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# Ru<sup>II</sup> and Ru<sup>III</sup> Chloronitrile Complexes: Synthesis, Reaction Chemistry, Solid State Structure, and (Spectro)Electrochemical Behavior

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Dedicated to Prof. Dr. Dr. h.c. mult. Herbert Roesky on the Occasion of his 85th Birthday

**Abstract.** The synthesis of  $[Ti_6O_4(OiPr)_8(O_2CPh)_8]$  (3) and  $[RuCl(N=CR)_5][RuCl_4(N=CR)_2]$  (4a, R = Me; 4b, R = Ph),  $[Ru(N=CPh)_6][RuCl_4(N=CPh)_2]$  (5) and  $[H_3O][RuCl_4(N=CMe)_2]$  (7a) is discussed. Crystallization of 5 from  $CH_2Cl_2$  gave *trans*- $[RuCl_2(N=CPh)_4]$  (6). The solid-state structures of 3, 4a,b, 5, 6 and 7a are reported. Complex 4b forms a 3D network, while 6 displays a 2D structure, due to  $\pi$ -interactions between the benzonitrile ligands. The (spectro)electrochemical behavior of 4a,b and 6 was studied at 25 and  $-72 \ ^{\circ}C$  and the results thereof are compared with [NEt<sub>4</sub>]

 $[\operatorname{RuCl}_4(N \equiv CMe)_2]$  (7b) and  $[\operatorname{RuCl}(N \equiv CPh)_5][\operatorname{PF}_6]$  (8). The electrochemical response of the cation and the anion in 4a,b are independent from each other.  $[\operatorname{RuCl}(N \equiv CR)_5]^+$  possesses one reversible  $\operatorname{Ru}^{II}/\operatorname{Ru}^{III}$ process. However,  $[\operatorname{RuCl}_4(N \equiv CMe)_2]^-$  was shown to be prone to ligand exchange and disproportionation upon formation of either a  $\operatorname{Ru}^{IV}$ and  $\operatorname{Ru}^{II}$  species at 25 °C, while at -72 °C the rapid conversion of the electrochemically formed species is hindered. In situ IR and UV/Vis/ NIR studies confirmed the respective disproportionation reaction products of the aforementioned oxidation and reduction, respectively.

## **1** Introduction

Recently, we got interested in the synthesis, structure-property relationship, and photocatalytic behavior of titanium oxo and titanium heterometal-containing oxo clusters, since they are of importance, for example, as photo-catalysts or photoelectrochemical materials in, i.e. photo-catalytic H<sub>2</sub> evolution,<sup>[1-4]</sup> water oxidation,<sup>[5]</sup> and as photosensitizers for dyesensitized solar cells.<sup>[6-9]</sup> In particular, titanium oxo clusters being doped with metal atoms, such as Ag, Cu, Cd and Fe, can be synthesized by solvothermal reactions<sup>[1]</sup> using titaniumalkoxides as titanium oxo source and metal alkoxides,<sup>[10]</sup> nitrates,<sup>[11,12]</sup> carboxylates,<sup>[13-16]</sup> acetylacetonate,<sup>[12,17]</sup> or halides<sup>[18-20]</sup> as heterometal components. This synthetic approach allowed the preparation of a variety of heterometal-titanium oxo clusters.<sup>[1]</sup> However, to the best of our knowledge, heterobimetallic titanium-ruthenium oxo clusters were not reported so far. Combining the numerous applications of titanium oxide

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/zaac.202000304 or from the author. materials with ruthenium containing clusters is desirable, as they offer promising applications such as catalysts, i.e. in the aforementioned photocatalytic H<sub>2</sub> evolution<sup>[21,22]</sup> or CO and CO<sub>2</sub> methanation.<sup>[23–25]</sup> We hoped, their well-defined structural information provides further insight into mechanistic studies and into the structure-property relationship of such mixed materials. They can additionally be used as singlesource precursors for the deposition of Ru-doped titanium oxide layers.<sup>[3,4,12,26,27]</sup>

Nitrile-modified ruthenium complexes of type  $[RuCl(N \equiv CMe)_5][RuCl_4(N \equiv CMe)_2]$  are of particular relevance.<sup>[28,29]</sup> Such Ru<sup>II</sup>/Ru<sup>III</sup> salts can successfully be used as reactive intermediates in, for example, homogeneously catalyzed hydrosilylation reactions in supercritical CO<sub>2</sub> to produce formoxysilanes R<sub>3</sub>SiO<sub>2</sub>CH.<sup>[29-31]</sup> They are accessible by either the reaction of [RuCl<sub>3</sub>·xH<sub>2</sub>O] with silanes in acetonitrile,<sup>[29]</sup> or as side products in the synthesis of  $[RuCl_3(N \equiv CMe)_3]$ .<sup>[28]</sup> In addition, ruthenium chloro-nitrile complexes can be applied in the electro-oxidation of hydrocarbons.<sup>[32]</sup> Likewise, they are of interest to study their (spectro)electrochemical behavior since they show multiple oxidation states.[32-34]

We herein report on the reaction chemistry of  $[RuCl_3 xH_2O]$ (1) towards  $Ti(OiPr)_4$  (2) and PhCO<sub>2</sub>H as well as the treatment of 1 with different nitriles in a reducing environment. The chemical, physical and structural properties of the cluster  $[Ti_6O_4(OiPr)_8(O_2CPh)_8],$ complexes  $[RuCl(N \equiv CR)_5]$  $[RuCl_4(N \equiv CR)_2]$ (R = Me, Ph),  $[Ru(N \equiv CPh)_6]$  $[RuCl_4(N \equiv CPh)_2]$ , trans- $[RuCl_2(N \equiv CPh)_4]$ ,  $[RuCl(N \equiv CPh)_5]$  $[PF_6]$  and *trans*- $[X][RuCl_4(N \equiv CMe)_2]$  (X = H<sub>3</sub>O; X = NEt<sub>4</sub>) are reported as well.

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# **2** Experimental Section

#### 2.1 Instruments and Materials

All synthetic procedures were carried out in an atmosphere of argon using standard Schlenk techniques unless otherwise stated. *Iso*-Propanol, acetonitrile, benzonitrile and pentane were dried and distilled prior to use according to common methods.<sup>[35]</sup> Dichloromethane and diethyl ether were taken from a M. Braun SBS-800 purification system (stationary drying with columns filled with molecular sieves, 3 Å). Compounds [NBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>[36]</sup> and *trans*-[NEt<sub>4</sub>][RuCl<sub>4</sub>(N≡CMe)<sub>2</sub>] (**7b**)<sup>[37]</sup> were prepared according to literature procedures. All other chemicals were purchased from commercial suppliers and used without further purification.

NMR spectra (500.3 MHz for <sup>1</sup>H, 125.7 MHz for <sup>13</sup>C{<sup>1</sup>H}) were recorded using a Bruker Avance III 500 FT-NMR spectrometer at ambient temperature. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent as reference signal (<sup>1</sup>H NMR,  $\delta$  ([D<sub>8</sub>]thf) 1.72 ppm, 3.58 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR,  $\delta$  ([D<sub>8</sub>]thf) 25.31 ppm, 67.21 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR,  $\delta$  (CD<sub>2</sub>Cl<sub>2</sub>) 53.84 ppm. <sup>1</sup>H NMR,  $\delta$  ([D<sub>6</sub>]DMSO) 2.50 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR,  $\delta$  ([D<sub>6</sub>]DMSO) 39.52 ppm. <sup>1</sup>H NMR,  $\delta$  ([D<sub>6</sub>]acetone) 2.05 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR,  $\delta$  ([D<sub>6</sub>]acetone) 29.84 ppm, 206.26 ppm).<sup>[38]</sup> Infrared spectra were recorded with a Thermo Nicolet 200 FT-IR spectrometer. Elemental analyses were performed with a Thermo FLASHEA 1112 Series instrument. The melting points were determined by using a Gallenkamp MFB 595 010 M melting point apparatus.

Single-crystal X-ray Diffraction Analysis: Diffraction data were collected with a Rigaku Oxford Gemini S diffractometer applying graphitemonochromated Cu- $K_a$  radiation ( $\lambda = 1.54184$  Å) at 100 K. Crystals were selected and mounted in Krytox®. The structures were solved by Direct Methods implemented within SHELXS-2013 (Sheldrick 2008, Version 2013/1)<sup>[39]</sup> using the WinGX software platform (Farrugia 2012, Version 2014.1).<sup>[40]</sup> The models were refined with SHELXL-2013 (Sheldrick 2008, Version 2013/4) by full-matrix least square procedures on  $F^2$ . All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. Graphics of the molecular structures were created by using SHELXTL and ORTEP. For the structural characterization of **5** and **7a** see the Supporting Information.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-2020603, CCDC-2020604, CCDC-2020605, and CCDC-2020607 for **3**, **4a**,**b** and **6**, respectively (Fax: +44-1223-336-033; E-Mail: deposit @ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

**Electrochemistry:** Measurements on 1.0 mmol·L<sup>-1</sup> solutions of the analytes **4a,b, 6, 7b** and **8** in anhydrous dichloromethane solutions or 5 vol-% N=CR (R = Me, Ph) / dichloromethane, containing 0.1 mol·L<sup>-1</sup> of [NBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as supporting electrolyte were conducted under an atmosphere of argon at 25 °C, -30 °C (**6**) or -72 °C (**4b**). A three electrode cell, which utilized a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm<sup>2</sup>) and an Ag/Ag<sup>+</sup> (0.01 mol·L<sup>-1</sup> AgNO<sub>3</sub>) reference electrode was used as described in reference.<sup>[36,41-50]</sup> Successive experiments under the same experimental conditions showed that all formal potentials were reproducible within ±5 mV. Experimental potentials were referenced against an Ag/Ag<sup>+</sup> reference electrode, but results are presented referenced against ferrocene [FcH/FcH<sup>+</sup> couple = 220 mV vs. Ag/Ag<sup>+</sup>,  $\Delta E_p = 61$  mV; FcH = Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] as an internal standard.<sup>[46]</sup> When decamethylferrocene [Fc<sup>\*</sup> = Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] was used as an internal standard, the

experimentally measured potentials were converted into E vs. FcH/ FcH<sup>+</sup> (under our conditions the Fc\*/Fc\*<sup>+</sup> couple was at -614 mV vs. FcH/FcH<sup>+</sup>,  $\Delta E_p = 60$  mV).

**Spectroelectrochemistry:** The spectroelectrochemical measurements of **4a,b** in anhydrous dichloromethane containing  $[NBu_4][B(C_6F_5)_4]$  (0.1 mol·L<sup>-1</sup>) as the supporting electrolyte were performed at 25 °C in an OTTLE (= Optically Transparent Thin-Layer Electrochemistry) cell<sup>[51]</sup> with quartz windows (UV/Vis/NIR) with a Varian Cary 5000 spectrophotometer or CaF<sub>2</sub> windows (IR) with a Nicolet IR 200 spectrometer (Fa. Thermo). Between the spectroscopic measurements the applied potentials were increased stepwise using step heights of 25, 50 or 100 mV. At the end of the measurements the analyte was reduced at –100 mV vs. Ag/AgCl for 20 min, and an additional spectrum was recorded to prove the irreversibility of the oxidations.

#### 2.2 Synthesis Procedures

2.2.1 Synthesis of  $[Ti_6O_4(OiPr)_8(O_2CPh)_8]$ · $3N \equiv CMe$  (3) and  $[RuCl(N \equiv CMe)_5][RuCl_4(N \equiv CMe)_2]$ · $2N \equiv CMe$  ( $[4a \cdot 2N \equiv CMe]$ )

Titanium *iso*propoxide Ti(OiPr)<sub>4</sub> (**2**) (0.5 mL, 1.50 mmol), benzoic acid (0.61 g, 5.5 mmol) and [RuCl<sub>3</sub>·xH<sub>2</sub>O] (**1**) (25 mg, 0.10 mmol) were dissolved in 2 mL of acetonitrile and heated to 100 °C for 24 h. Colorless crystals of **3** (53 mg, 38 µmol, 15% based on **2**) as well as orange crystals of [**4a**·2N=CMe] (12 mg, 17 µmol, 34% based on **1**) were obtained after three weeks after covering the reaction solution with hexane (2 mL) at ambient temperature. The crystals of **3** and **4a** were collected, washed with hexane, dried under vacuum, washed again with toluene, separated by hand and dried under vacuum.

**Titanium Oxo Cluster 3:** M.p.:  $\geq$  130 °C (decomp.).  $C_{80}H_{96}O_{28}Ti_6 \cdot 2C_7H_8$  ( $M_r = 1977.10$ ): calcd. C 57.11, H 5.71%; found C 57.25, H 5.67 %. **IR** (KBr):  $\tilde{v} = 3068$  (m), 2972 (s), 2930 (m), 2867 (m), 1718 (w), 1654 (w), 1608 (vs, v<sub>as</sub>CO), 1568 (vs, v<sub>as</sub>CO), 1542 (vs, v<sub>as</sub>CO), 1522 (w), 1494 (m), 1423 (vs, v<sub>s</sub>CO), 1360 (w), 1324 (m), 1277 (w), 1179 (w), 1164 (m), 1128 (vs), 1068 (m) 991 (vs), 859 (s), 821 (w), 721 (s), 712 (s), 684 (m), 672 (m), 629 (vs), 596 (vs), 552 (vs) cm<sup>-1</sup>. <sup>1</sup>H NMR ([D<sub>8</sub>]thf, ppm):  $\delta = 8.37$  (m, 4 H, PhCO<sub>2</sub>), 8.27 (m, 4 H, PhCO<sub>2</sub>), 8.20 (m, 4 H, PhCO<sub>2</sub>), 8.03-7.99 (m, 4 H, PhCO<sub>2</sub>), 7.75 (m, 2 H, PhCO<sub>2</sub>), 7.57-7.41 (m, 16 H, PhCO<sub>2</sub>), 7.30-7.13 (m, 6 H, PhCO<sub>2</sub>), 6.73(m, 3 H, 4-C<sub>6</sub>H<sub>5</sub>), 6.50 (m, 3 H, 3-C<sub>6</sub>H<sub>5</sub>), 5.81 (septet,  $J_{HH}$  = 6.1 Hz, 2 H, OCH(CH<sub>3</sub>)<sub>2</sub>), 5.46 (septet,  $J_{HH}$  = 6.1 Hz, 2 H, OCH(CH<sub>3</sub>)<sub>2</sub>), 5.20 (septet,  $J_{HH} = 6.1$  Hz, 1 H, OCH(CH<sub>3</sub>)<sub>2</sub>), 5.12–4.92 (m, 3 H, OCH(CH<sub>3</sub>)<sub>2</sub>), 1.56–1.28 (m, 48 H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR ([D<sub>8</sub>]thf, ppm):  $\delta = 177.7$  (PhCO<sub>2</sub>), 173.6 (PhCO<sub>2</sub>), 173.3 (PhCO<sub>2</sub>), 166.0 (PhCO<sub>2</sub>), 133.9 (PhCO<sub>2</sub>), 133.8 (PhCO<sub>2</sub>), 133.6 (PhCO<sub>2</sub>), 133.5 (PhCO<sub>2</sub>), 133.5 (PhCO<sub>2</sub>), 133.3 (PhCO<sub>2</sub>), 132.1 (PhCO<sub>2</sub>), 131.8 (PhCO<sub>2</sub>), 131.6 (PhCO<sub>2</sub>), 131.6 (PhCO<sub>2</sub>), 131.5 (PhCO<sub>2</sub>), 131.5 (PhCO<sub>2</sub>), 130.9 (PhCO<sub>2</sub>), 130.2 (PhCO<sub>2</sub>), 129.7 (PhCO<sub>2</sub>), 129.3 (PhCO<sub>2</sub>), 129.2 (PhCO<sub>2</sub>), 129.2 (PhCO<sub>2</sub>), 129.1 (PhCO<sub>2</sub>), 129.0 (PhCO<sub>2</sub>), 128.9 (PhCO<sub>2</sub>), 128.5 (PhCO<sub>2</sub>), 127.5 (PhCO<sub>2</sub>), 126.1 (PhCO<sub>2</sub>), 81.8 (OCH(CH<sub>3</sub>)<sub>2</sub>), 81.5 (OCH(CH<sub>3</sub>)<sub>2</sub>), 79.8 (OCH(CH<sub>3</sub>)<sub>2</sub>), 68.8 (OCH(CH<sub>3</sub>)<sub>2</sub>), 25.9(CH<sub>3</sub>), 25.8 (CH<sub>3</sub>), 25.7 (CH<sub>3</sub>), 22.2 (CH<sub>3</sub>).

**Complex 4a:** In addition to the analytical data given in reference<sup>[29]</sup> following NMR spectroscopic data are added: M.p.:  $\geq 168 \text{ °C}$  (decomp.). C<sub>14</sub>H<sub>21</sub>N<sub>7</sub>Cl<sub>2</sub>Ru<sub>2</sub> ( $M_r = 666.76$ ): calcd. C 25.22, H 3.17, N 14.71%; found C 24.97, H 3.02, N 14.30%. **IR** (KBr):  $\bar{v} = 2970$  (vs), 2915 (vs), 2737 (w), 2620 (w), 2410 (m), 2333 (w, v CN), 2286(m, v CN), 2253 (w, v CN), 1619 (m), 1415 (vs), 1365 (m), 1119 (s), 1031

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(s), 948 (m), 620 (m) cm<sup>-1</sup>. **UV/Vis**: (0.25 mmol·L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 477 (700), 413 (7500), 398 (6900), 305 (2800). <sup>1</sup>**H NMR** (CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta = [\text{RuCl}(N \equiv \text{CMe})_5]^+$ : 3.18 (s, 3 H, *axial*), 2.78 (s, 12 H, *equatorial*). Please, notice that for the paramagnetic part [RuCl<sub>4</sub>(N \equiv CMe)<sub>2</sub>]<sup>-</sup> (6 H) of **4a** no resonance signals could be detected. The low solubility of **4a** in non-coordinating and non-protic solvents did not give meaningful <sup>13</sup>C{<sup>1</sup>H} spectra.

# 2.2.2 Synthesis of $[RuCl(N \equiv CMe)_5][RuCl_4(N \equiv CMe)_2]$ $(4a)^{[29]}$

Complex **4a** was independently synthesized by a modified procedure published by *Pitter* and co-workers.<sup>[29]</sup> Ruthenium trichloride (1) (50 mg, 0.20 mmol) and HSiPh<sub>3</sub> (43 mg, 0.20 mmol) were dissolved in 1 mL of acetonitrile and heated at 80 °C without stirring for 48 h, whereby single crystals formed. After cooling the reaction mixture to ambient temperature the solid was collected and washed consecutively with acetonitrile, diethyl ether and pentane. Complex  $[4a \cdot 2N \equiv CMe]$  was obtained as orange crystals (49 mg, 65 µmol, 65 % based on 1). For analytical and spectroscopic data of **4a** see above.

# 2.2.3 Synthesis of $[RuCl(N \equiv CPh)_5][RuCl_4(N \equiv CPh)_2]$ (4b), $[Ru(N \equiv CPh)_6][RuCl_4(N \equiv CPh)_2]$ (5) and trans- $[RuCl_2(N \equiv CPh)_4]$ (6)

For the synthesis of the title complexes a modified procedure as published by *Pitter* and co-workers was used.<sup>[29]</sup> In this respect, complex **1** (50 mg, 0.20 mmol) and HSiPh<sub>3</sub> (43 mg, 0.20 mmol) were dissolved in 1 mL of benzonitrile and the reaction mixture was heated at 80 °C without stirring for 48 h. The thus formed solid was filtered off, consecutively washed with benzonitrile, diethyl ether and pentane. Complex **5** was obtained as a red solid. Recrystallization of **5** in a dichloromethane-diethyl ether mixture of ratio 1:1 ( $\nu/\nu$ ) at ambient temperature yielded **6** in form of orange crystals (11 mg, 8.9 µmol, 8% based on **1**). Upon addition of diethyl ether to the filtrate an orange solid precipitated, which was washed with diethyl ether and then with pentane in order to obtain **4b** as orange solid. Recrystallization by over-layering a concentrated dichloromethane solution containing **4b** with diethyl ether yielded **4b** as orange crystals (69 mg, 62 µmol, 62% based on **1**).

**Complex 4b:** M.p.:  $\geq$  193 °C (decomp.). C<sub>49</sub>H<sub>35</sub>N<sub>7</sub>Cl<sub>2</sub>Ru<sub>2</sub> ( $M_r$  = 1101.26): calcd. C 53.44, H 3.20, N 8.90%; found C 53.40, H 3.13, N 8.82%. IR (KBr): v = 3081 (w), 3059 (m), 3034(w), 3000(w), 2773 (w), 2255 (s, v CN), 1626 (w), 1595 (m), 1487 (s), 1446 (vs), 1318 (w), 1291 (w), 1199 (m), 1175 (m), 1162 (w), 1117 (w), 1071 (w), 1023 (w), 999 (s), 926 (w), 754 (vs), 685 (vs), 623 (w), 550 (s), 510 (s) cm<sup>-1</sup>. UV/Vis: (1 mmol·L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 488 (900), 422 (9400), 408 (9400), 305 (92700). <sup>1</sup>**H NMR** ([D<sub>6</sub>]DMSO, ppm):  $\delta$  = 8.11 (s, 8 H, equatorial, 3-C<sub>6</sub>H<sub>5</sub>), 7.93 (s, 2 H, axial, 3-C<sub>6</sub>H<sub>5</sub>), 7.82 (s, 4 H, equatorial, 4-C<sub>6</sub>H<sub>5</sub>), 7.77 (s, 1 H, axial, 4-C<sub>6</sub>H<sub>5</sub>), 7.66 (m, 10 H, Ph); Please, notice that for the paramagnetic part [RuCl<sub>4</sub>(N=CPh)<sub>2</sub>]<sup>-</sup> of 4b no resonance signals could be detected. <sup>13</sup>C{<sup>1</sup>H} NMR ([D<sub>6</sub>]DMSO, ppm):  $\delta$ = 134.9 (equatorial,  $4-{}^{c}C_{6}H_{5}$ ), 134.6 (axial,  $4-{}^{c}C_{6}H_{5}$ ), 132.1 (axial, 2-°C<sub>6</sub>H<sub>5</sub>), 131.4 (equatorial, 2-°C<sub>6</sub>H<sub>5</sub>),129.7 (axial, 3-°C<sub>6</sub>H<sub>5</sub>), 129.5 (equatorial,  $3^{-c}C_{6}H_{5}$ ), 124.5 (-C=N),110.0 (equatorial,  $1^{-c}C_{6}H_{5}$ ), 109.8 (axial, 1-<sup>c</sup>C<sub>6</sub>H<sub>5</sub>).

**Complex 6:** M.p.:  $\geq 238 \,^{\circ}$ C (decomp.).  $C_{28}H_{20}N_4Cl_2Ru \cdot 0.5CHCl_2$ ( $M_r = 1253.86$ ): calcd. C 54.60, H 3.38, N 8.94%; found C 54.19, H 3.10, N 8.97. **IR** (KBr):  $\tilde{v} = 3059$  (m), 3034(w), 3000(w), 2767 (w), 2244 (m, v CN), 1626 (vw), 1595 (m), 1487 (m), 1446 (s), 1318 (w), 1290 (w), 1199 (w), 1119 (vs), 1022 (w), 999 (w), 983 (w), 758 (s), 685 (s), 620 (s), 550 (s), 509 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm):  $\delta =$ 7.86 (m, 8 H, 2-C<sub>6</sub>H<sub>5</sub>), 7.63 (tt,  $J_{HH} =$  7.6,  $J_{HH} =$  1.8 Hz, 4 H, 4C<sub>6</sub>H<sub>5</sub>), 7.53 (t,  $J_{HH}$  = 7.7 Hz, 8 H, 3-C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ = 133.8 (2-<sup>c</sup>C<sub>6</sub>H<sub>5</sub>), 133.6 (4-<sup>c</sup>C<sub>6</sub>H<sub>5</sub>), 129.6 (3-<sup>c</sup>C<sub>6</sub>H<sub>5</sub>), 124.3 (-C≡N), 112.7(1-<sup>c</sup>C<sub>6</sub>H<sub>5</sub>).

# 2.2.4 Synthesis of trans- $[H_3O][RuCl_4(N \equiv CMe)_2] \cdot N \equiv CMe$ (7*a*)

Complex [RuCl<sub>3</sub>·xH<sub>2</sub>O] (1) (49 mg, 0.20 mmol) was dissolved in 1 mL of acetonitrile and 0.1 mL of *iso*-propanol and the solution was heated at 80 °C without stirring for 48 h, whereby orange single crystals formed. The crystals were washed first with acetonitrile, followed by diethyl ether and pentane, respectively. The title complex was obtained as orange-red crystals (12 mg, 35 µmol. 17% based on 1). In addition to the analytical data given in reference<sup>[32]</sup> the following data are added: M.p.:  $\geq$  218 °C. **IR** (KBr):  $\tilde{v} = 3173$  (vs), 3050 (w), 2979 (s), 2923 (s), 2321 (m), 2294 (m), 2254 (m, *v* CN), 1413 (vs), 1365 (s), 1021 (s), 947 (w) cm<sup>-1</sup>. **UV/Vis**: (0.25 mmol·L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 474 (1400), 413 (2400), 400 (2400), 302 (2600).

## 2.2.5 Synthesis of $[RuCl(N \equiv CPh)_5][PF_6]$ (8):

Complex 8 was synthesized by a modified procedure published by Duff et al.<sup>[34]</sup> [RuCl<sub>3</sub>•xH<sub>2</sub>O] (1) (62 mg, 0.24 mmol) was dissolved in 1 mL of benzonitrile and 0.25 mL of methanol. The respective solution was heated at 80 °C for 4 h and then at 120 °C for 48 h with stirring, whereby trans-[RuCl<sub>2</sub>(N=CPh)<sub>4</sub>]·N=CPh precipitated as a yellow solid, which was filtered off and dried under vacuum. The respective solid (150 mg, 0.22 mmol) was then suspended in 8 mL of benzonitrile. After addition of Ag[PF<sub>6</sub>] (75 mg, 0.3 mmol) the corresponding reaction mixture was stirred at 100 °C for 2 h. After cooling the reaction mixture to ambient temperature the suspension was filtered through a pad of Celite. Upon addition of diethyl ether to the eluate complex 8 precipitated. Crystallization from a benzonitrile-dichloromethane-diethyl ether mixture of ratio 1:10:10, (v/v/v) gave 8 as a pale yellow solid (46 mg, 58  $\mu$ mol, 23% based on 1). M.p.:  $\geq$  170 °C (decomp.).  $C_{35}H_{25}N_5PF_6ClRu \cdot H_2O$  ( $M_r = 815.12$ ): calcd. C 51.57, H 3.34, N 8.59%; found C 51.57, H 3.24, N 8.55%. **IR** (KBr):  $\tilde{v} = 3457$ (m), 3062 (m), 2773 (w), 2255 (m, v CN), 2227 (w, v CN), 1620 (bw), 1595 (w), 1489 (m) 1447 (s), 1199 (m), 1178 (w) 1135 (s), 976 (m) 837 (s), 755 (s), 684 (s), 550 (s), 510 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR ([D<sub>6</sub>]acetone, ppm):  $\delta$  = 8.06 (d,  $J_{HH}$  = 7.4 Hz, 8 H, equatorial, 3-C<sub>6</sub>H<sub>5</sub>), 8.01 (d,  $J_{HH}$ = 7.8 Hz, 2 H, axial, 3-C<sub>6</sub> $H_5$ ), 7.74 (t,  $J_{HH}$  = 7.6 Hz, 4 H, equatorial, 4-C<sub>6</sub>H<sub>5</sub>), 7.70 (t,  $J_{HH}$  = 7.4 Hz, 1 H, axial, 4-C<sub>6</sub>H<sub>5</sub>), 7.70 (t,  $J_{HH}$  = 7.8 Hz, 8 H, equatorial, 2-C<sub>6</sub> $H_5$ ), 7.66 (t,  $J_{HH}$  = 7.6 Hz, 2 H, axial, 2- $C_6H_5$ ). <sup>13</sup>C{<sup>1</sup>H} NMR ([D<sub>6</sub>]acetone, ppm):  $\delta = 135.3$  (axial, 4-<sup>c</sup>C<sub>6</sub>H<sub>5</sub>), 135.1 (equatorial, 4-<sup>c</sup>C<sub>6</sub>H<sub>5</sub>), 134.6 (equatorial, 2-<sup>c</sup>C<sub>6</sub>H<sub>5</sub>), 134.5 (axial, 2-°C<sub>6</sub>H<sub>5</sub>), 130.5 (axial, 3-°C<sub>6</sub>H<sub>5</sub>), 130.5 (equatorial, 3-°C<sub>6</sub>H<sub>5</sub>), 125.5  $(-C \equiv N)$ , 111.9 (equatorial,  $1-{}^{c}C_{6}H_{5}$ ), 111.7 (axial,  $1-{}^{c}C_{6}H_{5}$ ).

**Supporting Information** (see footnote on the first page of this article): Additional information on IR, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, CV's and SWV's of **4a,b**, **6**, **7a,b** and **8** as well as the single-crystal X-ray structure analysis (**5**, **7a**).

# **3** Results and Discussion

#### 3.1 Synthesis and Characterization

Heating  $[RuCl_3 \cdot xH_2O]$  (1),  $Ti(^iOPr)_4$  (2) and benzoic acid in the ratio of 1:15:55 in acetonitrile as solvent for 2 d resulted in the formation of the titanium oxo cluster  $[Ti_6O_4(OiPr)_8(O_2CPh)_8]$  (3) and the ruthenium complex  $[RuCl(N \equiv CMe)_5][RuCl_4(N \equiv CMe)_2]$  (4a)<sup>[29]</sup> (Scheme 1). After appropriate work-up (Experimental), cluster 3 could be ob-

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Scheme 2. Synthesis of 4a,b, 5 and 6.

tained as colorless crystals in a yield of 15% (based on 2), while [4a·2 N=CMe] was formed as orange needles in 34% (based on 1). Presumably, *iso*-propanol formed during the reaction is responsible for the reduction of Ru<sup>III</sup> to Ru<sup>II</sup> by forming acetone.<sup>[34,37]</sup> However, when 1 was solely reacted with *iso*-propanol under identical reaction conditions, then crystalline *trans*-[H<sub>3</sub>O][RuCl<sub>4</sub>(N=CMe)<sub>2</sub>](**7a**) was obtained (Experimental Section).

A further possibility to prepare **4a** is based on the synthetic protocol firstly described by Pitter.<sup>[29]</sup> Thus, **1** was treated with stoichiometric amounts of HSiPh<sub>3</sub> in refluxing acetonitrile for 4 h (Experimental Section). When acetonitrile is replaced by benzonitrile, the corresponding complex [RuCl(N=CPh)<sub>5</sub>][RuCl<sub>4</sub>(N=CPh)<sub>2</sub>] (**4b**) could be isolated in a yield of 62% (Scheme 2). While in acetonitrile solely **4a** was formed, it was found that in benzonitrile in addition to **4b** the Ru<sup>II</sup>/Ru<sup>II</sup> complex [Ru(N=CPh)<sub>6</sub>][RuCl<sub>4</sub>(N=CPh)<sub>2</sub>] (**5**) was produced in low yield (8%) (Experimental, Scheme 2). Attempts to recrystallize **5** from dichloromethane solutions at ambient temperature produced orange *trans*-[RuCl<sub>2</sub>(N=CPh)<sub>4</sub>] (**6**) (Scheme 2).

For comparison, complexes 7b and 8 were synthesized accordingly to references<sup>[34,37]</sup>. Hence, refluxing 1 in a methanol-acetonitrile mixture of ratio 2:1 ( $\nu/\nu$ ) in the presence of [NEt<sub>4</sub>]Cl gave *trans*-[NEt<sub>4</sub>][RuCl<sub>4</sub>(N=CMe)<sub>2</sub>] (**7b**),<sup>[30]</sup> while [RuCl(N=CPh)<sub>5</sub>][PF<sub>6</sub>] (**8**) was accessible in a consecutive reaction sequence by heating **1** in a benzonitrile-methanol mixture of ratio 4:1 ( $\nu/\nu$ ) to produce [RuCl<sub>2</sub>(N=CPh)<sub>4</sub>] first, which, when re-dissolved in benzonitrile, gave **8** on addition of Ag[PF<sub>6</sub>].

Cluster **3** and complexes **4a,b** and **5–7a,b** can be handled for a short period of time in air, however, long term exposure should be avoided, since they start to decompose giving undefined species. Solutions containing **3**, **4a,b** or **5–7a,b** should be best kept under an atmosphere of inert gas.

Solid **4a** is insoluble in non-polar common organic solvents, while in polar ones, such as dichloromethane and acetonitrile, it is somewhat soluble. In contrast, **4b** dissolves nicely in dichloromethane, chloroform and is moderately soluble in ben-zonitrile (Experimental Section).

The identities of **3**, **4a**,**b**, **6**, and **8** were confirmed by elemental analysis, IR and NMR ( ${}^{1}H$ ,  ${}^{13}C{{}^{1}H}$ ) spectroscopy (Experimental Section, see Supporting Information). The spectroscopic data of **7a**,**b** agree well with literature values.<sup>[32,37]</sup> The electrochemical behavior of **4a**,**b**, **6**, **7b** and **8** was studied by cyclic (CV) and square wave voltammetry (SWV), while

Zeitschrift für anorganische und allgemeine Chemie the spectroelectrochemical response was investigated by in situ UV/Vis/NIR and IR spectroscopy for **4a**,**b**. The molecular structures of **3**, **4–6** and **7a** in the solid state were determined

by single-crystal X-ray diffraction analysis.

The IR spectrum of **3** is characterized by typical v(CO) vibrations at 1608, 1568 and 1542 cm<sup>-1</sup>, which agree with similar titanium-oxo clusters reported elsewhere.<sup>[52–54]</sup> The respective ruthenium complexes show distinctive v(CN) vibrations at 2286 cm<sup>-1</sup> and 2254 cm<sup>-1</sup> (**4a**), 2255 cm<sup>-1</sup> (**4b**), 2244 cm<sup>-1</sup> (**6**), 2254 cm<sup>-1</sup> (**7a**) and 2255 and 2227 cm<sup>-1</sup> (**8**), which are characteristic for this type of species.<sup>[29,34,37]</sup>

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of diamagnetic **3**, **6** and **8** are in accordance with the proposed structures (Experimental). Specific to the <sup>13</sup>C{<sup>1</sup>H} NMR spectra is the appearance of a resonance signal for the N=C carbon atoms in the range of 124–126 ppm. Since **4a**,**b** features the  $[RuCl_4(N=CR)_2]^-$  (R = Me, Ph) anion as a paramagnetic part, less resolved and hence broad signals are observed for cationic  $[RuCl(N=CR)_5]^+$ , while for  $[RuCl_4(N=CR)_2]^-$  no signal could be observed (Experimental Section, see Supporting Information).

UV/Vis spectra of **4a,b** and **7a** for comparison confirmed the presence of Ru<sup>III</sup> ions typical for  $[RuCl_4(N \equiv CR)_2]^-$ , as it can be seen from Figure S28 (Supporting Information), depicting the two distinctive in-plane halide-to-Ru<sup>III</sup> chargetransfer bands (**4a**, 397 and 412 nm; **4b**, 410 and 422 nm; **7a**, 400 and 413 nm)<sup>[34]</sup> and the single  $d_{\pi}$ - $d_{\pi}$  transition (**4a**, 473 nm; **4b**, 488 nm; **7a**, 474 nm).<sup>[33,34,37]</sup>

#### 3.2 Solid State Structures

The molecular structures of 3, 4a, b, 5, 6 and 7a in the solidstate were determined by single-crystal X-ray diffraction analysis. The ORTEP of 3 is shown in Figure 1, the ones of **4a,b** in Figure 2 and that for **6** in Figure 3, while the ORTEP of **5** and **7a** along with key structural data can be found in the Supporting Information (Figures S5, S11, and S12, Tables S1 and S2). Selected crystal and structure refinement data of **3**, **4a,b** and **6** are given in Table 1.

Suitable crystals of **3** were obtained by layering the reaction solution with hexane for three weeks at ambient temperature. Complex **3** crystallizes in the triclinic space group  $P\overline{1}$ . Crystals are of the composition [**3**·3N $\equiv$ CMe] with the acetonitrile molecules acting as packing solvent. The asymmetric unit comprises of two crystallographically different and centrosymmetric halves of **3**, denoted as **3A** and **3B**, with the inversion center in the middle of the central Ti<sub>4</sub>O<sub>6</sub> rings (Figure 1). Related bond lengths and angles of **3A** and **3B** differ only marginally and hence the discussion refers to **3A** only. The molecular structure is shown in Figure 1, together with a complete and selective view on the centrosymmetric Ti<sub>6</sub>O<sub>26</sub> core.

The molecular structure of 3 is of the type

[Ti<sub>6</sub>O<sub>4</sub>(OR)<sub>8</sub>(O<sub>2</sub>CR')<sub>8</sub>] with four  $\mu$ -oxo (O1, O1A, O2, O2A) atoms, two  $\mu$ -bridging (O14, O14A) as well as six terminal *iso*-propxides (O4, O4A, O8, O8A, O13, O13A) and eight bridging bidentate carboxylate ligands (O3, O3A, O5, O5A, O6, O6A, O7, O7A, O9, O9A, O10, O10A, O11,O11A, O12, O12A) alongside one and a half acetonitrile molecule as packing solvent. A detailed structural discussion of the same type of titanium oxo clusters can be found elsewhere.<sup>[52–57]</sup>

Complex **4a** was obtained in form of single crystals during the reaction, if no stirring is applied, while suitable crystals of **4b** were formed by carefully covering a concentrated dichloromethane solution containing **4b** with a layer of diethyl ether at ambient conditions (Experimental). Complex **4a** crystallizes in the space group  $P\bar{1}$  with two acetonitrile packing solvent mol-



**Figure 1.** ORTEP (50% probability level) of **3A** (left) and its central  $Ti_6O_{23}$  core (right). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): O1–Ti1 1.750(2), O2A–Ti1 1.8985(18), O14A–Ti1 2.087(2), O1–Ti2 1.883(2), O2–Ti2 1.9218(19), O2–Ti3 2.058(2), O14–Ti3 1.961(2), O2–Ti1A 1.9011(19), O14–Ti1A 2.078(2), O1A–Ti1A 1.753(2), O1A–Ti2A 1.876(2), O2A–Ti2A 1.9156(19), O2A–Ti3A 2.053(2), O14A–Ti3A 1.965(2), Ti1–Ti3A 3.1037(7), Ti1–Ti2 3.3776(7), Ti3–Ti1A 3.1002(7), Ti2A–Ti1A 3.3694(7), Ti1–O1–Ti2 136.74(11), Ti1A–O2–Ti2 127.27(10), Ti1A–O2–Ti3 103.26(9), Ti2–O2–Ti3 128.58(10), Ti3–O14–Ti1A 100.08(9), Ti1A–O1A–Ti2A 136.34(12), Ti1–O14A–Ti2A 128.65(11), Ti1A–O2A–Ti3A 103.18(9), Ti2A–O2A–Ti3A 127.81(10), O1–Ti1–O2A 104.74(9), O1–Ti1–O14A 176.76(9), O2A–Ti1–O14A 77.08(8), O1–Ti2–O2 99.69(8), O14–Ti3–O2 76.44(8), O1A–Ti1A–O2 102.64(9), O1A–Ti1A–O14 179.27(9), O2–Ti1A–O14 77.66(8), O1A–Ti2A–O2A 99.94(8), O14A–Ti3A–O2A 76.87(8). Symmetry code; "A" = –x + 1, –y + 1, –z.

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5 6 1				
	3	4a	4b	6
Formula	C <sub>86</sub> H <sub>105</sub> N <sub>3</sub> O <sub>28</sub> Ti <sub>6</sub>	C18H27Cl5N9 Ru2	C49H35Cl5N7Ru2	$C_{29}H_{22}Cl_4N_4Ru$
$M_{\rm r}$ , g·mol <sup>-1</sup>	1916.12	748.87	1101.23	669.37
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Radiation / wavelength /Å	Cu-K <sub>a</sub> / 1.54184	$Cu-K_{\alpha}$ / 1.54184	$Cu-K_{\alpha}$ / 1.54184	$Cu-K_{\alpha}$ / 1.54184
a /Å	13.5290(5)	7.9383(4)	20.6205(7)	16.9895(3)
b /Å	14.0980(7)	13.0248(7)	10.9373(3)	10.9740(2)
c /Å	25.2512(11)	15.7137(10)	23.1788(8)	16.0847(3)
a /°	82.093(4)	78.945(5)		
βΙ°	82.536(3)	77.716(5)	105.721(4)	106.864(2)
y /°	81.793(4)	81.462(4)		
V/Å <sup>3</sup>	4691.6(4)	1548.21(16)	5032.0(3)	2869.91(9)
$\rho_{\rm calcd}$ /mg m <sup>-3</sup>	1.356	1.606	1.454	1.549
Z	2	2	4	4
$\mu$ /mm <sup>-1</sup>	4.784	12.065	7.618	8.052
Т, К	100	100	100	100
$\Theta$ range, deg	3.191-63.497	3.480-64.486	3.963-65.000	4.862-65.998
Reflections measured,	27715,	8871,	15604,	15074,
independent,	15327,	5158,	8517,	4976,
observed $[I > 2\sigma(I)]$	12578	4835	7530	4477
R <sub>int</sub>	0.0430	0.0378	0.0397	0.0334
$R_1 [I > 2\sigma(I)], R_1 (all)$	0.0505, 0.0638	0.0383, 0.0402	0.0695, 0.0771	0.0308, 0.0777
$wR_2 [I > 2\sigma(I)], wR_2$ (all)	0.1352, 0.1475	0.1005, 0.1027	0.1831, 0.1899	0.0777. 0.0810

Table 1. Crystallographic data and details of the data collection and structure determination for 3, 4a,b and 6.

ecules. Crystals are thus of the composition [**4a**·2N $\equiv$ CMe]. Complex **4b** crystallizes in the monoclinic space group  $P_{1/c}$  with one crystallographically independent [RuCl(N $\equiv$ CPh)<sub>5</sub>]<sup>+</sup> cation and two crystallographically independent centrosymmetric halves of [RuCl<sub>4</sub>(N $\equiv$ CPh)<sub>2</sub>]<sup>-</sup> anions (Figure 2). In [RuCl<sub>4</sub>(N $\equiv$ CPh)<sub>2</sub>]<sup>-</sup> the four chloride ligands are in equatorial positions, while the two nitrile groups are apically oriented. [RuCl(N $\equiv$ CPh)<sub>5</sub>]<sup>+</sup> features a Cl-Ru-N $\equiv$ CR moiety. The average Ru–N and Ru–Cl bond lengths in **4a**,**b** are comparable to those ones found in other ruthenium chloride nitrile complexes.<sup>[29,32,58–63]</sup> The average Ru–Cl bonds in the cationic part [RuCl(N $\equiv$ CR)<sub>5</sub>]<sup>+</sup> (**4a**, R = Me; **4b**, R = Ph) are with 2.3789(8) and 2.3863(18) Å longer than in  $[RuCl_4(N\equiv CR)_2]^-$ [4a: 2.3528(8) Å, 4b: 2.3539(17) Å], which is attributed to the chloride being in *trans* position to an acetonitrile ligand.<sup>[129, 32,58]</sup> The respective N–Ru–N, N–Ru–Cl, Cl–Ru–Cl, Ru–N–C and N–C–C bond angles are in accordance with literature values (Table 2).<sup>[29,32,58–63]</sup> One of the benzonitrile ligands (nitrile associated with N5) of  $[RuCl(N\equiv CPh)_5]^+$  is disordered and has been refined to split occupancies of 0.673/ 0.327 (Figure 2), resulting in bond angles of 155.2(9)° (Ru1– N5–C29') and 153.5(18)° (Ru1–N5–C29) with the bent nature of the benzonitrile ligand at an angle of 167(3)° (N5–C29–C30) and 176.6(3)° (N5–C29'–C30'), respec-



**Figure 2.** ORTEP (50% probability level) of **4a** (left) and **4b** (right) representing the orientation of Ru complexes to each other as observed in the asymmetric unit. Packing solvent molecules are omitted for clarity. Disordered atoms are labelled with suffix '. The broken line refers to a CH··· $\pi$  interaction within the asymmetric unit, whereby < indicates the interplanar angle and *d* the geometrical centroids distance of interaction phenyl rings. Symmetry code: "A" = 1 - *x*, 1 - *y*, -*z*. "B" = -*x*, -*y*, -*z*. For selected bond lengths (Å) and bond angles (°) see Table 2.

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	4a	4b
Ru1–Cl1	2.3789(8)	2.3863(18)
Ru2–Cl	2.3515(8), 2.3450(8), 2.3643(9), 2.3503(9)	2.3599(19), 2.3465(18), 2.3564(16), 2.3529(16)
Ru1–N1	2.020(3)	2.030(6)
Ru1–N	2.023(3), 2.019(3), 2.018(3), 2.005(3)	2.022(6), 2.011(6), 2.015(6), 2.024(7)
Ru2–N	2.013(3), 2.013(3)	1.992(6), 2.021(5)
N-Ru1-N (trans)	177.83(11), 178.74(11)	178.3(2), 174.4(3)
N–Ru1–N (cis)	89.45(12), 89.85(12), 90.50(12), 91.14(12), 90.92(12),	87.1(2), 93.4(2), 89.8(3), 89.5(3), 89.7(2), 88.9(2),
	91.30(12), 89.36(12), 90.49(12)	91.9(2), 95.8(3)
N-Ru2-N (trans)	179.09(12)	180.0
N–Ru1–Cl	88.43(9), 88.01(9), 89.91(9), 90.59(9)	88.12(17), 87.90(16), 90.28(16), 87.3(3)
N1–Ru1–Cl1 (trans)	178.64(8)	176.28(18)
N–Ru2–Cl	91.27(9), 88.74(9), 89.14(9), 90.84(9), 89.08(9),	91.44(18), 88.56(18), 91.49(19), 88.51(19), 87.31(17),
	90.01(9), 91.61(9), 89.29(9)	92.69(17), 90.43(16), 89.57(16)
Cl-Ru2-Cl (cis)	89.37(3), 89.50(3), 89.64(3), 91.49(3)	90.40(7), 89.60(7), 91.32(6), 88.69(6)
Cl-Ru2-Cl (trans)	178.93(3), 178.66(3)	180.0

Table 2. Selected bond parameters /Å/° of 4a,b.

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tively. The latter structural motif is also found in, i.e.  ${[RuCl_3(N=CMe)_3] \cdot N=CMe}_2$ .<sup>[32]</sup>

Complex **4b** forms in the solid state a 3D network of which the  $[\text{RuCl}_4(N\equiv\text{CPh})_2]^-$  (Figure S2, Supporting Information) and  $[\text{Ru}^{III}\text{Cl}(N\equiv\text{CPh})_5]^+$  (Figure S3, Supporting Information) parts assemble to 1D chains via parallel-displaced  $\pi$ - $\pi$  stacking interactions of the respective benzonitriles. As it can be seen from Figure S4 (Supporting Information), parallel (2D layer formation) and additional parallel and T-shaped CH··· $\pi$ interactions (3D structure formation) are completing the 3-dimensional network structure. Further information and graphical representations are given in the Supporting Information (Figures S1–S5).

Crystals of **6** were obtained by carefully layering a concentrated dichloromethane solution containing **6** with diethyl ether at ambient temperature. Complex **6** crystallizes in the  $P2_1/c$  space group and possesses one dichloromethane molecule in

the unit cell, resulting in [6·CH<sub>2</sub>Cl<sub>2</sub>]. Since the dichloromethane only acts as packing solvent it will be referred to as 6 further on. Complex 6 is centrosymmetric with two chlorides perpendicular to the Ru(N=C<sub>Ph</sub>)<sub>4</sub> plane. All bond lengths and angles in 6 are comparable to those in *trans*-[RuCl<sub>2</sub>(N=CMe)<sub>4</sub>]<sup>[60,62]</sup> with no distinguishable differences resulting from the change from acetonitrile to benzonitrile. In the solid state, 6 forms 2D layers due to  $\pi$ -interactions between the aromatic benzonitrile ligands (Figure 3). Further information and graphical representations are given in the Supporting Information (Figures S7–S10).

#### 3.3 Electrochemical Studies

The redox properties of ruthenium complexes **4a**,**b** and **6**, as well as, **7b** and **8** for comparison were investigated by cyclic voltammetry (= CV), square-wave voltammetry (= SWV) and



Figure 3. ORTEP (50% probability level) of 6 with the atom numbering scheme. Above: Perspective top view. Below: Two different perspective side views. Selected bond lengths (Å) and bond angles (°): N1–Ru1 1.997(2), N2–Ru1 2.014(2), N3–Ru1 2.001(2), N4–Ru1 2.006(2); N1–Ru1–N3 178.88(8), N1–Ru1–N4 90.88(8), N3–Ru1–N4 88.10(8), N1–Ru1–N2 88.59(8), N3–Ru1–N2 92.43(8), N4–Ru1–N2 179.34(8).

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Table 3. Cyclic voltammetry data (potentials vs. FcH/FcH <sup>+</sup> ) of 4a,b, 6, 7b and 8. <sup>a</sup> ).							
	$E_1^{\circ'} / \text{mV}^{\text{b}}$ [ <b>A</b> ] <sup>-</sup> /[ <b>A</b> ] <sup>2-</sup>	$E_2^{\circ}$ ' /mV <sup>b) h)</sup>	$E_3^{\circ} / \text{mV}^{\text{b) g)}$ $(\Delta E_p / \text{mV})^{\text{c)}}$	<i>E</i> <sub>4</sub> °' /mV <sup>b)</sup> [ <b>A</b> ] <sup>-</sup> /{ <b>A</b> }	$E_5^{\circ}$ '/mV <sup>b)</sup> ( $\Delta E_p$ /mV) <sup>c)</sup>	$E_6^{\circ'}$ /mV <sup>b) h)</sup> <b>B</b> /[ <b>B</b> ] <sup>+</sup>	$E_7^{\circ'}$ /mV <sup>b) f)</sup> $(\Delta E_p$ /mV) <sup>c)</sup>
4a 4b 6 7b 8	-1070 <sup>d)</sup> -980 <sup>d)</sup> - -1075 <sup>d)</sup>	-420 <sup>d)</sup> -350 <sup>d)</sup> - -425 <sup>d)</sup>	490 <sup>d)</sup> 525 <sup>d)</sup> 320 (59) <sup>e)</sup> 520 <sup>d)</sup>	775 <sup>d)</sup> 790 <sup>d)</sup> - 775 <sup>d)</sup>	1020 (72) 1080 (62) - - 1075 (89)	1250 <sup>d)</sup> 1240 <sup>d)</sup> - 1240 <sup>d)</sup>	1340 (104) 1330 (116) 1320 <sup>d)</sup> 1340 (104) 1345 (124)

a) 1.0 mmol·L<sup>-1</sup> solutions in anhydrous dichloromethane; 0.1 mol·L<sup>-1</sup> [NnBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as supporting electrolyte at 25 °C; sweep rate 100 mV s<sup>-1</sup>. b)  $E^{\circ}$  = Formal potential. c)  $\Delta E_{\rm p}$  = difference between  $E_{\rm pa}$  and  $E_{\rm pc}$  for a reversible redox process. d) Values determined with square wave voltammetry. e) Measured at -30 °C. f) Measured in the presence of Fc\*. g) Observed as follow up process of  $E_1^{\circ}$ . h) Observed as follow up process of  $E_4^{\circ}$ '.

#### Redox behavior of cationic part of 4a,b and 8

= [Ru<sup>III</sup>CI(NECR)<sub>5</sub>]<sup>2+</sup> [Ru<sup>II</sup>CI(NECR)<sub>5</sub>] - e<sup>-</sup> E5°

#### Redox behavior of anionic part of 4a,b and 7b



Scheme 3. Postulated reaction pathways for the chemical transformations of  $[RuCl(N=CR)_5]^+$  and  $[A]^-$  upon oxidation and reduction (4a, 7b: R = Me; **4b**, **8**: R = Ph. [A]<sup>-</sup>: [RuCl<sub>4</sub>(N $\equiv$ CR)<sub>2</sub>]<sup>-</sup>; **B**: [RuCl<sub>3</sub>(N $\equiv$ CR)<sub>3</sub>]; **C**: [RuCl<sub>5</sub>(N $\equiv$ CR)]).

spectroelectrochemistry (in situ UV/Vis/NIR and in situ IR spectroscopy, 4a,b). However, 7a could not be measured, due to its poor solubility in dichloromethane, acetonitrile and mixtures thereof.

As supporting electrolyte an anhydrous dichloromethane solution of 0.1 mol·L<sup>-1</sup> of [NBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was used.<sup>[36]</sup> In contrast to smaller counterions such as  $[PF_6]^-$  or  $[C1]^-$ , the weakly coordinating  $[B(C_6F_5)_4]^-$  is known to stabilize highly charged species in solution and to minimize ion pairing effects.<sup>[36,50,64-66]</sup> The CV measurements were performed at 25 °C (4a,b, 7b, 8), -30 °C (6) or -72 °C (4b) as noted in Table 3 and the Figure legends. All potentials are referenced to the FcH/FcH<sup>+</sup> (FcH = Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>) redox couple as an internal standard.<sup>[36,46,64]</sup> The CV data of all complexes at a scan rate of 100 mV·s<sup>-1</sup> are summarized in Table 3 and Scheme 3.

The Ru<sup>III</sup> ion in the  $[RuCl_4(N \equiv CR)_2]^-$  part (= [A]<sup>-</sup>) of 4a,b displays an irreversible oxidation at 775 mV (4a) or 790 mV (4b) giving  $\{A\}$ , which is most likely caused by an *EC* (E =

electron transfer, C = chemical follow reaction) and / or ligand dissociation / association process as shown in Scheme 3. This could be confirmed by studying complex 7b for comparison (Figure S37, Supporting Information). As described by Duff and *Heath*,<sup>[34]</sup> species  $\{A\}$  is not stable under the applied measurement conditions and hence undergoes a ligand exchangecoupled disproportionation reaction, forming **B** and **C** respectively, (Scheme 3) with Ru in the oxidation states III or V. In a follow-up process, in situ formed B undergoes a reversible oxidation at 1250 mV (4a) or 1240 mV (4b), respectively (Figure 4), producing  $[\mathbf{B}]^+$  (Scheme 3).<sup>[34]</sup> In contrast to the above studies at ambient temperature (Figure 4), measurements at -72 °C showed an additional reduction process at 480 mV (Figure 5) (see above) which can be assigned to the backformation of  $[A]^-$  from B and  $[C]^{2-}$  prior to the reduction event  $E_1^{\circ}$  (Figure 5 and S33), since in the initial scan the seeming oxidation at 520 mV is not observed. The reduction at 480 mV is only observable after oxidation of  $[A]^-$  ( $E_4^{\circ'}$ ) occurred.

Multi-cyclic measurements on 4a,b revealed an additional reduction process at -420 (4a) or -350 mV (4b), which is only

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**Figure 4.** Cyclic voltammograms of **4a** and **4a** with one eq. of Fc\* (left), and **4b** and **4b** with one equiv. of Fc\* (right); scan rate 100 mV·s<sup>-1</sup> at glassy carbon electrode, 1.0 mmol·L<sup>-1</sup> solution in anhydrous dichloromethane; 0.1 mmo·L<sup>-1</sup> of  $[NnBu_4][B(C_6F_5)_4]$  as supporting electrolyte at 25 °C. Fc\* = Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>.



**Figure 5.** Cyclic voltammograms of **4b** as well as **4b** and FcH at low temperature; 1.0 mmol·L<sup>-1</sup> solution in anhydrous dichloromethane; 0.1 mmol·L<sup>-1</sup> of [NnBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as supporting electrolyte at -72 °C with (solid) and without (dashed) ferrocene as standard.

detected after traversing the previously irreversible oxidation process at 775 or 790 mV (Figure 4, Table 3). This process represents a reduction of **C** to  $[\mathbf{C}]^{2-}$  which then undergoes ligand exchange with **B** to give  $[\mathbf{A}]^-$  (Scheme 4). Furthermore, an irreversible reduction event is observed at -1070 (**4a**) and -980 mV (**4b**) becoming reversible at -72 °C. It can be assigned to the  $[\mathbf{A}]^-/[\mathbf{A}]^{2-}$  redox couple (Scheme 3, Figure 5).<sup>[33,34]</sup>

$$[\operatorname{Ru}^{||}\operatorname{Cl}_{5}(N \equiv \operatorname{CR})] \xrightarrow{+2 \text{ e}^{-}} [\operatorname{Ru}^{|||}\operatorname{Cl}_{5}(N \equiv \operatorname{CR})]^{2-}$$

$$C \qquad [C]^{2-} \qquad 4a, R = Me$$

$$4b, R = Ph$$

$$[\operatorname{Ru}^{|||}\operatorname{Cl}_{5}(N \equiv \operatorname{CR})]^{2-} + [\operatorname{Ru}^{|||}\operatorname{Cl}_{3}(N \equiv \operatorname{CR})_{3}] \xrightarrow{-} 2 [\operatorname{Ru}^{|||}\operatorname{Cl}_{4}(N \equiv \operatorname{CR})_{2}]^{-}$$

[C]<sup>2-</sup> B [A]<sup>-</sup>

Scheme 4. Postulated reaction pathways for the re-formation of [A]<sup>-</sup>.

This reversibility of the  $[A]^{-/}[A]^{2-}$  wave increases with the scan rate (Figures S31 and S32, Supporting Information).

Both,  $[\mathbf{A}]^{2-}$  and  $\{\mathbf{A}\}$  are prone to ligand exchange and dissociation reactions (see earlier). Hence, a Cl<sup>-</sup> dissociation follows the  $[\mathbf{A}]^{2-}$  formation as an *EC* process generating coordinatively unsaturated  $[\operatorname{RuCl}_3(\mathbb{N}\equiv \mathbb{CR})_2]^-$ , which can be oxidized at 490 mV (**4a**) or 525 mV (**4b**) (Figure 4, Scheme 3). To suppress Cl<sup>-</sup> dissociation,  $[\operatorname{NBu}_4]$ Cl (10 mmol·L<sup>-1</sup>) was added to the respective analyte solution while keeping the experimental conditions identical. As result thereof, the irreversible reduction event for  $[\mathbf{A}]^{-/}[\mathbf{A}]^{2-}$  remained, while additional waves appeared between -800 to 0 mV and 250–1000 mV due to ligand exchanges by Cl<sup>-</sup> (Figure S35, Supporting Information).

The cationic Ru<sup>II</sup> part [RuCl(N=CR)<sub>5</sub>]<sup>+</sup> of **4a**,**b** possesses a reversible Ru<sup>II</sup>/Ru<sup>III</sup> redox process  $(E_5^{\circ})$  at 1020 (**4a**) or 1080 mV (**4b**), respectively (Figure 4), which is in accordance with the values reported elsewhere.<sup>[33,34]</sup> These results agree well with the studies carried out on **8** (1070 mV).

Appropriate measurements in the presence of either FcH [Fc =  $Fe(\eta^5-C_5H_4)(\eta^5-C_5H_5)$ ] or Fc\* [=  $Fe(\eta^5-C_5Me_5)_2$ ], however, led to the appearance of an additional redox process at anodic potential ( $E_7^{\circ \circ}$ ), the assignment of which was not possible (Table 3). Similar observations were made for **B** in reference<sup>[32]</sup>.

When the measurement window is limited to 0–1500 mV in order to exclude the reduction of Fc\*+, then the peak currents, due to the irreversible oxidations of the corresponding species  $[A]^-$  at 775 mV (**4a**, **7b**) or 790 mV (**4b**), decrease in multicyclic experiments, while those of all other processes remain rather constant (Figure 6). These findings point to activities of the ferrocenium ion, interacting with the ruthenium species **B** and **C**/[**C**]<sup>2–</sup> formed after oxidation (Scheme 3 and Scheme 4).<sup>[32]</sup> An alternative hypothesis is the reaction between the ferrocenium ion and  $[A]^-$ , leading to {**A**}, while the electro-generated Fc\* is continuously being regenerated at the working electrode. Due to the irreversible nature of this oxidation, {**A**} reacts to give **B** and **C** (see Scheme 3). Both factors drag the equilibrium towards **B** and **C** and therefore deplete the solution in the vicinity of the working electrode, causing

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**Figure 6.** Multi-cyclic cyclo voltammograms of **4b** with one equiv. of Fc\* from 0 to 1500 mV vs. FcH/FcH<sup>+</sup> (left) and -800 to 1500 mV vs. FcH/FcH<sup>+</sup> (right); scan rate 100 mV·s<sup>-1</sup> at a glassy carbon electrode, 1.0 mmol·L<sup>-1</sup> solution in anhydrous dichloromethane; 0.1 mmol·L<sup>-1</sup> of  $[NnBu_4][B(C_6F_5)_4]$  as supporting electrolyte at 25 °C.

the wave at 775 mV (4a, 7b) or 790 mV (4b) to disappear (Figure 6).

Studies at -72 °C led to a shift of the observed events to higher potentials (Figure 5). The previously observed wave at 1330 mV (**4b**) disappears, though it is either likely that it shifted outside of the measurement window or the subsequent species were not formed at low temperature.

Since **4a** is not soluble in acetonitrile and acetonitriledichloromethane mixtures (see earlier), further measurements were carried out with **4b** only. Concerning the influence of additional nitrile molecules on the reactivity of **4b**, studies with additional 5 vol-% of benzonitrile were performed at 25 °C to confirm the assumptions about this particular redox behavior (Figure 7). Within these studies, only an oxidation wave at 810 mV and a redox process at 1080 mV were found in the first CV cycle. In multi-cyclic experiments the process at 810 mV occurred with smaller current at 780 mV and an associated reduction at 750 mV. A new reversible event appeared at 405 mV (Figure 7), while the redox process at 1080 mV remains unchanged. In the potential window shown in Figure 7, the {A}/[A]<sup>-</sup> redox couple is in equilibrium with the disproportionation products **B** and **C** of {A} (Scheme 3).

In contrast to earlier studies without additional benzonitrile, following the irreversible reduction at  $-980 \text{ mV} ([\mathbf{A}]^{-/}[\mathbf{A}]^{2-})$  (Figure 8), an additional irreversible oxidation at -300 mV occurs and now no longer a reversible reduction at 400 mV can be seen. These two additional processes at more cathodic potentials compared to  $[\mathbf{A}]^{-/}[\mathbf{A}]^{2-}$  are related to the  $[\operatorname{RuCl}_3(\mathbf{N} \equiv \operatorname{CPh})_3]^{-/0}$  redox couple and further variations of  $[\operatorname{RuCl}_x(\mathbf{N} \equiv \operatorname{CPh})_y]$  ( $x = 6 - y; y = 0, 1, 2, \ldots, 6$ ), since additional benzonitrile is available for ligand exchange reactions.<sup>[33,34,67,68]</sup> Ferrocene containing analytes led to the disappearance of the event at 400 mV (Figure 8). Further measurements with higher concentrations of benzonitrile showed no additional influence to the redox behavior.

For complex **6** a reversible redox event was found (Figure S36, Supporting Information), which is characteristic for this type of compound.<sup>[33,34]</sup> However, the respective potentials differ, due to altered measurement conditions (320 mV at



**Figure 7.** Cyclic voltammogram of **4b** at 25 °C from 0 to 1400 mV vs. FcH/FcH<sup>+</sup>; 100 mV·s<sup>-1</sup> at a glassy carbon electrode, 1.0 mmol·L<sup>-1</sup> solution in anhydrous 5 vol-% benzonitrile/dichloromethane; 0.1 mmol·L<sup>-1</sup> of  $[NnBu_4][B(C_6F_5)_4]$  as supporting electrolyte.



**Figure 8.** Cyclic voltammograms of **4b** (dashed line) and **4b** with added FcH (solid line) at 25 °C, 100 mV·s<sup>-1</sup> at a glassy carbon electrode, 1.0 mmol·L<sup>-1</sup> solution in anhydrous 5 vol-% benzonitrile / dichloromethane; 0.1 mmol·L<sup>-1</sup> of  $[NnBu_4][B(C_6F_5)_4]$  as supporting electrolyte.

-30 °C and [NBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as supporting electrolyte (this work); 450 mV, -70 °C, [NBu<sub>4</sub>]BF<sub>4</sub>). However, no related re-

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dox behavior to the previously described compounds could be observed and therefore it is unlikely that 6 was generated in any chemical reaction following oxidation or reduction of 4a,b.

In order to analyze the in situ electrochemical behavior of **4a,b**, spectroelectro-IR measurements were carried out using an OTTLE<sup>[51]</sup> (Optically Transparent Thin-Layer Electrochemical) cell with CaF<sub>2</sub> windows, dichloromethane solutions of the analyte and Fc\*-containing mixtures (5.0 mmol·L<sup>-1</sup>), containing [NBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.1 mol·L<sup>-1</sup>) as supporting electrolyte.<sup>[51,66]</sup> During the measurements, the applied cell potential was increased stepwise (step width: 25 mV, 50 mV or 100 mV).

Neutral **4b** shows a v(N=C) absorption at 2255 cm<sup>-1</sup> for  $[RuCl(N \equiv CPh)_5]^+$  and at 2264 cm<sup>-1</sup> for  $[RuCl_4(N \equiv CPh)_2]^-$ ([A]<sup>-</sup>, Scheme 3, Table 4). On decreasing the potential to -1400 mV, a strong v(C=N) band at 2231 cm<sup>-1</sup> appears (Figure 9a) related to mer-[RuCl<sub>3</sub>(N=CPh)<sub>3</sub>]<sup>-</sup> ([**B**]<sup>-</sup>),<sup>[34]</sup> while a shoulder at 2255 cm<sup>-1</sup> remains for [RuCl(N≡CPh)<sub>5</sub>]<sup>+</sup>, confirming the EC mechanism observed in the CV experiments (Figure 4, Scheme 3). In this regard,  $[B]^-$  is electro-generated as an intermediate species which follows the  $[A]^{2-}$  formation as an EC process, generating coordinatively unsaturated  $[RuCl_3(N \equiv CPh)_2]^-$ , which is able to coordinate nearby nitriles and is additionally unstable under the conditions applied.<sup>[34]</sup> Upon oxidation afterwards to 900 mV, the former vibration decreases in intensity (Figure 9b), while the one at 2264 cm<sup>-1</sup> returns to its original form  $([A]^-)$  (vide supra). Further oxidation from 900 to 1800 mV results in the appearance of a strong, superimposing v(C=N) absorption at 2274 cm<sup>-1</sup>  $([RuCl_5(N \equiv CPh)])$ ,<sup>[37]</sup> leaving the vibration at 2231 cm<sup>-1</sup> as a shoulder (Figure 9d).

Table 4. In situ spectroelectrochemical IR studies of 4b.<sup>a)</sup>.

Potential/ mV vs. Ag/AgCl (vs. FcH/FcH <sup>+</sup> )	Compound	$v /cm^{-1}$ [ $v(C \equiv N)$ ]
Without potential	$[\operatorname{RuCl}_4(N \equiv \operatorname{CPh})_2]^- ([\mathbf{A}]^-)$ $[\operatorname{RuCl}(N \equiv \operatorname{CPh})_5]^+$	2264 (m)
		2255 (m)
0 to -300	$[\operatorname{RuCl}_4(N \equiv \operatorname{CPh})_2]^- ([\mathbf{A}]^-)$ $[\operatorname{RuCl}(N \equiv \operatorname{CPh})_5]^+$	2264 (m)
(-250 to -550)		2255 (m)
-800 to -1400-0	$[RuCl(N \equiv CPh)_5]^+$	2255 (m)
(-1050 to -1650 to -250)	$[RuCl_3(N \equiv CPh)_3]^- ([\mathbf{B}]^-)$	2231 (s)
700–900	$[\operatorname{RuCl}_4(N \equiv \operatorname{CPh})_2]^- ([\mathbf{A}]^-) / [\operatorname{RuCl}_3(N \equiv \operatorname{CPh})_3] (\mathbf{B})$	2262 (m)
(450-650)	$[RuCl(N \equiv CPh)_5]^+$	
	$[RuCl_3(N \equiv CPh)_3] (\mathbf{B})$	2255 (m) 2231 (m)
1600-1800	$[RuCl_5(N \equiv CPh)]^{[37]}$	2274 (vs)
(1350–1550)	$[RuCl_3(N \equiv CPh)_3] (\mathbf{B})$	2231 (w, sh

a) 5.0 mmol·L<sup>-1</sup> solution in anhydrous dichloromethane; 0.1 mol·L<sup>-1</sup> of  $[NnBu_4][B(C_6F_5)_4]$  as supporting electrolyte at 25 °C (vs = very strong, s = strong, m = medium, w = weak, sh = shoulder).

In contrast to the previous experiments, solely oxidizing **4b** from 0 to 1800 mV (Figure S43, Supporting Information) resulted in fewer changes in the IR spectra, which is in accordance with the results from electrochemical studies.<sup>[37]</sup>



**Figure 9.** IR spectra of **4b** with 1 equiv. of Fc\* at (a) -100 mV to -1400 mV, (b) -1400 mV to 900 mV, (c) 900 mV to 1475 mV, and (d) 1475 mV to 1800 mV vs. Ag/AgCl in an OTTLE cell; measurement conditions: 25 °C, 5.0 mmol·L<sup>-1</sup> analyte solution in dichloromethane, 0.1 mol·L<sup>-1</sup> of [NnBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], arrows indicate absorption changes.

Complex **4a** shows a similar behavior in its vibrational properties (Figure S40, Table S3, Supporting Information).

UV/Vis spectroscopy allows to distinguish between  $[\operatorname{RuCl}_x(N \equiv \operatorname{CPh})_y]$  (x = 6 - y; y = 0, 1, 2, ..., 6) species. Hence, additional in situ spectroelectrochemical UV/Vis/NIR measurements for **4b** have been carried out within an OTTLE cell with SiO<sub>2</sub> windows under identical conditions.

For  $[RuCl(N \equiv CPh)_5]^+$  and  $[RuCl_4(N \equiv CPh)_2]^-$  ([A]<sup>-</sup>) the respective absorptions were observed when no potential was applied.<sup>[33,34,37,69]</sup> Change to higher anodic potentials led to a decrease of the bands at 311, 408 (shifted from 410 nm vs. neat solvent) and 422 nm related to [A]<sup>-</sup> (Scheme 3), and at the same time the absorptions at 277 and 284 nm, characteristic for **B**, increased (Figure 10a, Table 3).<sup>[33,34]</sup> Additionally, a transition at 380 to 500 nm can be seen for either  $[RuCl_5(N \equiv CPh)]^-$  ([C]<sup>-</sup>) or  $[RuCl_6]^{2-[33,34,67,68]}$ . Shifting to more anodic potentials led to an intensity decrease of the band at 298 nm and an increase of the absorption at 490 nm (Figure 10b), belonging to the oxidation of  $[RuCl(N \equiv CPh)_5]^+$  to  $[RuCl(N \equiv CPh)_5]^{2+,[33,34]}$  These findings are consistent with the mechanism discussed earlier (Scheme 3 and Scheme 4), showing the formation of **B** after the oxidation of  $[A]^-$ , confirming the stability of  $[RuCl(N \equiv CPh)_5]^{2+}$ .

Upon decreasing the potential to -500 mV the absorptions at 408 and 422 nm ([RuCl<sub>4</sub>(N≡CPh)<sub>2</sub>]<sup>-</sup>) vanished, while the extinction coefficient of the shoulder at 370 nm increased (Figure 11a). Due to the width of the resulting absorption no specific assignment to particular species was possible. A corresponding effect was observed for [**B**]<sup>-</sup>, when the potential was further decreased (Table 5). However, a potential increase to 800 mV after this reduction makes the aforementioned absorption to disappear. The transitions at 270 and 280 nm increased, corresponding to the oxidation of [**B**]<sup>-</sup> to its neutral form (**B**).

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**Figure 10.** UV/Vis/NIR spectra of **4b** at (a) 0 mV to 1300 mV and (b) 1300 mV to 1550 mV vs. Ag/AgCl in an OTTLE cell; measurement conditions: 25 °C, 1.0 mmol·L<sup>-1</sup> analyte solution in dichloromethane, 0.1 mol·L<sup>-1</sup> [NnBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], arrows indicate absorption changes.



**Figure 11.** UV/Vis/NIR spectra of **4b** at (a) 0 mV to -500 mV, (b) -500 mV to -1400 mV, (c) -1400 mV to 800 mV, (d) 800 mV to 1300 mV, and (e) 1300 mV to 1750 mV vs. Ag/AgCl in an OTTLE cell; measurement conditions:  $25 \,^{\circ}$ C,  $1.0 \,\text{mmol}\cdot\text{L}^{-1}$  analyte solution in dichloromethane,  $0.1 \,\text{mol}\cdot\text{L}^{-1}$  of  $[NnBu_4][B(C_6F_5)_4]$ , arrows indicate absorption changes.

Increasing the potential further to 1750 mV led to oxidation of  $[RuCl(N \equiv CPh)_5]^+$  by forming  $[RuCl(N \equiv CPh)_5]^{2+}$ , which possesses a characteristic band at 490 nm. These results are in agreement with observations made by in situ IR spectroscopy.

## **4** Conclusions

The synthesis and characterization of the titanium oxo cluster  $[Ti_6O_4(OiPr)_8(O_2CPh)_8]$  (3), as well as the ruthenium complexes  $[RuCl(N\equiv CR)_5][RuCl_4(N\equiv CR)_2]$  (4a, R = Me; 4b, Ph), *trans*- $[RuCl_2(N\equiv CPh)_4]$  (6), *trans*- $[H_3O][RuCl_4(N\equiv CMe)_2]$  (7a) and  $[RuCl(N\equiv CPh)_5][PF_6]$  (8) is discussed. In the synthesis of 4b also complex  $[Ru(N\equiv CPh)_6][RuCl_4(N\equiv CPh)_2]$  (5) was formed in minor yields, which by ligand exchange reactions

gave 6. Single-crystal X-ray structure determinations of 3, 4a,b, 5, 6 and 7a were carried out of which 4b forms a 3D network, while 6 extends a 2D structure by  $\pi$  interactions between benzonitrile ligands. The (spectro)electrochemical behavior of 4a,b was determined by CV, SWV, in situ IR and UV/Vis/NIR studies and compared with 7b (*trans*-[NEt<sub>4</sub>][RuCl<sub>4</sub>(N=CMe)<sub>2</sub>])<sup>[37]</sup> and 8. It could be shown that the electrochemical response of 4a,b is analogous to that of their ionic counter-parts [RuCl(N=CR)<sub>5</sub>]<sup>+</sup> and [RuCl<sub>4</sub>(N=CR)<sub>2</sub>]<sup>-</sup> ([A]<sup>-</sup>) and that the combination of both still show their respective redox processes. Hence, electron transfer does not occur between the corresponding species. Cationic [RuCl(N=CR)<sub>5</sub>]<sup>+</sup> displays a reversible one-electron reaction, while [A]<sup>-</sup> engages in a ligand exchange-based equilibrium in solution that unZeitschrift für anorganische

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Potential/mV vs. Ag/AgCl (vs. FcH/	Compound [34]	Origin of transi- tion [33,34]	$\lambda$ /nm ( $\varepsilon_{max}$ / L·mol <sup>-1</sup> ·cm <sup>-1</sup> )
FcH <sup>+</sup> )			
-500 to -1400	$[\operatorname{RuCl}_3(N \equiv \operatorname{CPh})_3]^-$ $([\mathbf{B}]^-)$	Ru <sup>II</sup> →PhC≡N MLCT	380 (sh)
(-750 to -1650)	$[RuCl(N=CPh)_5]^+$	Ru <sup>II</sup> →PhC≡N MLCT	315 (5300)
-250 to 250	$[RuCl_4(N \equiv CPh)_2]^-$ $([A]^-)$	d–d	488(900)
(-500 to 0)	$[RuCl_4(N \equiv CPh)_2]^-$	d–d	422 (9400)
	$[RuCl_4(N \equiv CPh)_2]^-$	Cl→Ru <sup>III</sup> LMCT	408(9400) b)
	$RuCl(N=CPh)_5]^+$	Ru <sup>II</sup> →PhC≡N MLCT	305(92700)
250-1300	$[RuCl_5(N \equiv CPh)]$ $([C]^{-}) /$ $[RuCl_3(N \equiv CPh)_3]$ $(B)$		380 to 500 nm
(0–1050)	$RuCl(N \equiv CPh)_5]^+$	Cl→Ru <sup>III</sup> LMCT	(5700)
	$[RuCl_3(N \equiv CPh)_3]$ ( <b>B</b> )	Ru <sup>II</sup> →PhC≡N MLCT	298 (92000)
	$[RuCl_3(N \equiv CPh)_3]$ (B)		284(sh)
1300–1550	$[RuCl(N=CPh)_5]^{2+}$	Cl→Ru <sup>III</sup>	277(sh) 490(10300)
(1200–1200)	$[\operatorname{RuCl}_3(N \equiv \operatorname{CPh})_3]$	LMCT $Ru^{III} \rightarrow PhC \equiv N$ MICT	283 (sh)
	$[RuCl_3(N \equiv CPh)_3]$ (B)	$Ru^{III} \rightarrow PhC \equiv N$ MLCT	277(sh)

 Table 5. Spectroelectrochemical UV/Vis/NIR data of 4b under different in situ applied potentials.<sup>a)</sup>.

a) 1.0 mmol·L<sup>-1</sup> solution in anhydrous dichloromethane; 0.1 mol·L<sup>-1</sup> of  $[NnBu_4][B(C_6F_5)_4]$  as supporting electrolyte at 25 °C. Molar extinction coefficients in brackets (sh = shoulder). b) Shifted from 410 nm vs. neat compound.

dergoes a variety of various ligand exchange and disproportionation reactions at ambient temperatures under oxidative and reductive conditions, generating intermediary species  $\{[RuCl_4(N \equiv CR)_2]\}$ ({**A**}) and reduced complex  $[RuCl_4(N \equiv CR)_2]^{2-}$  ([A]<sup>2-</sup>). Further experiments allowed additional insight into the decomposition pathway and the identification of the resulting products  $[RuCl_3(N \equiv CR)_3]^-$  ([**B**]<sup>-</sup>),  $[RuCl_3(N \equiv CR)_3]$  (B) and  $[RuCl_5(N \equiv CR)]$  (C). At a temperature of -72 °C and at increased sweep rates the  $[A]^{-}/[A]^{2-}$  couple became chemically reversible, confirming the suppression of side reactions of the redox pairs  $([A]^{-}/{A})$  and  $([A]^{2-}/[A]^{-}$ ), thus decreasing the formation of the resulting decomposition products [B]<sup>-</sup> and B. Spectroelectrochemical measurements in the infrared and UV/Vis/NIR region additionally allowed approving the aforementioned proposed mechanism.

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