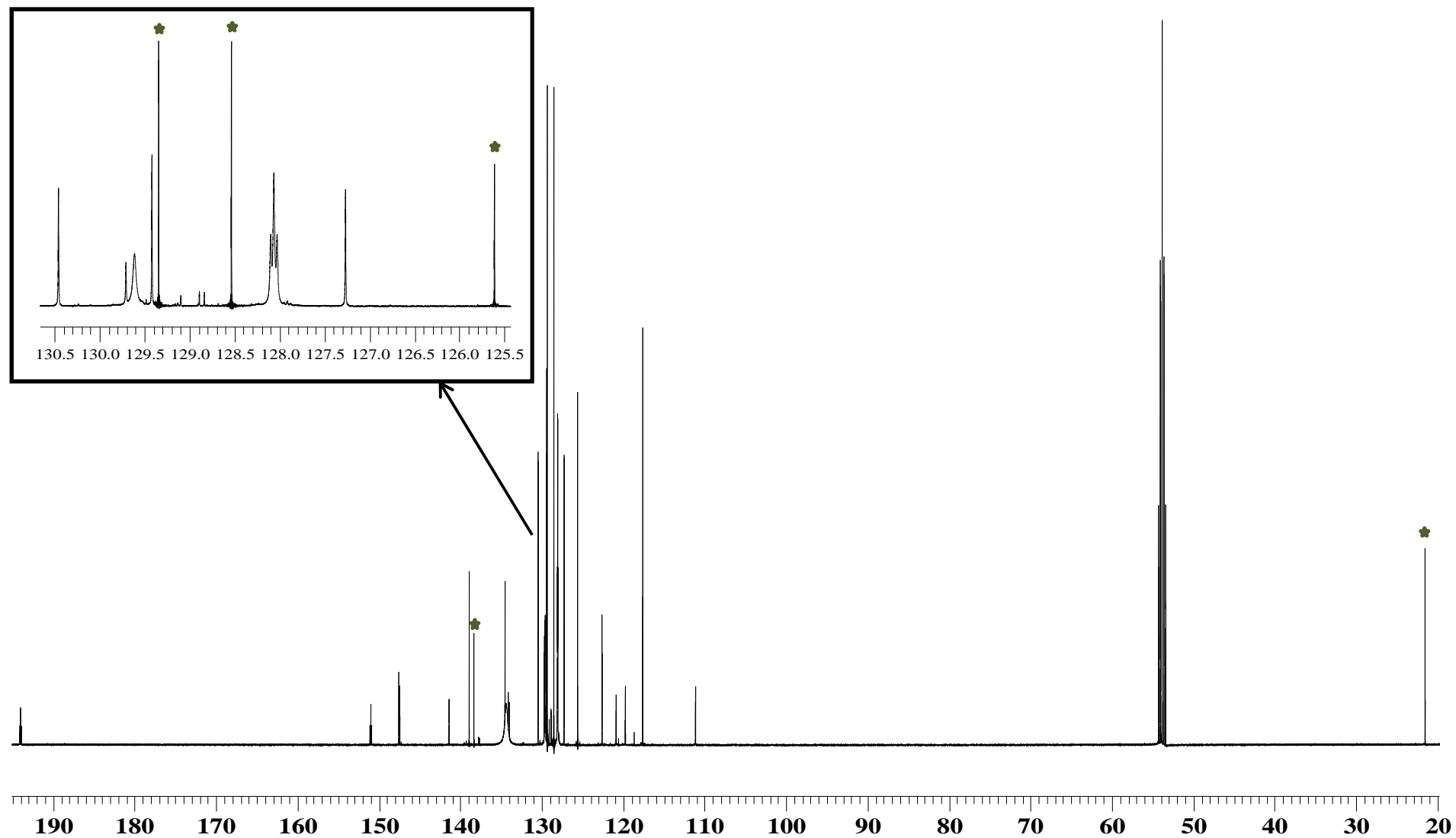
**Figure S2:**  $^{13}\text{C}$  NMR spectrum of  $[\text{RuCl}(\mathbf{3})(\text{PPh}_3)_2]$  in  $\text{CD}_2\text{Cl}_2$ . The inset shows a magnified view of the spectral region between ca. 130.2 and 125.3 ppm. Signals due to toluene are indicated by asterisks ( $\delta = 138.3, 129.3, 128.5, 125.6, 21.6$  ppm).



**Figure S3:** Top:  $^1\text{H}$  NMR spectrum of  $[\text{RuCl}(\mathbf{4})(\text{PPh}_3)_2]$  in  $\text{CD}_2\text{Cl}_2$ , the asterisk indicates the signal due to the methyl group of toluene ( $\delta = 2.36$  ppm). Bottom:  $^{31}\text{P}$  NMR spectrum of  $[\text{RuCl}(\mathbf{4})(\text{PPh}_3)_2]$  in  $\text{CD}_2\text{Cl}_2$ .



**Figure S4:**  $^{13}\text{C}$  NMR spectrum of  $[\text{RuCl}(\mathbf{4})(\text{PPh}_3)_2]$  in  $\text{CD}_2\text{Cl}_2$ . The inset shows a magnified view of the spectral region between ca. 130.5 and 125.5 ppm. Signals due to toluene are indicated by asterisks ( $\delta = 138.3, 129.3, 128.5, 125.6, 21.6$  ppm).



## 2. X-ray Diffraction Studies

### 2.1 General

For each data collection a single crystal was mounted on a glass fiber and all geometric and intensity data were taken from this sample. Data collection using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) was carried out on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. Absorption correction was done by integration using X-red.<sup>S3</sup> A dichloromethane solvent molecule was removed from the structure of  $[\text{RuCl}_2(\mathbf{3})(\text{PPh}_3)_2]\cdot\text{CH}_2\text{Cl}_2$  by using the SQUEEZE routine of PLATON.<sup>S4</sup> All data sets were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS97) and refined using alternating cycles of least squares refinements against  $F^2$  (SHELXL97).<sup>S5</sup> Graphical representations were made using ORTEP-3 win.<sup>S6</sup>

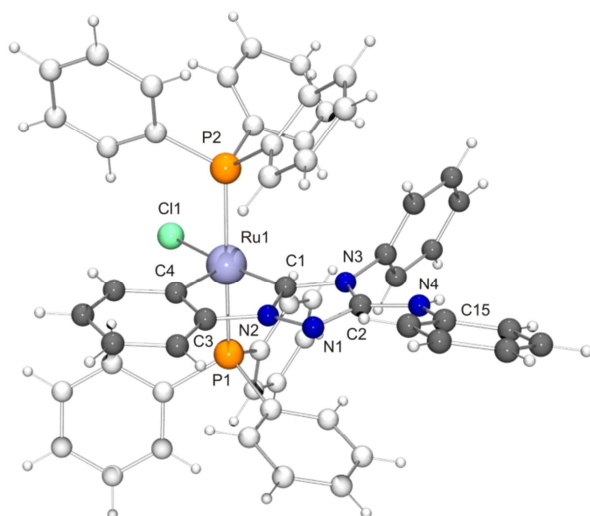
### 2.2 Discussion of the Structure of $[\mathbf{2}\text{-H}]\text{Cl}\cdot\text{CH}_3\text{OH}$

As a sideline of this work, we have been able to determine the crystal structure of the hydrochloride of Nitron (Figure S7), which crystallized as the solvate  $[\mathbf{2}\text{-H}]\text{Cl}\cdot\text{CH}_3\text{OH}$  from a methanol solution layered with diethyl ether. The crystal structure of the non-stoichiometric hydrochloride  $\mathbf{2}(\text{HCl})_{1.7}(\text{H}_2\text{O})_{3.3}$  was previously reported by Cannon et al.<sup>S7</sup>

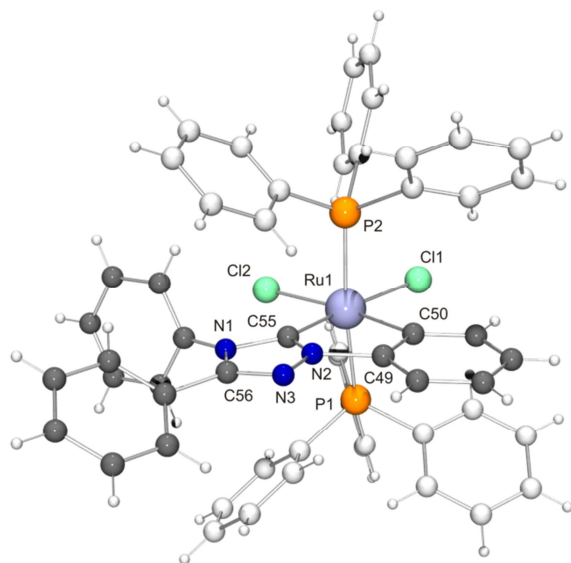
The bond parameters of the cation are indistinguishable within experimental error from those published earlier. However, the anion–cation interaction differs markedly from that described by Cannon et al. for their non-stoichiometric hydrochloride, where the chloride is involved in a hydrogen bond with the triazolium CH unit, the Cl–H distance being 2.43(5)  $\text{\AA}$ . In our case, the chloride is engaged in a hydrogen bond to the NH group. Pertinent parameters for this Cl $\cdots$ H–N interaction are the following: Cl–H–N 160.3 $^\circ$ , Cl–H 2.36  $\text{\AA}$ , Cl–N 3.15  $\text{\AA}$ . For reference, the sum of the van der Waals radii of Cl and N is 3.48  $\text{\AA}$ .<sup>S8</sup> This interaction is remarkable, since usually an ammonium unit, instead of an amine, is involved in such hydrogen bonding. We are aware of only a single comparable case, which was described by Natile and co-workers, who found a short Cl–N distance of 3.14(1)  $\text{\AA}$  in an acridine derivative.<sup>S9</sup> With ammonium units (Cl $\cdots$ H–N $^+$ ), shorter Cl–N distances down to ca. 3.0  $\text{\AA}$  can occur.<sup>S10</sup> The chloride ion in our compound is engaged in a second hydrogen bond of similar strength to the methanol of crystallization (Cl–H–O 169.5 $^\circ$ , Cl–H 2.32  $\text{\AA}$ , Cl–O 3.15  $\text{\AA}$ ).



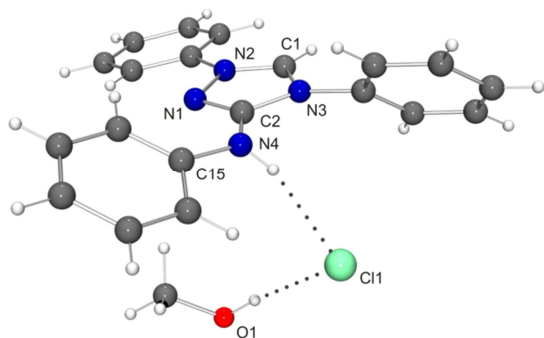
## 2.3 Molecular Structures



**Figure S5.** Molecular structure of  $[\text{RuCl}(\mathbf{4})(\text{PPh}_3)_2]$  in the crystal. Selected bond lengths ( $\text{\AA}$ ) and angles (deg): C1–N2 1.358(4), C1–N3 1.389(5), P1–Ru1 2.3494(10), P2–Ru1 2.3674(10); N2–C1–N3 101.4(3), P1–Ru1–P2 173.89(4).



**Figure S6.** Molecular structure of  $[\text{RuCl}_2(\mathbf{3})(\text{PPh}_3)_2]$  in the crystal. Selected bond lengths ( $\text{\AA}$ ) and angles (deg) not discussed in the text: C1–N2 1.350(12), C1–N3 1.441(11), P1–Ru1 2.421(3), P2–Ru1 2.406(3); N2–C1–N3 101.8(7), Cl1–Ru1–Cl2 98.96(10), P2–Ru1–P1 173.56(9).



**Figure S7.** Molecular structure of [2-H]Cl·CH<sub>3</sub>OH in the crystal. Selected bond lengths (Å) and angles (deg) not discussed in the text: C1–N2 1.317(2), C1–N3 1.345(2), C2–N1 1.310(2), C2–N3 1.392(2), C2–N4 1.358(2), N1–N2 1.391(2); N2–C1–N3 107.27(14), C2–N4–C15 126.79(15), C2–N4–H4 111.3(14), C15–N4–H4 117.3(13).

### 3. References

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