Structural Characterization of Cationic 16-Electron Pentamethylcyclopentadienyl Ruthenium(II) Complexes Containing the Binuclear [Cp*Ru(μ-Cl)$_3$RuCp*]$^-$ Anion

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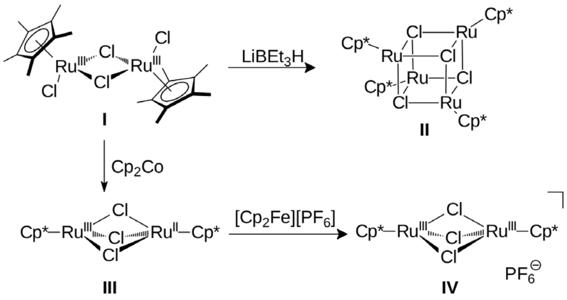
The reaction of the diimine ligand 1,2-bis(1,3-diisopropyl-4,5-dimethylimidazolin-2-imino)ethane (BL$^{i\mathrm{Pr}}$) with tetrameric [Cp*RuCl]$_4$ in a 1 : 0.75 ratio afforded the complex salt [**1**][**2**] containing the 16-electron half-sandwich cation [Cp*Ru(BL$^{i\mathrm{Pr}}$)]$^+$ (**1**) and the dinuclear anion [Cp*Ru(μ-Cl)$_3$RuCp*]$^-$ (**2**). The X-ray crystal structures of [**1**][**2**]·3½THF (monoclinic, space group $P2_1/n$, Z = 4) and of [**1**][**2**]·THF (monoclinic, space group $C2/m$, Z = 4) are reported, allowing the structural characterization of the unprecedented anion **2**, in which two [(η^5-C$_5$Me$_5$)Ru(II)] moieties are bridged by three μ_2-chlorine atoms.

Key words: Binuclear Complexes, Ruthenium, Cyclopentadienyl Ligands, 16-Electron Complexes, Coordinative Unsaturation

Introduction



Scheme 1.

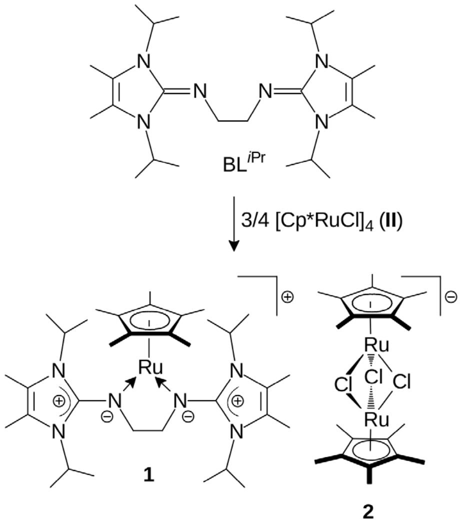
Binuclear chloro-bridged ruthenium complexes containing η^5-cyclopentadienyl ligands represent the most common precursors for the preparation of ruthenium half-sandwich complexes [1], and the accessibility and versatile reactivity of complexes such as [Cp*RuCl(μ-Cl)]$_2$ (**I**) have been responsible for the extensive use of these systems as precatalysts for a large number of organic transformations (Scheme 1) [2]. This Ru(III)-Ru(III) complex contains two terminal and two bridging chlorine atoms and exhibits an interesting bond-stretch or deformation isomerism with two distinctly different Ru–Ru separations in the solid state [3]. Complete reduction from Ru(III) to Ru(II) can be achieved in various ways, for instance with super hydride Li[BEt$_3$H], leading to a collapse of the dimeric structure and to the formation of the tetrameric Ru(II) complex [Cp*Ru(μ_3-Cl)]$_4$ (**II**) [4], which exhibits a distorted heterocubane structure [4, 5]. Stepwise reduction of [Cp*RuCl(μ-Cl)]$_2$ was also studied, and it has been reported that the mixed valence dimer [Cp*Ru(μ-Cl)$_3$RuCp*] (**III**) with three bridging chlorine atoms is formed electrochemically or by reaction with one equivalent of cobaltocene, Cp$_2$Co [6, 7]. Comproportionation between **I** and 0.5 eq. of **II** represents an alternative method for the preparation of **III**. Reoxidation of **III** with ferrocenium hexafluorophosphate, [Cp$_2$Fe][PF$_6$], affords complex **IV**, presumably containing the Ru(III)-Ru(III) cation [Cp*Ru(μ-Cl)$_3$RuCp*]$^+$. The corresponding Ru(II)-Ru(II) anion [Cp*Ru(μ-Cl)$_3$RuCp*]$^-$ (**2**), however, has been elusive and was reported to be unstable towards loss of one chloride ligand and subsequent oligomerization [7]. In addition, it should be emphasized that there are no single crystal X-ray structure data available for any [Cp*Ru(μ-X)$_3$RuCp*]^n system (n = +1, 0, −1, X = halide), which is quite surprising in view of the large number of structures reported for related [(η^6-arene)Ru(μ-Cl)$_3$Ru(η^6-arene)]$^+$ or [Cp*M(μ-Cl)$_3$MCp*]$^+$ systems (M = Rh, Ir) [8, 9].

Moreover, several heterobimetallic complexes of the type [Cp*Ru(μ-X)$_3$ML] (LM = η^6-arene-Ru, Cp*Rh, Cp*Ir) have been structurally characterized [10].

Recently, we have reported the isolation of very stable cationic 16-electron ruthenium complexes such as [Cp*Ru(BL$^{i\mathrm{Pr}}$)]$^+$ (**1**) containing the neutral 1,2-bis-(imidazolin-2-imino)ethane ligand BL$^{i\mathrm{Pr}}$ [11]. The reaction of BL$^{i\mathrm{Pr}}$ with 0.25 eq. of tetrameric **II** cleanly afforded [Cp*Ru(BL$^{i\mathrm{Pr}}$)]Cl, [**1**]Cl, in which the ruthenium atom resists coordination by the chloride counterion. This unusual stability can be ascribed to the strong π-basic nature of the bis(imidazoline) ligand, in which the ability of the imidazolium moiety to stabilize a positive charge leads to highly basic ligands with a high electron-donating capacity [11 – 13]. Consequently, the Ru atom exhibits a weak propensity to coordinate other π-donor ligands such as chloride, whereas strong binding of σ-donor/π-acceptor ligands such as CO or isocyanides can be observed [11]. In this contribution, we wish to report that the reaction of BL$^{i\mathrm{Pr}}$ with **II** in a 1 : 0.75 ratio (or in a 1 : 3 ligand-to-metal ratio, respectively) affords the complex salt [**1**][**2**], which contains the previously unknown anion [Cp*Ru(μ-Cl)$_3$RuCp*]$^-$ (**2**) with the coordinatively unsaturated 16-electron ruthenium complex **1** acting as the counterion.

Results and Discussion

The formation and precipitation of the complex salt [**1**][**2**] was initially observed from THF solutions containing the chloride salt [**1**]Cl, which had been left in the glove box at r. t. for a prolonged time in order to grow single crystals by hexane diffusion. The ^{1}H NMR spectrum of the crystalline material in [D$_6$]acetone showed resonances that are in full agreement with the presence of the cation **1** [11]. In addition to the Cp* resonance of **1** at 1.35 ppm, a singlet at 1.34 ppm with double intensity was observed, which can be assigned to the Cp* hydrogen atoms of the anion **2**. The formation of [**1**][**2**] must be accompanied by the release of two equivalents of the free diimine ligand, and NMR spectroscopic analysis of the supernatant solution confirmed the presence of BL$^{i\mathrm{Pr}}$. Apparently, the driving force for the decomposition of [**1**]Cl is based on the tendency of the free chloride ion to seek coordination, which is achieved by ligand substitution and combination of one Cl$^-$ and two [Cp*RuCl] moieties to furnish the anion **2**.



Scheme 2.

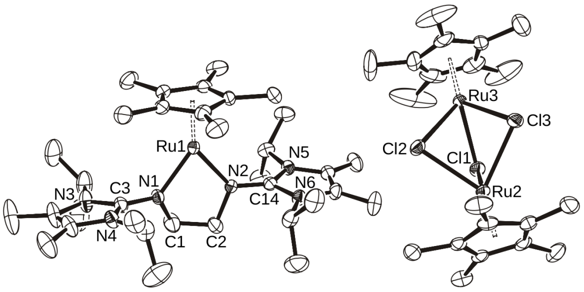


Fig. 1. ORTEP diagram of the cation **1** (left) and of the anion **2** (right) in the asymmetric unit of [**1**][**2**]·3½THF with displacement parameters drawn at the 50 % probability level.

Changing the stoichiometry between BL$^{i\mathrm{Pr}}$ and [Cp*Ru(μ_3-Cl)]$_4$ (**II**) from 1 : 0.25 to 1 : 0.75 allowed direct access to [**1**][**2**], which could be isolated as a red crystalline solid in high yield (Scheme 2). Recrystallization by diffusion of hexane into a THF solution afforded single crystals suitable for X-ray diffraction analysis. [**1**][**2**]·3½THF crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit containing the molecules **1** and **2** is shown in Fig. 1. The cationic half-sandwich complex **1** exhibits a two-legged piano stool geometry with the Cp* and the diimine ligands adopting a slightly distorted pseudo trigonal-planar coordination sphere around the ruthenium atom. The Ct–Ru1–N1–N2 torsion angle (Ct = centroid of the Cp* ring) is 177.9°, and the sum of the N1–Ru1–N2 angle [77.8(1)°] and the two Ct–Ru1–N angles is 360.0°. In accordance with the strong binding ability of the BL$^{i\mathrm{Pr}}$ ligand, short Ru1–N distances of 2.081(3) and 2.066(2) Å are observed (Table 1). The Ru1 atom does not exhibit intramolecular C–H···Ru contacts as

Table 1. Selected bond lengths (Å) and angles (deg) for [**1**][**2**]·3$^1/_2$THF and [**1**][**2**]·THF with estimated standard deviations in parentheses.

[**1**][**2**]·3$^1/_2$THF		[**1**][**2**]·THF[a]	
Ru1-N1	2.081(3)	Ru1-N1	2.066(2)
Ru1-N2	2.066(2)	Ru1-N1a	2.066(2)
Ru1-C(Cp*)	2.111(3) - 2.152(3)	Ru1-C(Cp*)	2.110(4) - 2.148(3)
Ru2-Cl1	2.5100(8)	Ru2-Cl1	2.4891(6)
Ru2-Cl2	2.5344(8)	Ru2-Cl2	2.5318(7)
Ru2-Cl3	2.5075(8)	Ru2-Cl1a	2.5005(6)
Ru3-Cl1	2.5185(8)		
Ru3-Cl2	2.5277(8)		
Ru3-Cl3	2.5025(8)		
Ru2-C(Cp*)	2.096(3) - 2.118(3)	Ru2-C(Cp*)	2.097(2) - 2.110(2)
Ru3-C(Cp*)	2.088(3) - 2.114(4)		
N1-C3	1.348(4)	N1-C2	1.353(3)
N2-C14	1.353(4)		
N1-Ru1-N2	77.77(10)	N1-Ru1-N1a	76.92(11)
Ru2-Cl1-Ru3	83.74(3)	Ru2-Cl1-Ru2a	84.73(2)
Ru2-Cl2-Ru3	83.06(2)	Ru2-Cl2-Ru2a	83.21(3)
Ru2-Cl3-Ru3	84.12(3)		
Cl1-Ru2-Cl2	79.19(3)	Cl1-Ru2-Cl2	79.86(2)
Cl1-Ru2-Cl3	81.58(3)	Cl1a-Ru2-Cl2	79.64(2)
Cl2-Ru2-Cl3	80.28(3)	Cl1-Ru2-Cl1a	80.33(3)
Cl1-Ru3-Cl2	79.16(3)		
Cl1-Ru3-Cl3	81.51(3)		
Cl2-Ru3-Cl3	80.51(3)		

[a] The label a refers to symmetry-equivalent atoms; the cation has mirror symmetry, and the anion has twofold symmetry; for symmetry operations see Fig. 2.

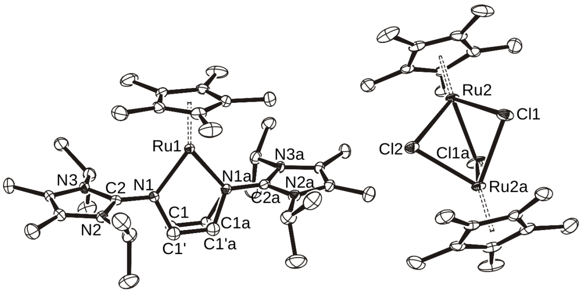


Fig. 2. ORTEP diagram of the cation **1** (left) and of the anion **2** (right) in [**1**][**2**]·THF with displacement parameters at the 50 % probability level. The ethylene bridge and the THF molecule (not shown) are disordered. Symmetry operations to equivalent positions a: cation x, $1-y$, z; anion $-x$, y, $1-z$.

observed for the triflate salt [**1**]OTf [11], and any intermolecular interactions between the cation and anion can also be excluded, since the shortest Ru–Cl distance is 7.82 Å.

The anion $[\mathrm{Cp^*Ru}(\mu\text{-Cl})_3\mathrm{RuCp^*}]^-$ (**2**) consists of two $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(II)}]$ moieties that are bridged by three μ_2-chlorine atoms. Both metal atoms are in a pseudotetrahedral environment, and the structure can thus be regarded as being composed of two face-sharing $\mathrm{Cp^*RuCl_3}$ tetrahedra. The Cp* rings adopt a mutually eclipsed conformation, rendering the ion almost $C_{2\mathrm{v}}$ symmetric. The Ru–Cl distances range from 2.5075(8) to 2.5344(8) Å for Ru2 and from 2.5025(8) to 2.5277(8) Å for Ru3 (Table 1), which is as expected longer than observed for the bridging chlorine atoms in Ru(III) complexes such as $[\mathrm{Cp^*RuCl}(\mu\text{-Cl})]_2$ (**I**) [3], but falls in the range reported for the corresponding bond lengths in the Ru(II) cluster $[\mathrm{Cp^*Ru}(\mu_3\text{-Cl})]_4$ (**II**) [4, 5] and in the binuclear complex $[\mathrm{Cp^*Ru}(\mu\text{-Cl})_3\mathrm{Ru}(p\text{-cymene})]$ [10]. The Ru2–Ru3 separation is 3.36 Å, precluding any direct metal-metal interaction.

Cooling of a THF/hexane solution of [**1**][**2**] to −20 °C afforded single crystals of a different solvate [**1**][**2**]·THF, which crystallizes in the monoclinic space group $C2/m$. The cation **1** and the anion **2** are located around the special positions x, $^1/_2$, z and 0, y, $^1/_2$ of the monoclinic unit cell and display crystallographic mirror symmetry (**1**) or C_2 symmetry (**2**), respectively; the actual symmetry of the anion is again close to $C_{2\mathrm{v}}$. An ORTEP presentation of **1** and **2** in [**1**][**2**]·THF is shown in Fig. 2, and Table 1 assembles selected bond lengths and angles. The structural parameters are very similar to those discussed above for the solid state structure of [**1**][**2**]·3$^1/_2$THF. Interaction of the Ru1 atom in the cationic 16-electron complex **1** with the anion **2** or with the THF solvate molecule can be excluded, since the shortest Ru–O and Ru–Cl separations are 5.22 and 7.87 Å, respectively. The distance between the Ru atoms in **2** (Ru2–Ru2a = 3.36 Å) is identical with that in [**1**][**2**]·3$^1/_2$THF.

Conclusion

The structural characterization of [**1**][**2**]·3$^1/_2$THF and [**1**][**2**]·THF reveals that the previously unknown anion $[\mathrm{Cp^*Ru}(\mu\text{-Cl})_3\mathrm{RuCp^*}]^-$ (**2**) can be isolated in the presence of an appropriate counterion and stabilized towards decomposition, which presumably proceeds *via* loss of chloride and formation of the tetrameric complex $[\mathrm{Cp^*Ru}(\mu_3\text{-Cl})]_4$ (**II**). Because of the strong electron-donating capability of the diimine ligand $\mathrm{BL}^{i\mathrm{Pr}}$, the 16-electron complex $[\mathrm{Cp^*Ru}(\mathrm{BL}^{i\mathrm{Pr}})]^+$ (**1**) exhibits a weak propensity to coordinate additional ligands such as Cl^- and is therefore able to stabilize **2** by exhibiting the properties of a weakly coordinating counterion [14].

Experimental Section

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. All solvents

Table 2. Crystal structure data for [**1**][**2**]·3½THF and [**1**][**2**]·THF.

	[**1**][**2**]·3½THF	[**1**][**2**]·THF
Formula	$C_{68}H_{117}Cl_3N_6O_{3.5}Ru_3$	$C_{58}H_{97}Cl_3N_6ORu_3$
M_r	1484.24	1303.98
Cryst. size, mm^3	$0.27 \times 0.23 \times 0.18$	$0.25 \times 0.12 \times 0.08$
Temperature, K	133	100
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/m$
a, Å	10.6250(6)	21.4028(16)
b, Å	34.8157(19)	31.401(2)
c, Å	19.0801(11)	10.5344(8)
β, deg	90.7170(10)	117.170(4)
V, Å^3	7057.5(7)	6298.5(8)
Z	4	4
$D_{\text{calcd.}}$, g cm^{-3}	1.397	1.375
μ(MoK_α), cm^{-1}	0.796	0.878
F(000), e	2552	2712
hkl range	±15, ±49, ±27	±32, ±47, ±15
2θ(max), deg	61	65
Refl. measured	150609	145853
Refl. unique	21595	11641
R_{int}	0.0739	0.0564
Param. refined	662	361
$R(F)$/ $wR(F^2)$[a] (all refls.)	0.077/ 0.121	0.058/ 0.099
GoF (F^2)[b]	1.044	1.120
$\Delta\rho_{\text{fin}}$(max/min), e Å^{-3}	1.27/−1.31	1.75/−0.94

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\} / \Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [F_o^2 + 2F_c^2]/3$; *a* and *b* are constants selected by the refinement program. [b] $\text{GoF} = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n-p)]^{0.5}$ with *n* data and *p* parameters.

were purified by standard methods and distilled prior to use. ^{1}H NMR spectra were recorded on a Bruker DPX 200 instrument. Elemental analysis (C, H, N) was performed on an Elementar Vario EL III CHNS elemental analyzer. The ligand BL$^{i\text{Pr}}$ [11] and the ruthenium heterocubane $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ [4] were prepared according to literature procedures.

*Preparation of [Cp*Ru(BL$^{i\text{Pr}}$)][Cp*Ru(μ-Cl)$_3$RuCp*], [1][2]*

The title compound was prepared by the reaction of 1,2-bis(1,3-diisopropyl-4,5-dimethylimidazolin-2-imine)ethane (BL$^{i\text{Pr}}$) (51.2 mg, 0.123 mmol) with $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ (100 mg, 0.092 mmol) in THF (10 mL). After stirring the mixture for 48 h at ambient temperature, the product was precipitated with an excess of *n*-hexane, filtered off and washed several times with *n*-hexane. Drying in high vacuum afforded 133 mg of a red solid (yield 81 %). – ^{1}H NMR (600 MHz, [D$_6$]acetone): δ = 5.26 (sept, 4H, $NCHCH_3$), 2.59 (s, 4H, CH_2CH_2), 2.40 (s, 12H, CCH_3), 1.80 (d, 12H, $NCHCH_3$), 1.48 (s, 15H, Cp*-CH_3 cation), 1.47 (s, 30H, Cp*-CH_3 anion), 1.43 (d, 12H, $NCHCH_3$). – Elemental analysis for $[C_{20}H_{30}Ru_2Cl_3][C_{34}H_{59}N_6Ru]$: calcd. C 52.65, H 7.28, N 6.82; found C 52.83, H 7.35, N 6.68.

Crystals of [**1**][**2**]·3½THF could be obtained as dark red prisms by diffusion of *n*-hexane into a tetrahydrofuran solution. Crystals of [**1**][**2**]·THF were also isolated as dark red prisms by diffusion of *n*-hexane into a tetrahydrofuran solution at −20 °C.

X-Ray structure determinations

Data were measured using MoK_α radiation (λ = 0.71073 Å) on a Bruker SMART 1000 CCD diffractometer for [**1**][**2**]·3½THF and on a Bruker APEX2 diffractometer for [**1**][**2**]·THF. Absorption corrections were applied on the basis of multi-scans. The structures were subjected to full-matrix least-squares refinement on F^2 (SHELXL-97 [15]). All non-hydrogen atoms were refined anisotropically. H atoms were included using a riding model. See Table 2 for crystallographic data. Special features: The THF molecules of the 3½-solvate were badly disordered (one of them about an inversion center) and could not be refined adequately. The routine SQUEEZE, as incorporated in PLATON [16], was therefore used to remove mathematically the effects of the solvent. Because of the approximations involved, the results should be interpreted with caution. For the monosolvate, the THF was again disordered, this time over a mirror plane, but could be refined using a suitable system of restraints. The CH_2–CH_2 bridge of the cation was disordered over two positions.

CCDC 691986 and 691987 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.

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