

Structural Characterization of Cp*Ru-Intermediates of Phenylacetylene Cyclotrimerization

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Abstract. Phenylacetylene reacts depending on the reaction conditions with Cp*Ru(COD)Cl under formation of the neutral dicarbene complex 2,5-diphenyl-Cp*ruthena-cyclopentatriene (**1**) or the cationic sandwich compound [Cp*Ru(1,2,4-triphenyl)benzene] (**2**). The X-ray structures and spectroscopic data of both complexes are presented. The complexes can be interpreted as intermediates in the CpRu-catalyzed cyclotrimerization of acetylenes.

Cyclotrimerization of acetylenes is catalyzed by various complex compounds from the early to the late transition metals [1]. On the cyclotrimerization using Ru-complexes only few is reported [2].

We report here on the reaction of a Cp*RuCl-fragment, which is isolobal to the CpCo-fragment [3], with acetylenes and the formation of the organometallic products obtained from this reaction.

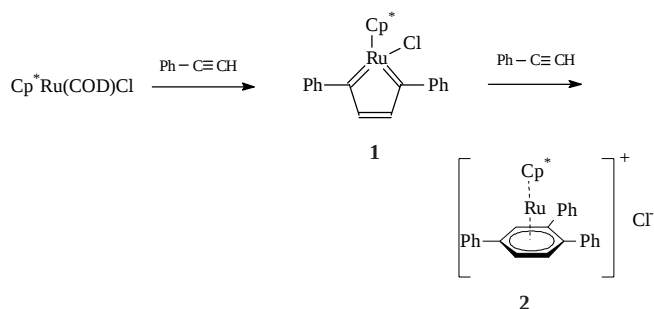
Results and Discussion

Phenylacetylene reacts with Cp*Ru(COD)Cl depending on the reaction conditions under formation of the neutral dicarbene complex, 2,5-diphenyl-Cp*ruthena-cyclopentatriene (**1**), or the cationic sandwich compound [Cp*Ru(1,2,4-triphenyl)benzene] (**2**) (Scheme 1). The main difference in

the preparation is the reaction time which has to be longer to build the Ru-sandwich compound **2**. The formation of **2** can be explained by further reaction of **1** with another molecule of phenylacetylene under elimination of a chloride ligand. In contrast at the CpCo-fragment only a η^4 -coordination of the benzene built from cyclotrimerization of acetylenes is observed [4]. Elimination of the benzene derivative and recoordination of the chloride ligand can reform the Cp*RuCl-fragment, which comes to a catalytic cycle according to that known from CpCo-catalysis [5].

Single crystals of **1** were grown from a CH₂Cl₂ solution layered with *n*-hexane at -30 °C during one week [6]. Compound **1** crystallizes in the orthorhombic space group Pnma with half a molecule **1** in the crystallographic independent unit of the elementary cell (Table 1, Fig. 1), the other half of the molecule is symmetry equivalent and generated by a mirror plane.

The coordination of the Ru-centre in **1** is very similar to its bromine derivative [2a] and can be described as distorted tetrahedral when the coordination of the Cp-ring is reduced to its centre. However, the Cp-ring is not coordinated symmetrically to the Ru-atom which causes different C-Ru-distances (Table 2). The embedding of the Ru-metal in the metallacyclopentatriene leads to a smaller C-Ru-C-bond angle of 78.9° than expected for an idealized tetrahedral environment (Table 2, Fig. 1). The bond angles at the Ru-atom between the centre of the Cp-ring and the chlorine ligand as well as between the carbene C-atom (C1, Fig. 1) are widened to circa 121° (Table 2). The coupling of the phenylacetylene leads to the formation of a C-C-bond with a C-C-distance of 137 (1) pm in **1** which has double bond character. The C-C-

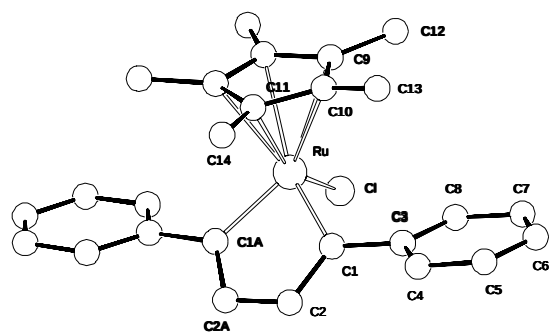


Scheme 1 Reaction of Cp*Ru(COD)Cl with phenylacetylene

Table 1 Crystallographic data of the neutral complex **1** and the cationic complex **2**

Compound	1	2
Empirical formula	C ₂₆ H ₂₇ ClRu	2Cl·CH ₂ Cl ₂ C ₃₅ H ₃₅ Cl ₃ Ru
Formula weight	476.00	661.03
Crystal size	0.4 × 0.38 × 0.36 mm ³	0.4 × 0.3 × 0.2 mm ³
Crystal system	orthorhombic	monoclinic
Space group	Pnma (No. 62)	P2 ₁ /n (No. 14)
Unit cell dimensions	a = 1885.8 (4) pm b = 1575.2 (3) pm c = 724.9 (1) pm	a = 1101.0 (1) pm b = 1303.3 (3) pm c = 2126.6 (3) pm β = 95.64 (1)°
Volume	2153.3 (7) × 10 ⁶ pm ³	3036.9 (9) × 10 ⁶ pm ³
Z	Z = 4	Z = 4
Density (calculated)	1.468 g/cm ³	1.446 g/cm ³
Diffractometer	Enraf Nonius CAD4	Siemens SMART 5000 CCD-Diffractometer
Wavelength	MoK _α Graphit-Monochromator	
Temperature	200 K	200 K
θ-Range	2.52 ≤ θ ≤ 27.42 °	1.84 ≤ θ ≤ 28.38 °
Scan	ω-Scan, Δ ω = 0.3 °	ω-Scan, Δ ω = 0.3 °
Index ranges	−24 ≤ h ≤ 0, 0 ≤ k ≤ 20, 0 ≤ l ≤ 9	−14 ≤ h ≤ 14, −17 ≤ k ≤ 17, −28 ≤ l ≤ 27
Number of reflections measured	2543	31625
independent reflections	2543	7475
reflections observed	2172	6026
Number of parameters refined	188	362
Residual electron density	0.801 × 10 ^{−6} e/pm ³	0.948 × 10 ^{−6} e/pm ³
Corrections	Lorentz and Polarisation, Absorption correction (SADABS) [11]	
Structure solution	direct methods	
Structure refinement	full matrix least square on F ²	
Programs and weightings used	SHELXS-86 [12], SHELXL-93 [14]	SHELX-97 [13], xpma, zortep [15]
R indices	R ₁ = 0.0436 (I > 2σ) R _w = 0.1121 (all data on F ²)	R ₁ = 0.0261 (I > 2σ) R _w = 0.0697 (all data on F ²)

Standard deviations in parentheses.

**Fig. 1** View to the molecular structure of **1** in the crystal

distance between the former C-atoms belonging to the triple bond is elongated to 140.2(7) pm (Table 2). The distance of the quaternary C-atom of the phenylacetylene to the Ru-centre is with 196.9(4) pm in the range for a double bond. Both carbon atoms of the former acetylene unit show sp²-hybridization. All these findings are conform with those reported from the bromine derivative of **1** [2]. So, the coupling of phenylacetylene at a Cp*Ru-centre leads to the formation of a new C–C-bond involving the necessary change of hybridization and the formation of metal-carbon bonds.

Table 2 Selected bond lengths (pm) and angles (°) for **1**

Ru–Cl	236.5(2)	C1–Ru–C1a	78.9(3)
Ru–C1	196.9(4)	C1–Ru–Cl	102.7(1)
Ru–C9	235.1(4)	Cp–Ru–Cl	120.8
Ru–C10	229.2(4)	Cp–Ru–C1	121.5
Ru–C11	219.6(6)	C2–C1–C3	119.5(4)
C1–C2	140.2(7)	C2–C1–Ru	116.6(4)
C1–C3	147.3(7)	C3–C1–Ru	123.8(4)
C2–C2a	137(1)	C2a–C2–C1	113.7(3)

Standard deviations in parentheses. The suffix a indicates an atom which is symmetry-equivalent to the atom without the suffix. The abbreviation Cp symbolizes the centre of the Cp-ring coordinated to the Ru-centre.

When **1** is allowed to react with a further molecule of phenylacetylene by longer stirring at room temperature, the cationic sandwich complex [Cp*Ru(1,2,4-triphenyl)benzene] **2** (Scheme 1) is built. The counter anion is a chloride which left the coordination sphere of the Ru-centre. Single crystals of **2**Cl were obtained from a CH₂Cl₂ solution layered with *n*-hexane at −30 °C during two weeks [6]. **2**Cl crystallizes in the monoclinic space group P2₁/n with one molecule CH₂Cl₂ per unit (Table 1, Fig. 2). The coordination of both ring systems to the Ru-centre in **2** is nearly ideal. The angle at the Ru-atom formed by the two centres of the ring system is very

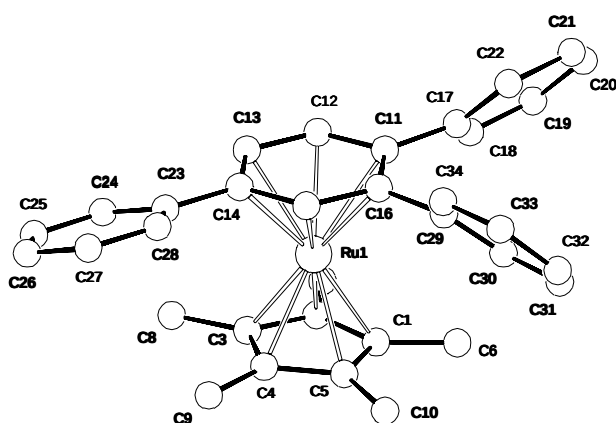


Fig. 2 View to the molecular structure of the cation 2 in the crystal

Table 3 Selected bond lengths (pm) and angles (°) for 2 lengths

Ru–C(Cp)	218.0(2) to 220.3(2)
Ru–C(Ph)	220.5(2) to 226.8(2)
Ru–CentreCp	182.0
Ru–CentrePh	171.8
angles	
CentrePh–Ru–CentreCp	176.9
plane Ph to plane Cp	4.6

Standard deviations in parentheses.

close to 180° (Table 3, Fig. 2). This is also expressed in the nearby coplanarity of the Ph- and Cp-ring. As the Ph-ring has a larger diameter than the Cp-ring its centre is closer to the Ru-metal-atom than the centre of the Cp-ring even when the Ru–C-distances for the C-atoms of the Cp-ring are shorter than the corresponding Ru–C-distances of the Ph-ring (Table 3). This behaviour is typical for complexes of this type [7].

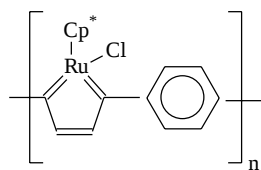


Fig. 3 Ru-containing polymer

The results confirm the knowledge about the CpRu-catalyzed cyclotrimerization of acetylenes [2] according to a mechanism similar to the CpCo-catalysis [5].

The possibility of the use of bisacetylenes in this reaction would lead to polymeric materials containing the Ru-metal in the main chain of the polymer, which have attracted great attention [8] (Fig. 3). As monomeric compounds of this type show interesting electronic properties the polymeric material should be of high potential [9]. These are topics of present

work and the knowledge of the purest preparation method is essential to produce pure polymeric materials.

Experimental

Chemicals were purchased from Aldrich and used as received. Solvents and reagents were purified by literature methods. Cp*Ru(COD)Cl was synthesized according to the literature [10]. NMR-spectra were registered on a Varian Unity Inova spectrometer in CDCl₃ solution at 25 °C referring to the rest proton signal of the solvent (δ = 7.27 ppm) or its carbon frequency (δ = 77.0 ppm). The spectra were obtained at the operating frequency of 400 MHz for proton spectroscopy or 100 MHz for ¹³C NMR spectra, respectively. Infrared spectra were recorded on a BIORAD FT spectrometer in KBr-pellets in the region of 400–4000 cm^{–1}. For the details of the single crystal X-ray diffraction measurements see table 1 and [6].

2,5-Diphenyl-Cp*ruthena-cyclopentatriene (1)

0.085 g (8.38 mmol) of phenylacetylene were added at 0 °C to a solution of 0.0453 g (0.16 mmol) Cp*Ru(COD)Cl in 40 ml THF. The mixture was stirred overnight and allowed to warm up to room temperature. The solvent was removed *in vacuo* and the residue washed with 10 ml cold (0 °C) *n*-hexane to give a dark red powder. Single crystals suitable for X-ray diffraction were obtained by crystallization from a CH₂Cl₂ solution of 1, layered with *n*-hexane at –30 °C during 7 days. Yield 0.068 g (0.14 mmol, 89%). – ¹H NMR: δ /ppm = 7.56 (m, 2H, Ph-H), 7.26 (s, 2H, CH, metallacyclopentatriene), 7.18 (m, 8H, Ph-H), 1.19 (s, 15H, Cp-CH₃). – ¹³C NMR: δ /ppm = 264.1, 160.3, 156.4, 130.8, 128.2, 126.0, 107.8, 11.1 (C₅Me₅). – IR ν /cm^{–1} = 2962 (m), 1447(m), 1261 (s), 1093 (s), 1022 (s), 802 (s).

[Cp*Ru(1,2,4-triphenyl)benzene]⁺Cl[–] (2Cl)

0.085 g (8.38 mmol) of phenylacetylene were added at 0 °C to a solution of 0.045 g (0.16 mmol) Cp*Ru(COD)Cl in 30 ml CH₂Cl₂. The mixture was allowed to warm up to room temperature and stirred for 72 h at room temperature. The solvent was removed *in vacuo* and the residue washed three times with 10 ml cold (0 °C) *n*-hexane to give a light yellow powder. Single crystals were obtained by crystallization from a CH₂Cl₂ solution of 2Cl, layered with *n*-hexane at –30 °C during 14 days. Yield 0.046 g (0.078 mmol, 49%). – ¹H NMR: δ /ppm = 7.92 (d, 2H), 7.74 (d, 1H), 7.55–7.12 (m, 12H), 6.81 (d, 1H), 6.28 (s, 1H), 5.27 (s, 1H), 1.68 (s, 15H). – ¹³C NMR: δ /ppm = 134.6, 132.9, 130.9–128.4, 127.2, 127.1, 95.6, 10.1. – IR ν /cm^{–1} = 3053 (m), 2922 (m), 1492 (m), 1475 (m), 1449 (m), 1384 (s), 1074 (m), 1028 (m), 699 (s).

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