



# The bis(trifluoroacetate) analogue of the first-generation Grubbs catalyst: Synthesis, X-ray structure, and metathesis activity of $[\text{Ru}(\text{CF}_3\text{CO}_2)(\eta^2\text{-CF}_3\text{CO}_2)(=\text{CHPh})(\text{PCy}_3)_2]$

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## ABSTRACT

A simple synthesis of  $[\text{Ru}(\text{CF}_3\text{CO}_2)(\eta^2\text{-CF}_3\text{CO}_2)(=\text{CHPh})(\text{PCy}_3)_2]$  from dimeric  $[\text{Ru}_2(\text{CF}_3\text{CO}_2)_2(\mu\text{-CF}_3\text{CO}_2)_2(=\text{CHPh})_2(\text{PCy}_3)_2(\mu\text{-H}_2\text{O})]$  is described. The new complex crystallizes in monoclinic system ( $P2(1)/c$  space group) with distorted octahedral coordination. The very low metathesis activity of this new ruthenium benzylidene complex demonstrates that substitution of chlorides with trifluoroacetates in  $[\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2]$  results in loss of the catalytic activity.

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## 1. Introduction

Alkene metathesis is a useful method for the formation and cleavage of carbon–carbon double bonds [1]. The discovery of the first-generation Grubbs catalyst  $[\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2]$  (**1**) [2] has allowed for the widespread use of metathesis in both organic and polymer chemistry [3]. Numerous modifications of **1** have been reported so far. The efforts to improve the catalytic performance of **1** have involved replacement of one phosphine ligand with a nucleophilic *N*-heterocyclic carbene [4]. A number of research groups have designed and synthesized analogues of **1** with an *o*-chelating phenyl group to develop the Grubbs–Hoveyda catalysts [5]. On the other hand, only few attempts to substitute the anionic ligands in **1** have been reported [6]. Mol and co-workers studied reactions of **1** or its vinylcarbene derivative with silver carboxylates as a plausible route for attachment of Ru–carbene species to a polymeric support. Instead of the expected five-coordinate chloride-substitution products  $[\text{Ru}(\text{R}'\text{CO}_2)_2(=\text{CHR})(\text{PCy}_3)_2]$ , a series of six-coordinate, metathesis-active dimeric complexes **2** was obtained (Scheme 1) [7].

Consequently, the reaction of complex **1** with a suitably designed silver carboxylate was used as the key step in the synthesis of a polymer-supported metathesis catalyst by Nieczydor et al. (Scheme 2) [8]. Subsequently, the same principle of immobilization was applied to the second-generation Ru-based metathesis catalysts in a number of reports [9].

Despite this considerable amount of work on the supported, trifluoroacetate-bound Ru(II) metathesis catalysts, the exact structure of these species, in particular the binding mode of the carboxylate, remains undisclosed. Moreover, to the best of our knowledge, only one first-generation bis(trifluoroacetate) Ru(II) alkylidene, namely  $[\text{Ru}(\text{CF}_3\text{CO}_2)_2(=\text{CHMe})(\text{PCy}_3)_2]$ , was described so far. However, its crystal structure was not determined, and the carboxylate ligands were described as probably monodentate according to the IR data [10]. Therefore, we sought to synthesize and structurally characterize the hitherto unknown bis(carboxylate) counterpart of  $[\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2]$ .

## 2. Experimental

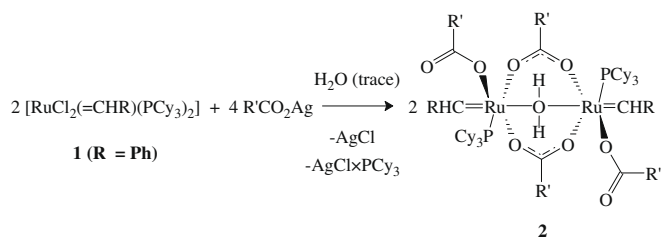
All manipulations were performed under an atmosphere of purified argon using standard Schlenk tube techniques. All solvents and alkenes were purified by reported methods [11]. Complex **2a** (Scheme 1; R = Ph, R' = CF<sub>3</sub>) was obtained as described earlier [7a]. All other chemicals were purchased from commercial sources and used as received. Unless otherwise noted, NMR spectra were recorded on a Mercury-400BB spectrometer at ambient temperature.

### 2.1. Synthesis of $[\text{Ru}(\text{CF}_3\text{CO}_2)(\eta^2\text{-CF}_3\text{CO}_2)(=\text{CHPh})(\text{PCy}_3)_2]$ (**3**)

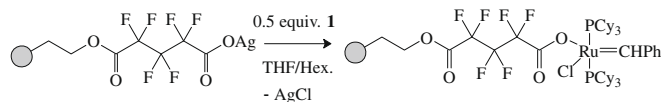
A solution of PCy<sub>3</sub> (44.4 mg, 0.158 mmol) in hexane (3.0 mL) was added to a stirred solution of **2a** (110 mg, 0.0778 mmol) in hexane (60 mL) and Et<sub>2</sub>O (2.0 mL) at –78 °C in the presence of activated MS

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**Scheme 1.** Synthesis of dimeric Ru carbene complexes **2** (R = Ph or CH=CPh<sub>2</sub>; R' = CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>, CCl<sub>3</sub>, or C<sub>6</sub>F<sub>5</sub>) [7].



**Scheme 2.** Immobilization of the first-generation ruthenium carbene on a functionalized polystyrene via halogen exchange [8].

4A. The resulting mixture was stirred at this temperature for 15 min and filtered. The green filtrate was reduced in volume and kept at  $-30\text{ }^{\circ}\text{C}$  for a few days to yield bright green crystals of **3** which were separated from the mother liquor and washed with hexane at  $-78\text{ }^{\circ}\text{C}$ . Yield: 108 mg (70%).  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  (ppm) 21.20 (s, 1H, Ru=CH), 8.61 (d,  $^3J_{\text{HH}} = 7.6$  Hz, 2H, *o*-H of Ph), 7.26 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 1H, *p*-H of Ph), 7.18 (*m*-H of Ph, partially obscured by the solvent signal), 2.24 (m, 6H, C-1 of Cy), 1.9–0.9 (m, 80H, Cy and C<sub>6</sub>H<sub>14</sub>).  $^{31}\text{P}$  NMR (C<sub>6</sub>D<sub>6</sub>, 162 MHz):  $\delta$  (ppm) 34.71 (PCy<sub>3</sub>).  $^{19}\text{F}$  NMR (C<sub>6</sub>D<sub>6</sub>, 376 MHz):  $\delta$  (ppm)  $-73.92$  (CF<sub>3</sub>CO<sub>2</sub>).  $^{19}\text{F}$  NMR (toluene-*d*<sub>8</sub>, 470 MHz, 25  $^{\circ}\text{C}$ ):  $\delta$  (ppm)  $-73.90$  ( $\Delta\nu_{1/2} = 2.8$  Hz) (CF<sub>3</sub>CO<sub>2</sub>).  $^{19}\text{F}$  NMR (toluene-*d*<sub>8</sub>, 470 MHz,  $-40\text{ }^{\circ}\text{C}$ ):  $\delta$  (ppm)  $-73.63$  ( $\Delta\nu_{1/2} = 55$  Hz) (CF<sub>3</sub>CO<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>, 101 MHz):  $\delta$  (ppm) 310.1 (s, Ru=CH), 164.5 (q,  $^2J_{\text{CF}} = 36$  Hz, CO<sub>2</sub>CF<sub>3</sub>), 153.7, 130.9, 130.4, 129.9 (all s, Ph), 114.6 (q,  $^1J_{\text{CF}} = 292$  Hz, CO<sub>2</sub>CF<sub>3</sub>), 34.9 (t,  $J_{\text{CP}} = 8.5$  Hz), 29.8 (s), 27.8 (t,  $J_{\text{CP}} = 4.8$  Hz), 26.64 (s), all Cy. IR (KBr):  $\nu$  (cm<sup>-1</sup>) 2932 (CH), 2852 (CH), 1694 (COO)<sub>a</sub>, 1626 (COO)<sub>a</sub>, 1448 (COO)<sub>s</sub>, 1194 (COO)<sub>s</sub>, 1152, 1143, 728 (CF<sub>3</sub>). Anal. Calc. for C<sub>47</sub>H<sub>72</sub>F<sub>6</sub>O<sub>4</sub>P<sub>2</sub>Ru: C, 57.7; H, 7.42. Found: C, 57.1; H, 7.55%.

## 2.2. X-ray structure determination

Crystals suitable for the X-ray study were grown from an *n*-hexane solution at  $-20\text{ }^{\circ}\text{C}$ . The data have been collected using the BRUKER KAPPA APEXII ULTRA system equipped with TXS rotating anode and controlled by APEXII software (Bruker, 2007). The crystal of the size  $0.12 \times 0.09 \times 0.06$  mm has been mounted on a cactus fiber with a drop of Pantone-N oil. The experiment has been carried out at 90 K using the Oxford Cryostream cooling device with liquid nitrogen. The Mo K $\alpha$  X-ray radiation (50 kV, 22 mA) was further monochromatized by multi-layer optics. A total of 33 686 reflections have been collected in four  $\omega$  scans with various  $\chi$  offsets and 45 s exposure times for  $0.5^{\circ}$  oscillation angle per frame.

Indexing, integration and initial scaling were performed with SAINT and SADABS software (Bruker, 2007). The numerical absorption correction from crystal shape was applied in the scaling procedure. The average mosaicity was refined to the value of  $0.5^{\circ}$ . Relatively weak scattering of the compound indicated significant disorders in the structure. The data collection and processing statistics are given in Table 1.

The crystals have grown as twins, related by mirror plane perpendicular to the crystallographic *x*-axis. Due to the characteristic lattice parameters the twinning resulted in nearly ideal overlap of the reflections in the reciprocal space and gave rise to the pseudo-orthorhombic symmetry. Structure refinement was possible only

**Table 1**

The data collection and processing statistics for complex **3**.

Empirical formula	C <sub>53</sub> H <sub>86</sub> F <sub>6</sub> O <sub>4</sub> P <sub>2</sub> Ru
Formula weight	1064.23
Crystal system, space group	Monoclinic, <i>P</i> 2(1)/ <i>c</i>
<b>Unit cell dimensions</b>	
<i>a</i> (Å)	11.1275(5)
<i>b</i> (Å)	22.5707(14)
<i>c</i> (Å)	23.5929(10)
$\alpha$ ( $^{\circ}$ )	90
$\beta$ ( $^{\circ}$ )	118.141(2)
$\gamma$ ( $^{\circ}$ )	90
Volume (Å <sup>3</sup> )	5225.0(5)
<i>Z</i> , Calculated density (Mg/m <sup>3</sup> )	4, 1.353
Absorption coefficient (mm <sup>-1</sup> )	0.425
<i>F</i> (0 0 0)	2256
$\theta$ Range for data collection ( $^{\circ}$ )	1.33–27.16
Reflections collected/unique	33 686/33 686 [ <i>R</i> <sub>int</sub> = 0.0000]
Completeness to $\theta = 27.16$	99.5%
Absorption correction	Numerical
Max. and min. transmission	0.98 and 0.90
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	33 686/299/803
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.002
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0589, <i>wR</i> <sub>2</sub> = 0.1218
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1168, <i>wR</i> <sub>2</sub> = 0.1446
Largest difference in peak and hole (e Å <sup>-3</sup> )	1.535 and $-0.691$

after the twinning matrix was introduced by TWIN instruction. The proportion of the twin components was refined with BASF instruction to 0.6 for main component and 0.4 for second component accordingly. The structure was solved by direct methods approach using the SHELXS-97 program and then refinement was carried out with the SHELXL-97. The refinement was based on *F*<sup>2</sup> for all reflections except those with negative intensities. Weighted *R* factors *wR* and all goodness-of-fit *S* values were based on *F*<sup>2</sup>, whereas conventional *R* factors were based on the amplitudes, with *F* set to zero for negative *F*<sup>2</sup>. The *F*<sub>o</sub> > 2 $\sigma$ (*F*<sub>o</sub>) criterion was applied only for *R* factors calculation and was not relevant to the choice of reflections for the refinement. The hydrogen atoms were located in idealized geometrical positions. Also there were some special constraints applied to the anisotropic displacement parameters of disordered atoms. The significantly disordered solvent molecule was refined isotropically after assignment of three alternative conformations. Scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 from the International Crystallographic Tables Vol. C.

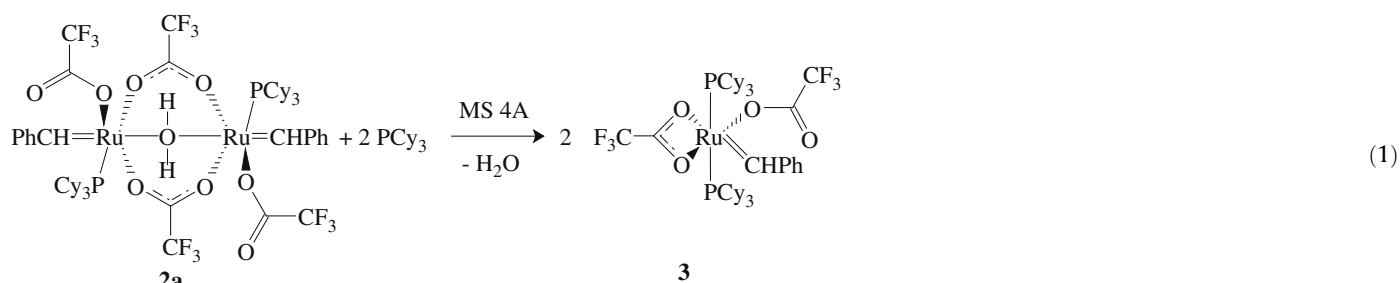
## 2.3. Catalytic activity

The metathesis activity of **3** was evaluated with selected substrates in toluene or C<sub>6</sub>D<sub>6</sub> as described earlier [12]. In a typical experiment, neat 1-octene (115  $\mu\text{L}$ , 0.733 mmol) was added to a toluene (2.45 mL) solution of complex **3** (7.20 mg,  $7.36 \times 10^{-3}$  mmol). The resulting mixture was stirred at 25  $^{\circ}\text{C}$ . The progress of the reaction was followed by GC (1-octene, methyl oleate) or by  $^1\text{H}$  NMR (diethyl diallylmalonate, 1,5-cyclooctadiene).

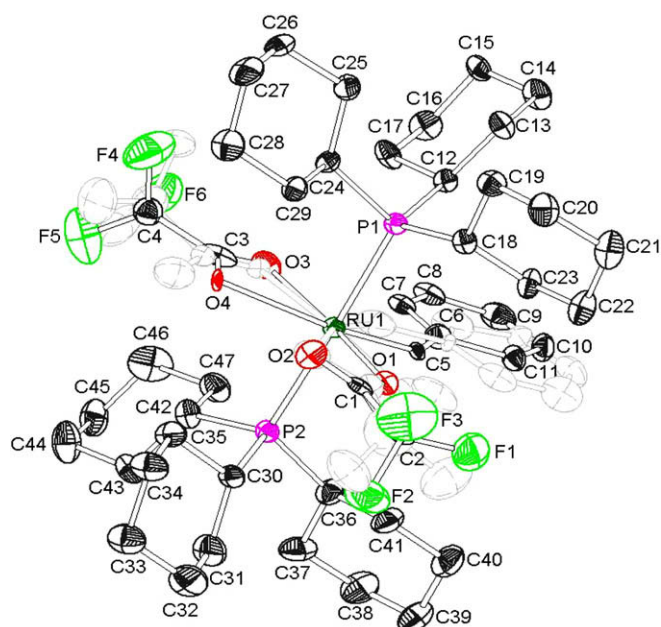
## 3. Results and discussion

Our initial unsuccessful attempts to obtain [Ru(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(=CHPh)(PCy<sub>3</sub>)<sub>2</sub>] consisted in substitution of the chloride ligands in complex **1** using CF<sub>3</sub>CO<sub>2</sub>Ag under rigorously water-free conditions [13]. A reaction of **1** with an excess of CF<sub>3</sub>CO<sub>2</sub>Na was also tested; however after 3 days at room temperature the substrate was the major carbene species detected by  $^1\text{H}$  NMR [14]. Therefore, we decided to turn our attention to the aqua-bridged complexes **2** (Scheme 1). Dimers **2** are moderately stable in solution and react

under ambient conditions with weak ligands and donor solvents, such as pyridine, THF, or MeOH [7b]. Since Mol and co-workers suggested that the bridging water molecule was replaced by the incoming ligand, we envisaged that addition of PCy<sub>3</sub> to complexes **2** may result in the desired bis(trifluoroacetate) monomeric products. Apparently, addition of a PCy<sub>3</sub> solution to a hexane solution of **2a** does not result in any significant chemical event because the original green color of the substrate persisted. However, NMR analysis of the solid product obtained after the solvent removal clearly indicated that a new complex was selectively obtained (Eq. (1)).



The diagnostic signal of the bridging aqua ligand of **2a** at 12.50 ppm (C<sub>6</sub>D<sub>6</sub>) disappeared and the carbene proton doublet at 20.79 ppm was replaced by a singlet at 21.20 ppm. Interestingly, only one signal was observed in the <sup>19</sup>F NMR spectrum, similarly a singlet at 34.71 ppm appeared in the <sup>31</sup>P NMR. The corresponding changes were observed in the <sup>13</sup>C NMR spectrum indicating that the new complex **3** consisted of one benzylidene ligand, two equivalent phosphines and two equivalent carboxylic groups. To fully elucidate the structure of **3** we have undertaken a single-crystal X-ray diffraction study.



**Fig. 1.** ORTEP representation of complex **3**. The thermal ellipsoids are drawn at the 50% probability level. The alternative conformations of the disordered molecule are drawn in light grey. Hydrogen atoms have been omitted for clarity.

Complex **3** crystallizes in monoclinic system, in centrosymmetric *P2(1)/c* space group. One molecule of the ruthenium complex together with one solvent (*n*-hexane) molecule constitute the crystallographic asymmetric unit. There are no atoms in special positions. The ORTEP representation of complex **3** is presented in Fig. 1. Bond lengths and angles are given in Table 2.

In contrast to distorted square-pyramidal complex [RuCl<sub>2</sub>(=CH-*p*-C<sub>6</sub>H<sub>4</sub>Cl)(PCy<sub>3</sub>)<sub>2</sub>] (**1-Cl**) [2], the coordination of the central ruthenium ion in **3** takes shape of a distorted octahedron. Two phosphine ligands occupy the tops of the octahedron. They are equally far from the coordinated cation (2.452 and 2.461 Å)

and considerably further than phosphines in **1-Cl** (2.397 and 2.435 Å). The P1, Ru1 and P2 atoms are nearly collinear (the P1–Ru1–P2 angle is 176.2°, compared with 161.1° in **1-Cl**), indicating the tendency of phosphines to bend away from the benzylidene moiety. The two bulky substituents shield a plane perpendicular to the P1–P2 axis, where the other three coordinating moieties are located. There is an asymmetry in the interactions of the two trifluoroacetates with the ruthenium cation. In the case of the first moiety, O1 oxygen is significantly closer to the ruthenium than O2, which can hardly be described as interacting with the ruthenium (a distance of 3.284 Å), while in the second moiety the O3–Ru1 and O4–Ru1 distances are comparable (Table 2). We assume that in solution these ligands exchange rapidly, and consequently a single resonance appears on the NMR spectra [15]. In agreement with the theory postulating double bond formation between ruthenium and the carbene carbon, the C5–Ru1 bond (1.852 Å) is the shortest of the metal–ligand contacts. Similarly to **1-Cl**, the phenyl ring lays exactly in the plane perpendicular to the P1–P2 direction.

The whole complex displays a tendency to non-crystallographic symmetry. The two opposite phosphine moieties are related by two-fold axis that crosses the ruthenium atom and lies in the plain of the benzylidene moiety, in between C6 and C6B atoms, which nearly overlap. The tendency to maintain this symmetry together with shielding by phosphine ligands is responsible for the static

**Table 2**  
Selected bond lengths (Å) and angles (°) for complex **3**.

Ru(1)–C(5)	1.852(6)	O(1)–Ru(1)–O(4)	114.5(3)
Ru(1)–O(1)	2.064(9)	O(3)–Ru(1)–O(4)	57.8(2)
Ru(1)–O(2)	3.284(11)	C(5)–Ru(1)–P(2)	93.28(19)
Ru(1)–O(3)	2.206(10)	O(1)–Ru(1)–P(2)	88.6(2)
Ru(1)–O(4)	2.399(4)	O(3)–Ru(1)–P(2)	91.4(3)
Ru(1)–P(2)	2.4517(11)	O(4)–Ru(1)–P(2)	87.85(12)
Ru(1)–P(1)	2.4605(11)	C(5)–Ru(1)–P(1)	89.87(18)
C(5)–Ru(1)–O(1)	81.4(3)	O(1)–Ru(1)–P(1)	89.8(2)
C(5)–Ru(1)–O(3)	106.2(3)	O(3)–Ru(1)–P(1)	89.8(3)
O(1)–Ru(1)–O(3)	172.3(3)	O(4)–Ru(1)–P(1)	89.71(12)
C(5)–Ru(1)–O(4)	164.1(2)	P(2)–Ru(1)–P(1)	176.20(4)

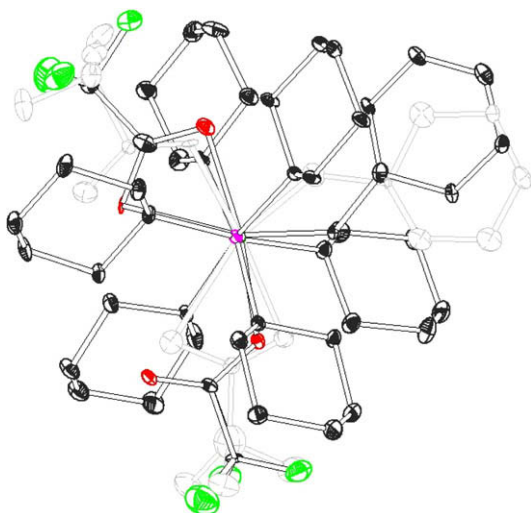


Fig. 2. Illustration of the non-crystallographic symmetry in complex **3**.

disorder of the substituents located in the equatorial plane. The disordered moieties are related with their alternative conformations by the already mentioned two-fold axis. The axis is nearly, but not exactly parallel to the crystallographic *x*-axis (Fig. 2).

The occupancies of the main and alternative conformation for all three equatorial substituents are 0.6 and 0.4, respectively. Large values of thermal displacement parameters refined for fluorine atoms suggest additional high mobility of the trifluoro groups.

The crystal packing of complex **3** explains both ordered structure of phosphine groups and heavily disordered structure of the solvent hexane molecules. The ruthenium complexes form columns along *X* direction, so as the phosphine moieties are directed along *Z* direction and the benzylidene moiety from one complex forms close C–H...O contacts with the O2 oxygen from the next complex (Fig. S1a; Supplementary material). The columns then form layers perpendicular to the crystallographic *Y* direction. The cyclohexyl rings from adjacent columns interact closely, as the C18–C23 ring belonging to one column is located in between two C42–C47 rings from the next column, forming a kind of hydrophobic zip-locks along the *X* direction (Fig. S1a). Between the two layers of the complexes there are broad channels aligned with trifluoro groups, along *X* direction, filled with the disordered solvent (Fig. S1b). Such porous structure and lack of strong complex–solvent interactions may also explain the instability of the crystals to air.

The metathesis activity of complex **3** with selected alkenes (1-octene, methyl oleate, diethyl diallylmalonate, 1,5-cyclooctadiene) was examined under standard conditions [12]. The complex showed negligible activity in the metathesis of 1-octene, methyl oleate or diethyl diallylmalonate (toluene or C<sub>6</sub>D<sub>6</sub> solution, molar ratio substrate: catalyst = 100:1, ca. 1% conversion after 24 h at 25 °C; ca. 2% conversion after 24 h at 50 °C with methyl oleate) and very low ROMP activity with 1,5-cyclooctadiene (30% conversion after 24 h at 25 °C). A conversion of 26% was reached in CH<sub>2</sub>Cl<sub>2</sub> (methyl oleate, 100:1, 24 h, 25 °C), however the reported propensity of Ru–carbene complexes to exchange anionic ligands in solution [16] strongly suggests that this result should be attributed to the regeneration of the chloride-substituted catalyst.

The previously reported aqua-bridged complexes **2** displayed significant metathesis activity [7]. The current results with **3** are rather disappointing because we supposed that cleavage of the bridging moiety in the six-coordinate **2** would yield an active, five-coordinate bis(trifluoroacetate) analogue of **1**. Unexpectedly, the trifluoroacetate in **3** adopts a bidentate binding mode, and

the Ru(II) coordination sphere in **3** does not resemble that in **1**. We note that [Ru(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(=CHMe)(PCy<sub>3</sub>)<sub>2</sub>] was completely inactive in cross-metathesis of allyl alcohol with cyclopentene [10].

The mechanism of olefin metathesis catalyzed by **1** and its analogues [RuX<sub>2</sub>(=CHR)(PCy<sub>3</sub>)<sub>2</sub>] (X = Cl, Br, I) was investigated in detail [17]. The key steps of the catalytic cycle involve phosphine dissociation to generate the four-coordinate intermediate [RuX<sub>2</sub>(=CHR)L], an olefin coordination, and metallacycle formation. It was shown that both steric and electronic properties of the anionic ligand significantly influence the overall reactivity, however these effects are not particularly well understood. We suppose that the chelating carboxylate in **3** and in the plausible intermediate [Ru(CF<sub>3</sub>CO<sub>2</sub>)(η<sup>2</sup>-CF<sub>3</sub>CO<sub>2</sub>)(=CHPh)(PCy<sub>3</sub>)] prevents an incoming olefin from coordination to the Ru-centre, and renders complex **3** almost inactive.

#### 4. Conclusions

In conclusion, we have prepared and fully characterized [Ru(CF<sub>3</sub>CO<sub>2</sub>)(η<sup>2</sup>-CF<sub>3</sub>CO<sub>2</sub>)(=CHPh)(PCy<sub>3</sub>)<sub>2</sub>] (**3**). Despite twinning of the crystals – the ratio of occupancies equal 0.6 and 0.4 for the main and second components, respectively – and a complex static disorder of the solvent molecules, the crystal structure of this complex has been established. Complex **3** displays very low metathesis activity with benchmark substrates, e.g. diethyl diallylmalonate. Our results are particularly relevant to the field of supported Grubbs-type catalysts immobilized via the perfluoroglutaric acid linker and suggest that this approach may result in species with low catalytic activity.

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#### Appendix A. Supplementary material

CCDC 705020 contains 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](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.05.008](https://doi.org/10.1016/j.jorganchem.2009.05.008).

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