

## Structural Characterization of Cp\*Ru-Intermediates of Phenylacetylene Cyclotrimerization

C. Ernst, O. Walter, and E. Dinjus\*

Karlsruhe, ITC-CPV, Forschungszentrum

S. Arzberger

Jena, Projektgruppe "CO<sub>2</sub>-Chemie" an der Friedrich-Schiller-Universität

H. Görls

Jena, Institut für Anorganische und Analytische Chemie der Universität

Received August 26th, 1999

Dedicated to Professor Egon Uhlig on the Occasion of his 70th Birthday

**Keywords:** Alkynes, Cyclopentadienes, Cyclotrimerization, Metallacycles, Ruthenium

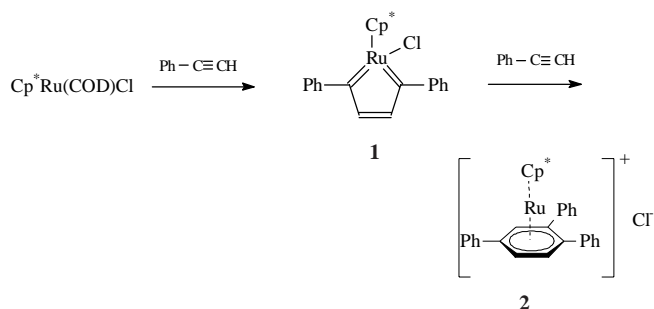
**Abstract.** Phenylacetylene reacts depending on the reaction conditions with Cp\*Ru(COD)Cl under formation of the neutral dicarbene complex 2,5-diphenyl-Cp\*ruthena-cyclopentatriene (**1**) or the cationic sandwich compound [Cp\*Ru(1,2,4-triphenyl)benzene] (**2**). The X-ray structures and spectroscopic 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



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

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  $\eta^4$ -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].

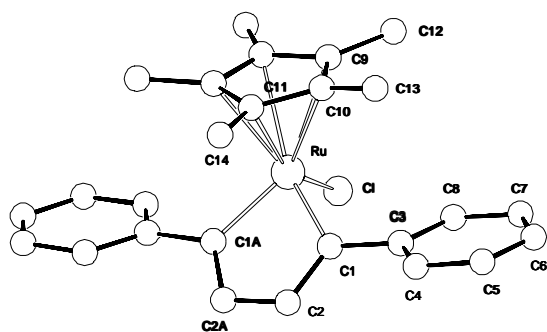
Single crystals of **1** were grown from a CH<sub>2</sub>Cl<sub>2</sub> solution layered with *n*-hexane at -30 °C during one week [6]. Compound **1** crystallizes in the orthorhombic space group Pnma with half a molecule **1** in the crystallographic independent unit of the elementary cell (Table 1, 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-

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

Compound	<b>1</b>	<b>2Cl·CH<sub>2</sub>Cl<sub>2</sub></b>
Empirical formula	C <sub>26</sub> H <sub>27</sub> ClRu	C <sub>35</sub> H <sub>35</sub> Cl <sub>3</sub> Ru
Formula weight	476.00	661.03
Crystal size	0.4 × 0.38 × 0.36 mm <sup>3</sup>	0.4 × 0.3 × 0.2 mm <sup>3</sup>
Crystal system	orthorhombic	monoclinic
Space group	Pnma (No. 62)	P2 <sub>1</sub> /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 <sup>6</sup> pm <sup>3</sup>	3036.9 (9) × 10 <sup>6</sup> pm <sup>3</sup>
Z	Z = 4	Z = 4
Density (calculated)	1.468 g/cm <sup>3</sup>	1.446 g/cm <sup>3</sup>
Diffractometer	Enraf Nonius CAD4	Siemens SMART 5000 CCD-Diffractometer
Wavelength	MoK <sub>α</sub> 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 <sup>-6</sup> e/pm <sup>3</sup>	0.948 × 10 <sup>-6</sup> e/pm <sup>3</sup>
Corrections	Lorentz and Polarisation, Absorption correction (SADABS) [11]	
Structure solution	direct methods	
Structure refinement	full matrix least square on F <sup>2</sup>	
Programs and weightings used	SHELXS-86 [12], SHELXL-93 [14]	SHELX-97 [13], xpma, zortep [15]
R indices	R <sub>1</sub> = 0.0436 (I > 2σ) R <sub>w</sub> = 0.1121 (all data on F <sup>2</sup> )	R <sub>1</sub> = 0.0261 (I > 2σ) R <sub>w</sub> = 0.0697 (all data on F <sup>2</sup> )

Standard deviations in parentheses.

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

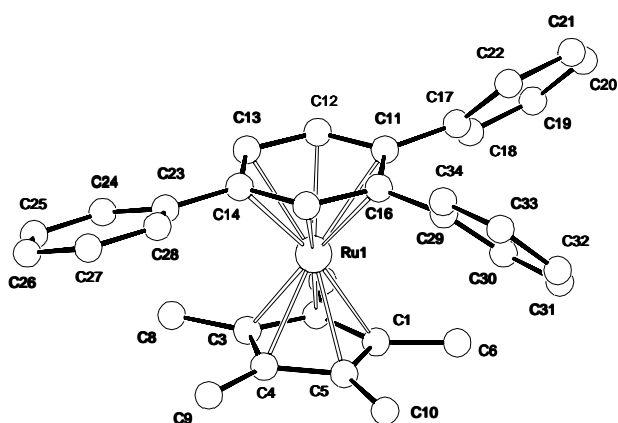
distance between the former C-atoms belonging to the triple bond is elongated to 140.2(7) pm (Table 2). The distance of the quaternary C-atom of the phenylacetylene to the Ru-centre is with 196.9(4) pm in the range for a double bond. Both carbon atoms of the former acetylene unit show sp<sup>2</sup>-hybridization. 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-C1	236.5(2)	C1-Ru-C1a	78.9(3)
Ru-C1	196.9(4)	C1-Ru-C1	102.7(1)
Ru-C9	235.1(4)	Cp-Ru-C1	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 **2Cl** were obtained from a CH<sub>2</sub>Cl<sub>2</sub> solution layered with *n*-hexane at -30 °C during two weeks [6]. **2Cl** crystallizes in the monoclinic space group P2<sub>1</sub>/n with one molecule CH<sub>2</sub>Cl<sub>2</sub> per unit (Table 1, Fig. 2). The coordination of both ring systems to the Ru-centre in **2** is nearby ideal. The angle at the Ru-atom formed by the two centres of the ring system is very



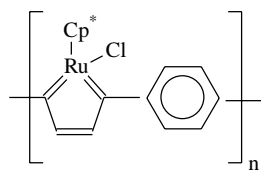
**Fig. 2** View to the molecular structure of the cation **2** in the crystal

**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 CDCl<sub>3</sub> solution at 25 °C referring to the rest proton signal of the solvent ( $\delta$  = 7.27 ppm) or its carbon frequency ( $\delta$  = 77.0 ppm). The spectra were obtained at the operating frequency of 400 MHz for proton spectroscopy or 100 MHz for <sup>13</sup>C NMR spectra, respectively. Infrared spectra were recorded on a BIORAD FT spectrometer in KBr-pellets in the region of 400–4000 cm<sup>-1</sup>. 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 CH<sub>2</sub>Cl<sub>2</sub> solution of **1**, layered with *n*-hexane at –30 °C during 7 days. Yield 0.068 g (0.14 mmol, 89%). – <sup>1</sup>H NMR:  $\delta$ /ppm = 7.56 (m, 2H, Ph-H), 7.26 (s, 2H, CH, metallacyclopentatriene), 7.18 (m, 8H, Ph-H), 1.19 (s, 15H, Cp-CH<sub>3</sub>). – <sup>13</sup>C NMR:  $\delta$ /ppm = 264.1, 160.3, 156.4, 130.8, 128.2, 126.0, 107.8, 11.1 (C<sub>5</sub>Me<sub>5</sub>). – IR  $\nu$ /cm<sup>-1</sup> = 2962 (m), 1447(m), 1261 (s), 1093 (s), 1022 (s), 802 (s).

### [Cp\**Ru*(1,2,4-triphenyl)benzene]<sup>+</sup>Cl<sup>-</sup> (**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 CH<sub>2</sub>Cl<sub>2</sub>. 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 CH<sub>2</sub>Cl<sub>2</sub> solution of **2Cl**, layered with *n*-hexane at –30 °C during 14 days. Yield 0.046 g (0.078 mmol, 49%). – <sup>1</sup>H NMR:  $\delta$ /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). – <sup>13</sup>C NMR:  $\delta$ /ppm = 134.6, 132.9, 130.9–128.4, 127.2, 127.1, 95.6, 10.1. – IR  $\nu$ /cm<sup>-1</sup> = 3053 (m), 2922 (m), 1492 (m), 1475 (m), 1449 (m), 1384 (s), 1074 (m), 1028 (m), 699 (s).

## References

- [1] K. S. Chio, M. K. Park, B. H. Han, J. Chem. Res., Synop. **1998**, 9, 518, 2348; E. S. Johnson, G. J. Balaich, I. P. Rothwell, J. Am. Chem. Soc. **1997**, *119*, 7685; A. v. d. Linden, C. J. Schaverien, N. Meijboom, C. Ganter, A. G. Orpen, J. Am. Chem. Soc. **1995**, *117*, 3008; P. Diversi, L. Ermini, G. Ingrassio, A. Lucherini, J. Organomet. Chem. **1993**, *447*, 291;

- P. M. Boorman, M. Wang, M. Parvez, *J. Chem. Soc. Dalton Trans.* **1996**, 24, 4533; K. S. Jerome, E. J. Parsons, *Organometallics*, **1993**, 12, 2991; I. Amer, T. Bernstein, M. Eisen, J. Blum, K.P.C. Vollhardt, *J. Mol. Catal.* **1990**, 60, 313; J. B. Hartung Jr., S. F. Pedersen, *Organometallics* **1990**, 9, 1414
- [2] M. O. Albers, D. J. A. de Waal, D. C. Liles, D. J. Robinson, E. Singleton, M. B. Wiege, *J. Chem. Soc. Chem. Commun.* **1986**, 1680; J.-U. Peters, S. Blechert, *J. Chem. Soc. Chem. Commun.* **1997**, 1983; T. Naota, H. Takaya, S.-I. Murahashi, *Chem. Rev.* **1998**, 98, 2599
- [3] R. Hoffmann, *Science* **1981**, 211, 959
- [4] R. Diercks, B. A. Eaton, S. Gürtzgen, S. Jalisatgi, A. J. Matzger, R. H. Radde, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1998**, 120, 8247
- [5] E. O. Fischer, *Z. Naturforsch.* **1955**, B 10, 355; H. Boenne-  
mann, N. J. Brijoux, *New Journal of Chemistry* **1987**, 11,  
549; K. P. C. Vollhardt, *Pure Appl. Chem.* **1993**, 65, 153; H.  
Yamazaki, Y. Wakatsuki, *Tetrahedron Lett.* **1973**, 3383
- [6] Crystallographic data of the structures have been deposited  
at the Cambridge Crystallographic Data Centre as supple-  
mentary publication no. CCDC 135128 (1) and 135129 (2).  
The data can be obtained on application to CCDC, 12 Union  
Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.  
cam.ac.uk).
- [7] S. C. Hockett, L. L. Miller, *Organometallics* **1988**, 7, 686; C.  
Gemel, A. La Pensee, K. Mauthner, K. Mereiter, R. Schmid,  
K. Kirchner, *Monatsh. Chem.* **1997**, 128, 1189
- [8] N. Hagihara, K. Sonogashira, S. Takahashi, *Adv. Poly. Sci.*  
**1981**, 41, 149; I. Manners, *Angew. Chem.* **1996**, 108, 1713;  
P. Nguyen, P. Gomez-Elipse, I. Manners, *Chem. Rev.* **1999**,  
99, 1515; S. Setayesh, U. H. F. Bunz, *Organometallics* **1996**,  
15, 5470; V. Wing-Wah Yam, K. Kam-Wing Lo, K. Man-  
Chung Wong, *J. Organomet. Chem.* **1999**, 578, 3; J. E. Sheats,  
C. E. Carraher Jr., C. U. Pittman Jr. (Eds.), *Metal-Contain-  
ing Polymer Systems*, Plenum Press, N.Y. and London, **1985**
- [9] N. J. Long, *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 21; H.  
Sasabe, T. Wada, M. Hosoda, H. Ohkava, A. Yamada, A. F.  
Garito, *Mol. Cryst. Liq. Cryst.* **1990**, 189, 155; K. Nishi-  
hara, T. Shimura, A. Ohkubo, N. Matsuda, K. Aramaki, *Adv.  
Materials* **1993**, 5, 752; G. C. Jia, W. F. Wu, R. C. Y. Yeung,  
H. P. Xia, *J. Organomet. Chem.* **1997**, 539, 53; T. Skotheim,  
R. L. Elsenbaumer, J.R. Reynolds (ed.), *Handbook of Con-  
ducting Polymers*, second edition, Marcel Dekker Inc., N.Y.,  
1998; and literature cited therein
- [10] N. Oshima, H. Suzuki, Y. Moro-Oka, *Chem. Lett.* **1984**, 1161
- [11] Siemens Area Detector Absorption Correction, Siemens.
- [12] SHELXS-86, G. M. Sheldrick, Universität Göttingen 1990
- [13] SHELXL-93, G. M. Sheldrick, Universität Göttingen 1993
- [14] SHELX-97, G. M. Sheldrick, Universität Göttingen 1997
- [15] xpma, zortep, L. Zsolnai, Universität Heidelberg 1997

Address for correspondence:  
Prof. Dr. E. Dinjus  
Forschungszentrum Karlsruhe  
Institut für Technische Chemie  
Bereich Chemisch-Physikalische Verfahren  
PF 3640  
D-76021 Karlsruhe  
Fax: Internat. code (0)7247 822244  
e-Mail: office@itc-cpv.fzk.de