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Journal of Organometallic Chemistry 627 (2001) 249–254

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Cp*Ru-allylcarbene complexes by nucleophilic attack of cyclic Cp*Ru-dicarbenes

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Received 21 December 2000; accepted 1 March 2001

Abstract

Phenylacetylene and its derivatives react with Cp*Ru(COD)Cl under formation of the neutral 2,5-bis-substituted dicarbene ruthenacycles chloro-Cp*ruthenacyclopenta-1,3,5-trienes (**1a** R = phenyl, **1b** R = *p*-bromophenyl). Nucleophilic attack of PMe_3 or $P(OMe)_3$ occurs at one α-atom of the ruthenacyclopentatrienes **1** and leads under metal–chlorine bond cleavage to the corresponding Cp*Ru-allylcarbene complexes **2**. The X-ray structures and spectroscopic data of the complexes confirm the results.

Keywords: Ruthenium; Metallacycles; Carbene complexes; Allyl complexes

1. Introduction

CpRu-complexes, in coupling reactions with acetylenes, form metallavinylidenes, -cyclopentadienes or -cyclopentatrienes [1]. The metal in the ruthenacyclopentatriene complexes is embedded in a planar, five-membered aromatic ring. Suitable substituents at the ruthenacyclopentatriene such as phenyl rings enable further conjugation. The introduction of functional groups at these phenyl rings allowing coupling reactions could offer the possibility of building conjugated polymeric materials containing a transition metal in the main chain. These metalorganic polymers could possess interesting properties for material sciences such as non-linear optics.

To obtain detailed information on the polymeric material, profound knowledge of the corresponding monomeric compounds possibly acting as precursors for the polymer and of their reactivities is essential.

Here we report on the effects of introducing a bromo substituent in the *p*-position of phenylacetylene and on the further reaction of the resulting metallacyclopentatrienes with nucleophiles such as PMe_3 and $P(OMe)_3$.

2. Results and discussion

p-Bromophenylacetylene reacts with Cp*Ru(COD)Cl in CH_2Cl_2 at 0°C during 2 h to yield in 20% the neutral dicarbene complex chloro-2,5-bis-(*p*-bromophenyl)-Cp*ruthenacyclopenta-1,3,5-triene (**1b**) (Scheme 1). In contrast, the reaction of phenylacetylene with Cp*Ru(COD)Cl yields around 80% of chloro-2,5-bis-(phenyl)-Cp*ruthenacyclopenta-1,3,5-triene (**1a**) [2].

The introduction of a bromo substituent at the phenyl ring in *p*-position to the acetylene leads to much lower yields in the formation of the corresponding Cp*ruthenacyclopentatriene, which is more sensitive than its bromine free derivative but can be stored for weeks at −30°C in the dark.

Single crystals of **1b** were grown from a $CHCl_3$ solution at −80°C during 14 days (see Section 5). **1b** crystallises in the triclinic space group $P\bar{1}$ with half a molecule of bromobenzene as decomposition product per unit (Table 4).

The coordination of the Ru-centre in **1b** can be described as a distorted tetrahedron reducing the coordination of the Cp-ring to its centre (Table 1, Fig. 1). The Cp-ring is not coordinated symmetrically to the Ru-atom, which is reflected in different Cp*–C–Ru distances in the range 219.4–238.4 pm (Table 1). The asymmetrical coordination of the Cp*-ring to the Ru-

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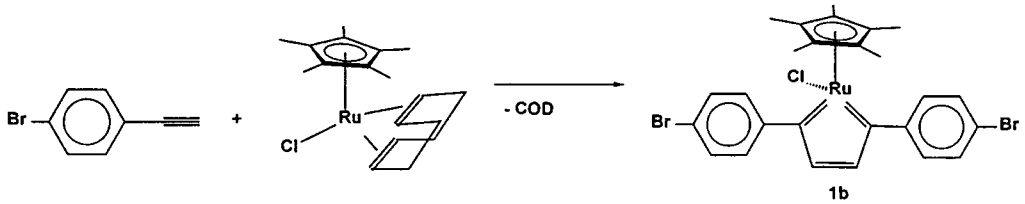
0022-328X/01/$ - see front matter
PII: S0022-328X(01)00757-4



Scheme 1. Reaction of *p*-bromophenylacetylene with Cp*Ru(COD)Cl.

centre is caused by the embedding of the Ru-atom in the metallacyclopentatriene unit, where Ru–C bond lengths of 194.6 and 196.7 pm were found, corresponding to Ru–C double bonds [3] (Table 1). The double bond character of these Ru–C bonds is caused by a strong back donation from the Ru-atom to these carbene C-atoms. This lowers the electron transfer from the Ru-centre to the part of the Cp-ring in opposite position to the dicarbene C–Ru–C unit and finally causes longer Ru–C distances for these Cp–C atoms and its asymmetric coordination. These findings are typical for complexes of this type [2,4]. The coupling of the *p*-bromophenylacetylene leads to the formation of a new C–C bond which has a C–C distance of 132.9(11) pm of double bond character. The C–C distances between the C-atoms of the former acetylene unit are elongated to ca. 145 pm (Table 1). All carbon atoms of the former acetylene units show sp^2-hybridisation (Table 1). So the coupling of two acetylene units in the coordination sphere of a metal atom leads to the formation of a new C–C bond and change of hybridisation of all sp-C atoms of the acetylenes.

With the aim of studying the electronic properties and reactivities of the metallacycles, the ruthenacyclopentatrienes were treated with PMe_3 or $P(OMe)_3$ (Scheme 2). When **1a**,**b** are reacted with PMe_3, the cationic allylcarbene complexes **2a**,**b** are formed immediately (Scheme 2), the colour of the reaction solution turning from red to dark blue. Under elimination of chloromethane, the complex **2c** was formed by reaction of **1b** with $P(OMe)_3$, accompanied by a colour change of the reaction solution from red to green, giving blue crystals after recrystallisation.

The solution of the reaction of **1a** with $P(OMe)_3$ does not show any dramatic colour change; after removal of the solvent a red powder with spectroscopic data differing from **2c** and presently unknown constitution is obtained.

The transformation of the ruthenacyclopentatrienes to their corresponding allylcarbene complexes is reflected in the most significant $^{13}C\{^1H\}$-NMR spectra. For the carbene C-atoms of the ruthenacyclopentatrienes **1**, resonances around 260 ppm are observed [2], while for the allylcarbene complexes **2** a carbene C-resonance at $\sim$240 ppm in the $^{13}C\{^1H\}$-NMR spectra appears. The allyl unit of the allylcarbenes **2** causes three resonances in the $^{13}C\{^1H\}$-NMR spectra well separated at $\sim$140, $\sim$91 and $\sim$49 ppm (see Section 4). Using $^{13}C\{^1H\}$-NMR-DEPT spectroscopy, the first two signals may be assigned to the two allylic tertiary C-atoms and the last at 49 ppm appearing as a doublet with a $^1J_{PC}$ coupling constant of 65 Hz to the quaternary C-atom at which the P-atom has been added. This assignment is in agreement with Ref. [5] and the results are confirmed by X-ray analyses of some of the allylcarbenes **2**.

Single crystals of **2a**·Cl·3$CHCl_3$ were obtained from a $CHCl_3$ solution at -80°C during 2 weeks. **2a**·Cl·3$CHCl_3$ crystallises in the triclinic space group $P\bar{1}$ (Table 4). The nucleophilic attack of the phosphine at the α-C atom to the Ru-centre of the metallacyclopentatriene leads under elimination of the chloride ligand to a change in the arrangement of the former planar cyclopentatriene unit. For the cation **2a** the Ru-atom is localised above the plane of the four C-atoms of the earlier cyclopentatriene unit (Fig. 2). This enables the double bond connecting its two β-C atoms to perform π-bonding to the Ru-centre, resulting in an allylic coordination and coordinative saturation of the Ru-centre. The bond distance of the α-C atom to the Ru-centre not involved in this allylic system is with 193.4 pm in the range of a double bond (Table 2, Fig. 2) and significantly shorter than the Ru–C bond lengths of the π-coordinated allylic unit [2,3].

Table 1
Selected bond lengths [pm] and angles [°] for **1b** [a]

Ru1–C1	194.6(8)	C1–Ru1–C4	79.5(4)
Ru1–C4	196.7(8)	C1–Ru1–C5	95.6(3)
Ru1–Cl1	235.6(2)	C4–Ru1–C5	102.4(3)
Ru1–C5	219.4(4)	Cl1–Ru1–C8	94.6(2)
Ru1–C6	226.5(9)	Cl1–Ru1–C7	97.1(2)
Ru1–C7	238.4(8)	C2–C1–C15	119.1(8)
Ru1–C8	235.8(8)	C2–C1–Ru1	115.9(6)
Ru1–C9	227.4(8)	C15–C1–Ru1	124.9(4)
C1–C2	145.0(10)	C3–C2–C1	113.5(7)
C2–C3	132.9(11)	C2–C3–C4	114.6(8)
C3–C4	142.7(11)	C3–C4–C21	120.0(7)
C1–C15	145.9(11)	C3–C4–Ru1	115.6(7)
C4–C21	146.6(11)	C21–C4–Ru1	124.4(6)
C24–Br1	189.7(9)		
C18–Br2	190.3(9)		

[a] Standard deviations in parentheses.

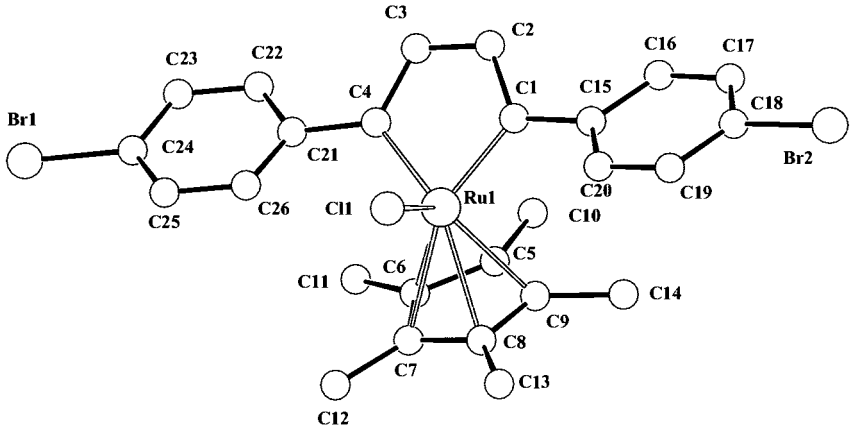


Fig. 1. View of the molecular structure of **1b** in the crystal.

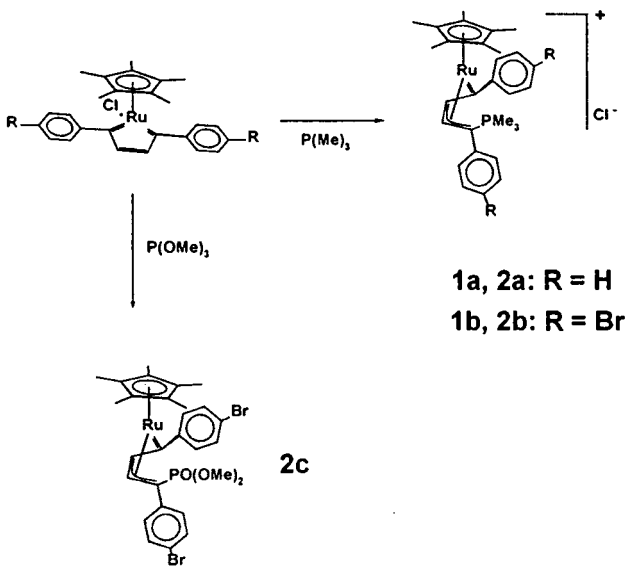
Due to the addition of a phosphine to the planar metallacyclopentatriene, the Ru-centre moves above the plane under formation of an allylcarbene-species.

Single crystals of **2c** were obtained from a CH_2Cl_2 solution layered successively with diethylether and pentane at $-80°C$ during 2 weeks. **2c** crystallises in the triclinic space group $P\bar{1}$ (Table 4). The overall structure and binding features of **2c** can be described as for the complex cation **2a**.

As for **2a**, due to the nucleophilic attack of a phosphite on the planar metallacyclopentatriene, the Ru-centre moves above the plane under formation of an allylcarbene species with corresponding changes in bond lengths and angles for **2c** (Table 3, Fig. 3).

For both complexes **2a**,**c** the backdonation from the Ru-centre to the Cp-ring is no longer disturbed as the cyclic dicarbene structure of the educts no longer exists. This is demonstrated in the symmetrical coordination and the nearly identical bond distances of about 222 pm from the Cp-ring atoms to the Ru-centre (Tables 2 and 3). These findings conform with allylcarbene complexes published by Kirchner et al. [5]. They describe the formation of the allylcarbene complex as a result of the reaction of cationic CpRu-bis(acetonitrile)phosphine complexes with acetylenes, proposing an intermediate ruthenacyclopentatriene. Our results confirm their postulated reaction pathway by reacting the phosphines or phosphites with isolated ruthenacyclopentatrienes **1** forming the allylcarbene complexes **2**.

In the literature other regioselectivities for the nucleophilic attack of phosphines in similar CpRu-systems at the metal itself are discussed. The reaction of bromo-2,5-diphenyl-Cpruthenacyclopenta-1,3,5-triene with phosphines forms bromo-phosphine-2,5-diphenyl-Cpruthenacyclopenta-2,4-diene [4]. In another case the reaction of $Cp^*Ru(PPh_3)_2Cl$ with acetylene leads directly to the corresponding chloro-phosphine-Cpruthenacyclopentadiene [6]. The differences in regioselectivity for the nucleophilic addition could be explained by different electronic and steric reasons in the substrates or different possible reaction pathways and the details are objectives of present research.



Scheme 2. Reaction of **1a**,**b** with PMe_3 or $P(OMe)_3$.

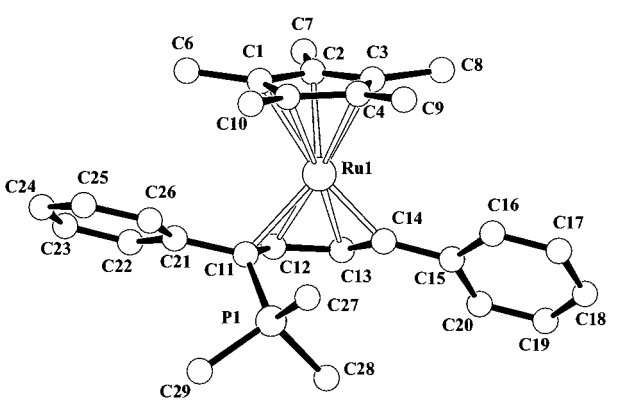


Fig. 2. View of the molecular structure of the cation **2a** in the crystal.

Table 2
Selected bond lengths [pm] and angles [°] for **2a** [a]

Ru1–C(1–5)	~222	C12–C11–C21	117.6(3)
Ru1–C11	221.4(3)	C12–C11–P1	120.3(3)
Ru1–C12	213.9(4)	C21–C11–P1	112.2(2)
Ru1–C13	219.4(4)	C12–C11–Ru1	68.0(2)
Ru1–C14	193.4(3)	C21–C11–Ru1	120.0(2)
P1–C11	181.0(3)	P1–C11–Ru1	112.2(2)
C11–C12	143.6(5)	C13–C14–C15	126.2(3)
C12–C13	141.7(5)	C13–C14–Ru1	80.2(2)
C13–C14	141.7(5)	C15–C14–Ru1	145.6(3)
		C14–Ru1–C11	86.8(1)

[a] Standard deviations in parentheses.

Table 3
Selected bond lengths [pm] and angles [°] for **2c** [a]

Ru1–C(1–5)	~223	C11–Ru1–C14	85.61(8)
Ru1–C11	192.8(2)	C12–C11–C21	127.3(2)
Ru1–C12	220.0(2)	C21–C11–Ru1	144.0(2)
Ru1–C13	215.3(2)	C12–C11–Ru1	80.8(1)
Ru1–C14	221.7(2)	C13–C14–Ru1	68.3(1)
P1–C14	179.8(2)	C15–C14–Ru1	116.9(1)
P1–O1	147.0(2)	P1–C14–Ru1	112.6(1)
C11–C12	141.0(3)	O1–P1–C14	117.6(9)
C12–C13	141.3(3)		
C13–C14	144.4(3)		

[a] Standard deviations in parentheses.

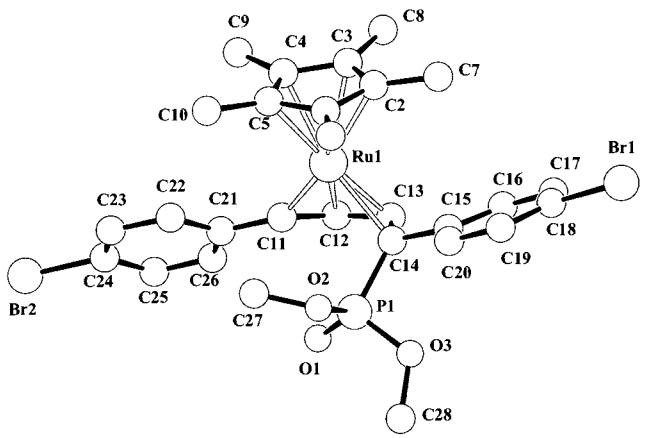


Fig. 3. View of the molecular structure of **2c** in the crystal.

3. Summary

We have shown that in the reaction of phenylacetylenes with Cp*Ru(COD)Cl the amounts of the formed chloro - 2,5 - (bis - substituted) - Cp*ruthenacyclopenta-1,3,5-trienes **1** are decreased by introducing a bromo substituent at the phenylacetylene and we have studied their reactivity towards PMe_3 and $P(OMe)_3$ respectively. In this reaction Cp*Ru-allylcarbene complexes **2** are formed by attack of the nucleophile at one of the α-C atoms of the metallacyclopentatriene unit under metal chlorine bond cleavage. The Ru-centre is shifted out of the former planar metallacyclopentatriene unit and its coordination sphere is saturated due to the still double bonded α-C atom and the new allylic π-coordination.

The simple attack of a nucleophile in α-position to the Ru-atom of the metallacyclopentatriene unit causes a structural rearrangement towards a sandwich type coordination of the ligands, retaining the carbene type coordination of the C-atom where nucleophilic addition has not taken place.

The results confirm a proposed reaction mechanism of CpRu-fragments in the presence of acetylenes and phosphines by introducing the phosphines or phosphites at a later reaction step [5].

4. Experimental

Chemicals were purchased from Aldrich and used as received. Solvents and reagents were purified by standard methods. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Cp*Ru(COD)Cl and *p*-bromophenylacetylene were synthesised according to the literature [7,8] and **1a** was synthesised following the method of Ref. [2]. The NMR spectra were registered on a Varian Unity Inova spectrometer in $CDCl_3$ solution at -60°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 ^{13}C-NMR spectra respectively. ^{31}P-NMR spectroscopy was carried out against 85% phosphoric acid as external standard at an operating frequency of 161.8 MHz. Infrared spectra were recorded on a BIORAD FT spectrometer in KBr pellets in the region of 400–4000 cm^{-1}. For details of the single crystal X-ray diffraction measurements see Table 4, Refs. [9–11], and Section 5. The single crystal X-ray determinations were carried out with an irradiation time of 10 s per frame for **2a** and **2c**, collecting a full sphere of data, and 40 s per frame for **1b**, collecting a hemisphere of data. Mass spectrometry was carried out on a Hewlett Packard series 1100 MSD mass spectrometer. The allylcarbene complexes **2** were purified by crystallisation; purification by chromatography on silicagel or aluminium oxide was not successful because of the sensitivity of the substances.

*4.1. Chloro-2,5-bis(p-bromophenyl)-Cp*ruthenacyclopenta-1,3,5-triene (**1b**)*

1.51 g (8.38 mmol) of *p*-bromophenylacetylene was added at 0°C to a solution of 0.06 g (0.16 mmol) Cp*Ru(COD)Cl in 40 ml THF. The mixture was stirred at 0°C for 6 h. The solvent was removed in vacuum at 0°C and the residue washed twice with 10 ml cold (0°C)

n-hexane, followed by a short, cooled (dry-ice) silica-gel column with CH_2Cl_2 as eluent. The red fraction was collected and the solvent removed in vacuum at 0°C to give a dark red powder yielding 0.020 g (0.032 mmol, 20%) **1b**. Single crystals suitable for X-ray diffraction were obtained by crystallisation from a $CHCl_3$ solution of **1b** at −80°C during 14 days.

Crystals for CH analyses were obtained by recrystallisation from a solution of **1b** in CH_2Cl_2 layered with Et_2O and pentane at −80°C during 10 days, affording crystals of the composition **1b**·0.5CH_2Cl_2.

^{1}H-NMR: δ (ppm) 7.26 (m, 4H, Ph–H), 7.16 (s, 2H, CH, metallacyclopentatriene), 7.03 (m, 4H, Ph–H), 1.19 (s, 15H, Cp–CH_3).

^{13}C-NMR: δ (ppm) 258.6 (Ru=*C*), 157.4 (Ru=C–*C*), 156.0 (Ru=C–*C*), 133.5, 131.5, 126.3, 120.8, 107.8 (C_5Me_5), 10.4 (C_5Me_5).

IR [cm^{-1}]: 2958 (m), 1568 (m), 1458 (m), 1261 (s), 1098 (s), 1023 (s), 801 (s).

ESI-MS *m*/*z*: 631 (M^+), 597 (M − Cl).

1b·0.5CH_2Cl_2 ($C_{26.5}H_{26}Br_2Cl_2Ru$): C 47.81 (calc. 47.06), H 4.14 (calc. 3.88%).

4.2. [Cp*Ru-allylcarbene]$^+$ Cl^- (**2a**·Cl)

To a solution of 0.055 g **1a** (0.1 mmol) in 10 ml CH_2Cl_2, 0.1 ml of PMe_3 solution (1 M in THF) was added at 0°C. The mixture immediately turned dark blue. The solvent was removed at 0°C in vacuum and the residue washed with 5 ml pentane to give a dark blue powder yielding 0.062 g (0.1 mmol, 100%) **2a**·Cl. Single crystals were obtained by crystallisation from a $CHCl_3$ solution of **2**·Cl, at −80°C during 14 days, forming crystals of composition **2a**·Cl·3$CHCl_3$.

^{1}H-NMR ($CDCl_3$): δ (ppm) 7.70–7.23 (m, 10 H), 6.87 (d, $^3J_{PH} = 12.3$ Hz, 1H), 4.82 (s (br), 1H), 1.42 (s, 15H), 1.39 (d, $^3J_{PH} = 13.2$ Hz, 9H).

^{13}C-NMR ($CDCl_3$): δ (ppm) 240.0 (Ru=*C*), 140.8 (Ru=C–*C*), 131.1–127.1 (aryl-C), 96.7 (C_5Me_5), 91.8 (allyl-C), 50.0 (P–*C*, d, $^1J_{PC} = 65.9$ Hz), 13.7 (PMe_3, d, $^1J_{PC} = 58.5$ Hz), 10.1 (C_5Me_5).

Table 4
Crystallographic data for the neutral complexes **1b** and **2c** and the cationic complex **2a** [a]

	1b·0.5C_6H_5Br	**2a**·Cl·3$CHCl_3$	**2c**
Empirical formula	$C_{29}H_{27}Br_{2.5}ClRu$	$C_{32}H_{39}Cl_{10}PRu$	$C_{28}H_{31}Br_2O_3PRu$
Formula weight	711.80	910.17	707.39
Crystal size (mm^3)	0.12 × 0.12 × 0.03	0.3 × 0.3 × 0.2	0.4 × 0.4 × 0.2
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Unit cell dimensions			
a (pm)	971.7(1)	1186.43(9)	955.88(6)
b (pm)	1205.1(2)	1201.07(9)	1190.57(7)
c (pm)	1279.8(2)	1548.7(1)	1338.80(8)
α (°)	95.746(2)	84.047(1)	111.212(1)
β (°)	111.221(2)	71.703(1)	101.854(1)
γ (°)	97.221(2)	73.680(1)	90.100(1)
Volume (pm^3)	1368.6(3) × 10^6	2010.6(3) × 10^6	1385.2(1) × 10^6
Z	2	2	2
Density (calculated) (g cm^{-3})	1.727	1.503	1.696
Diffractometer	Siemens SMART 5000 CCD diffractometer		
Wavelength	Mo–K_α, graphite monochromator		
Temperature (K)	200	200	200
θ range (°)	1.72 ≤ θ ≤ 28.33	1.39 ≤ θ ≤ 28.31	1.39 ≤ θ ≤ 28.31
Scan	ω-scan, $\Delta\omega = 0.45°$	ω-scan, $\Delta\omega = 0.3°$	ω-scan, $\Delta\omega = 0.3°$
Index ranges	−12 ≤ *h* ≤ 9	−15 ≤ *h* ≤ 15	−12 ≤ *h* ≤ 12
	−15 ≤ *k* ≤ 16	−16 ≤ *k* ≤ 15	−15 ≤ *k* ≤ 15
	−15 ≤ *l* ≤ 16	−20 ≤ *l* ≤ 20	−17 ≤ *l* ≤ 17
Reflections measured	9460	21732	14391
Independent reflections	6445	9575	6533
Reflections observed	2111	6612	5793
Refined parameters	307	497	335
Residual electron density (e pm^{-3})	1.586 × 10^{-6}	1.065 × 10^{-6}	0.976 × 10^{-6}
Corrections	Lorentz and polarisation, absorption correction (SADABS) [9]		
Structure solution	Direct methods		
Structure refinement	Full-matrix least-squares on F^2		
Programs used	SHELX-97 [11] XPMA, ZORTEP [10]		
R indices	$R_1 = 0.0488$ ($I > 2\sigma$)	$R_1 = 0.0472$ ($I > 2\sigma$)	$R_1 = 0.0263$ ($I > 2\sigma$)
	$R_w = 0.1299$ (all data on F^2)	$R_w = 0.1245$ (all data on F^2)	$R_w = 0.0705$ (all data on F^2)

[a] Standard deviations in parentheses.

^{31}P-NMR ($CDCl_3$): δ (ppm) 32.8.

IR [cm^{-1}]: 3054 (m), 2954 (m), 2900 (m), 1597 (m), 1493 (m), 1432 (m), 1296 (m), 926 (s), 729 (s), 636 (m).

ESI-MS m/z: 516 (M^+)

4.3. [Cp*Ru-allylcarbene]$^+$ Cl^- (**2b**·Cl)

To a solution of 0.063 g **1b** (0.1 mmol) in 10 ml CH_2Cl_2, 0.1 ml of a 1 M solution of PMe_3 in THF was added at 0°C. The mixture immediately turned dark blue. The solvent was removed in vacuum at 0°C and the residue washed successively with 5 ml pentane and 5 ml diethylether at 0°C to give a dark blue powder of **2b** yielding 0.033 g (0.05 mmol, 50%).

^{1}H-NMR ($CDCl_3$): δ (ppm) 7.51–7.29 (m, 8H), 6.88 (dd, $^3J_{HH} = 3.8$ Hz, $^3J_{PH} = 13.6$ Hz, 1H), 4.83 (d, $^3J_{HH} = 3.8$ Hz, 1H), 1.40 (s, 15H), 1.33 (d, $^3J_{PH} = 12.3$ Hz, 9H).

^{13}C-NMR ($CDCl_3$): δ (ppm) 237.1 (Ru=*C*), 139.5 (Ru=C–*C*) 133.1–127.1 (aryl-C), 96.0 (C_5Me_5), 91.4 (allyl-C), 47.8 (P–*C*, d, $^2J_{PC} = 65.6$ Hz), 13.5 (P*Me*$_3$, d, $^2J_{PC} = 58.3$ Hz), 10.1 (C_5*Me*$_5$).

^{31}P-NMR ($CDCl_3$): δ (ppm) 33.08.

ESI-MS m/z: 673 ($M^+ - Cl$),

4.4. Cp*Ru-allylcarbene (**2c**)

To a solution of 0.063 g **1b** (0.1 mmol) in 10 ml CH_2Cl_2, 0.1 ml of a 1 M solution of $P(OMe)_3$ in CH_2Cl_2 was added at 0°C. The mixture immediately turned dark green. The solvent was removed in vacuum at 0°C and the residue washed successively with 5 ml pentane and 5 ml diethylether at 0°C to give a dark blue powder of **2c** yielding 0.035 g (0.05 mmol, 50%). Single crystals were obtained by crystallisation from a CH_2Cl_2 solution of **2c**, layered with diethylether and pentane at −80°C during 14 days.

^{1}H-NMR ($CDCl_3$): δ (ppm) 7.69–7.37 (m, 8H), 6.77 (dd,$^3J_{HH} = 4.2$ Hz, $^3J_{PH} = 17.9$ Hz, 1H), 4.78 (d, $^3J_{HH} = 4.2$ Hz, 1H), 3.30 (d, $^3J_{PH} = 11.1$ Hz, 3H), 3.31 (d, $^3J_{PH} = 11.1$ Hz, 3H), 1.42 (s, 15H).

^{31}P-NMR ($CDCl_3$): δ (ppm) 31.3.

IR [cm^{-1}]: 2963 (m), 2943 (m), 2908 (m), 1261 (m), 1084 (s), 1032 (s), 802 (s), 561 (w).

ESI-MS m/z: 707 (M^+),

2c ($C_{28}H_{31}Br_2O_3PRu$): C 47.92 (calc. 47.54), H 4.94 (calc. 4.42%).

5. Supplementary material

Crystallographic data for the structures have been deposited at the Cambridge Crystallographic Data Centre, supplementary publication Nos. CCDC 155920 (**1b**), CCDC 155921 (**2a**) and CCDC 155922 (**2b**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We wish to thank the Forschungszentrum Karlsruhe GmbH for financial support of this work and are very grateful to Dr T. Zevaco and Mr G. Zwick for recording the NMR spectra and mass spectra respectively. Elemental analysis was carried out by the Institute of Inorganic Chemistry, University of Karlsruhe.

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