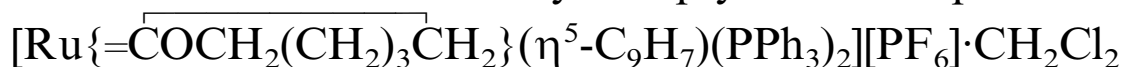


## Synthesis and characterization of 2-oxacycloalkylideneruthenium(II) complexes: X-ray crystal structure of the 2-oxacycloheptylidene complex



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### Abstract

The oxacyclocarbene complexes  $[\text{Ru}\{\overline{\text{COCH}_2(\text{CH}_2)_n\text{CH}_2}\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}'][\text{PF}_6]$  ( $\text{L} = \text{L}' = \text{PPh}_3$ ,  $n = 1$  (**2a**), 2 (**3a**), 3 (**5a**);  $\text{L} = \text{L}' = \text{PMe}_2\text{Ph}$ ,  $n = 1$  (**2b**), 2 (**3b**), 3 (**5b**);  $\text{LL}' = \text{dppm}$ ,  $n = 1$  (**2c**), 2 (**3c**), 3 (**5c**);  $\text{L} = \text{PPh}_3$ ,  $\text{L}' = \text{PMe}_3$ ,  $n = 1$  (**2d**), 2 (**3d**), 3 (**5d**)) have been prepared by reaction of  $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)\text{LL}']$  with 3-butyne-1-ol, 4-pentyne-1-ol and 5-hexyne-1-ol in refluxing ethanol and in the presence of  $\text{NaPF}_6$ . The process involves alkyne to vinylidene tautomerization to give hydroxyalkylvinylidene intermediate complexes. The vinylidene complexes  $[\text{Ru}\{\text{C}=\text{C}(\text{H})(\text{CH}_2)_3\text{CH}_2\text{OH}\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}'][\text{PF}_6]$  ( $\text{L} = \text{L}' = \text{PPh}_3$  (**4a**),  $\text{L} = \text{L}' = \text{PMe}_2\text{Ph}$  (**4b**),  $\text{L} = \text{PPh}_3$ ,  $\text{L}' = \text{PMe}_3$  (**4d**)) have been isolated from the reaction of  $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)\text{LL}']$  with 5-hexyne-1-ol. The first structure for a 2-oxacycloheptylidene complex, **5a**, has been determined by X-ray diffraction methods. The molecular structure shows the typical pseudoctahedral three-legged piano-stool geometry around the ruthenium atom, which is linked to the phosphorus atoms of the triphenylphosphine ligands and to the  $\text{C}_\alpha$  of the oxacyclic carbene ligand; the coordination around the ruthenium atom is completed by a  $\eta^5$ -bonded indenyl ligand with the benzo ring orientated nearly *trans* to the carbene group ( $\text{CA} = 16.6(6)^\circ$ ). The  $\text{Ru}-\text{Cl}$  distance, 1.89(1) Å, is somewhat shorter than that found for other oxacyclic carbene ruthenium(II) complexes. The oxacycloheptylidene ring adopts a ‘pseudochair’ conformation for the seven member ring and shows an appreciable deviation from vertical orientation ( $\text{DA} = 29.7(5)^\circ$ ). © 2002 Published by Elsevier Science B.V.

**Keywords:** Ruthenium; Oxacycloalkylidene complexes; Oxacycloalkenyl complexes; Indenyl complexes

### 1. Introduction

The chemistry of 2-oxacycloalkylidene transition metal complexes  $[\text{M}]\overline{\text{CO}(\text{CH}_2)_n\text{CH}_2}$  has experienced a remarkable development in the last years due to their ready accessibility [1] and to the potential usefulness of the oxacyclic fragment in chemical transformations [2]. Moreover, their utility in stoichiometric [3] as well as in

catalytic [4] processes, has been confirmed [1].

Most of the 2-oxacycloalkylidene complexes hitherto described contain a five-membered or, to a minor extent, a six-membered ring carbene ligand [1]. To the best of our knowledge, only two 2-oxacycloheptylidene complexes,  $[(\text{CO})_5\text{Mn}-\text{Mn}(\text{CO})_4\{\overline{\text{CO}(\text{CH}_2)_4\text{CH}_2}\}]$  [5a] and  $[\text{Re}\{\overline{\text{CO}(\text{CH}_2)_4\text{CH}_2}\}(\text{triphos})(\text{CO})_2][\text{BF}_4]$  (triphos =  $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ ) [5b] have been reported [5c], although their structures have not been confirmed by X-ray diffraction.

In the course of our studies on the reactivity of unsaturated carbene complexes containing indenyl-ruthenium(II) moieties as metal auxiliary [6] we have explored the behaviour of the cationic vinylidene com-

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plexes  $[\text{Ru}(\text{C}=\text{CR}^1\text{R}^2)(\eta^5\text{-C}_9\text{H}_7)\text{L}_2]^+$  towards alcohols [6a] and have examined the effect of the steric and electronic properties of the vinylidene substituents  $\text{R}^1$  and  $\text{R}^2$  and of the ligands  $\text{L}$  in their reactivity. We observed that only the unsubstituted vinylidene  $[\text{Ru}(\text{C}=\text{CH}_2)(\eta^5\text{-C}_9\text{H}_7)\text{L}_2]^+$  and the monosubstituted  $[\text{Ru}(\text{C}=\text{CHR})(\eta^5\text{-C}_9\text{H}_7)(\text{dppm})]^+$  complexes reacted with ethanol or methanol to give the corresponding alkoxycarbene derivatives. In contrast, all disubstituted vinylidene complexes were unreactive (see Chart 1).

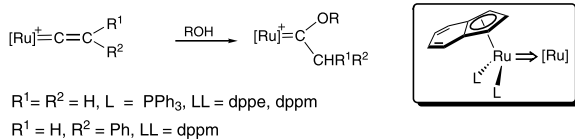


Chart 1.

On the basis of this reactivity, we believed it to be of interest to develop the intramolecular version since the cyclization of  $\omega$ -alkyn-1-ols constitutes one of the most useful methods for the preparation of oxacycloalkylidene complexes [1] (Scheme 1). It has been observed experimentally that the intramolecular attack by the hydroxy group is increasingly disfavoured as the number of  $\text{CH}_2$  spacers between the triple bond and the OH group in the alkynol increases. For instance, the reaction of  $[\text{Mo}(\text{Me}_2\text{CO})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$  with 3-butyn-1-ol led to the oxacyclopentylidene complex, while mixtures of oxacyclohexylidene and the hydroxyvinylidene complexes were formed when 4-pentyn-1-ol was employed [7].

In this paper, we report the synthesis and characterization of a series of 2-oxacycloalkylidene complexes (**2a–d**, **3a–d**, **5a–d**), as well as a number of their corresponding hydroxyvinylidene precursors (**4a–b**, **4d**), (see Chart 2). Complexes **5a–d** are the first ruthenium oxacycloheptylidene complexes described to date. In addition, the X-ray crystal structure of **5a**, which to the best of our knowledge is the first oxacycloheptylidene transition metal complex crystallographically characterized, is also reported.

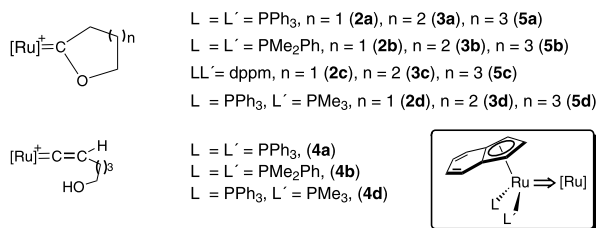
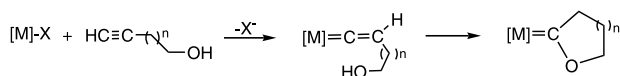


Chart 2.



Scheme 1.

## 2. Results and discussion

### 2.1. Synthesis of 2-oxacyclopentylidene (**2a–d**) and 2-oxacyclohexylidene (**3a–d**) complexes

The reaction of complexes  $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)\text{LL}']$  ( $\text{L} = \text{L}' = \text{PPh}_3$  (**1a**);  $\text{PMe}_2\text{Ph}$  (**1b**);  $\text{LL}' = \text{dppm}$  (**1c**);  $\text{L} = \text{PPh}_3, \text{L}' = \text{PMe}_3$  (**1d**)) with 3-butyn-1-ol and 4-pentyn-1-ol in refluxing ethanol and in the presence of  $\text{NaPF}_6$  gave, after 20–30 min, 2-oxacyclopentylidene ( $n = 1$ , **2a–d**) and 2-oxacyclohexylidene ( $n = 2$ , **3a–d**) complexes  $[\text{Ru}\{\text{COCH}_2(\text{CH}_2)_n\text{CH}_2\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}']\text{-}[\text{PF}_6]$ . They were isolated as yellow, air stable hexafluorophosphate salts (60–90% yield). The reaction was monitored at  $-20^\circ\text{C}$ , but the expected hydroxyvinylidene intermediate could not be detected by  $^{31}\text{P}$ -NMR presumably because of the rapid intramolecular attack by the hydroxy group.

All the complexes are soluble in chlorinated solvents and tetrahydrofuran. They have been characterized by elemental analyses, conductance measurements, IR and NMR ( $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$  and  $^{13}\text{C}\{^1\text{H}\}$ ) spectroscopy (details are given in the Section 4 and in Tables 1 and 2). A medium intensity  $\nu(\text{COC})$  absorption [5b] at ca. 1163 (**2a–d**) and ca. 1246  $\text{cm}^{-1}$  (**3a–d**) in the IR spectra (KBr) confirms the presence of the oxacyclic carbene group (see Section 4).

The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the complexes **2a–c** and **3a–c** show at room temperature a single resonance which is consistent with a rapid rotation of the carbene group around the  $\text{Ru}=\text{C}$  bond on the NMR time scale. This is also in agreement with the data reported for related indenylruthenium(II) Fischer type carbene and vinylidene complexes [6a]. The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the complexes **2d** and **3d** exhibit two doublet signals ( $^2J_{\text{PP}}$  ca. 30 Hz) corresponding to the inequivalent phosphorus atoms of  $\text{PPh}_3$  and  $\text{PMe}_3$  ligands (see Table 1). The typical low-field carbene resonance in the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra appears as a triplet at  $\delta$  295.06–308.05 ( $^2J_{\text{CP}} = 12.0\text{--}13.5$  Hz), a chemical shift similar to that reported for other oxacyclic carbene ruthenium complexes [8]. The values of other oxacycloalkylidene carbon nuclei are in accordance with those reported for other oxacycloalkylidene ruthenium complexes [8a].

Several 2-(oxacyclopentylidene)ruthenium(II) complexes have been described in the literature [1]. However, to the best of our knowledge, only the oxacyclohexylidene ruthenium complexes  $[\text{Ru}\{\text{CO}(\text{CH}_2)_3\text{CH}_2\}(\eta^5\text{-C}_5\text{H}_5)\text{LL}']^+$  ( $\text{L} = \text{PPh}_3$  [8a],  $\text{LL}' = \text{dppe}$  [8d]) are known to date.

### 2.2. Synthesis of the hydroxybutylvinylidene (**4a–b**, **4d**) and 2-oxacycloheptylidene (**5a–d**) complexes

When a mixture of 5-hexyn-1-ol,  $\text{NaPF}_6$  and  $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)\text{LL}']$  was refluxed in ethanol for 15 min,

Table 1  
 $^3\text{P}\{^1\text{H}\}$ - and  $^1\text{H}$ -NMR data for the oxacyclocarbene complexes <sup>a</sup>

Compound	$^1\text{H}$									
	$\eta^5\text{-C}_9\text{H}_7$ <sup>i</sup>									
	$^3\text{P}\{^1\text{H}\}$	H-1,3	H-2	$J_{\text{HH}}$	H-4,7, H-5,6	$\text{OCH}_2$ <sup>d</sup>	$=\text{CCH}_2$ <sup>d</sup>	$-\text{CH}_2-$	Others	
$[\text{Ru}\{\text{C}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\}(\eta^5\text{-C}_9\text{H}_7)\text{-}(\text{PPh}_3)_2][\text{PF}_6]$ ( <b>2a</b> )	44.88 s	5.22 br	6.19 br	–	6.92 m <sub>b</sub>	3.63 t (7.3)	3.50 m	1.56 m	6.67–7.46 (m, PPh <sub>3</sub> )	
$[\text{Ru}\{\text{C}(\text{OCH}_2(\text{CH}_2)_2\text{CH}_2)\}(\eta^5\text{-C}_9\text{H}_7)\text{-}(\text{PPh}_3)_2][\text{PF}_6]$ ( <b>3a</b> )	45.50 s	5.21 m	6.14 t	2.7	6.91 m <sub>b</sub>	3.41 m	3.41 m	1.05 m 1.60 m	6.67–7.46 (m, PPh <sub>3</sub> )	
$[\text{Ru}\{\text{C}(\text{OCH}_2(\text{CH}_2)_3\text{CH}_2)\}(\eta^5\text{-C}_9\text{H}_7)\text{-}(\text{PPh}_3)_2][\text{PF}_6]$ ( <b>5a</b> )	45.03 s	5.23 br	6.09 br	–	6.94 m <sub>b</sub>	3.64 m	3.20 m	1.08 m 1.53 m 1.87 m	6.72–7.72 (m, PPh <sub>3</sub> )	
$[\text{Ru}\{\text{C}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\}(\eta^5\text{-C}_9\text{H}_7)\text{-}(\text{PMe}_2\text{Ph})_2][\text{PF}_6]$ ( <b>2b</b> )	19.83 s	5.34 d	5.71 t	2.6	6.75 m <sub>c</sub>	4.50 t (7.3)	3.05 t (7.7)	2.04 m	1.45 (vt, $^2J_{\text{HP}} + ^4J_{\text{HP}} = 8.9$ , $\text{PMe}_a + \text{PMe}_b$ ) 1.60 (vt, $^2J_{\text{HP}} + ^4J_{\text{HP}} = 9.1$ , $\text{PMe}_b + \text{PMe}_c$ ) 6.99–7.42 (m, PPh)	
$[\text{Ru}\{\text{C}(\text{OCH}_2(\text{CH}_2)_2\text{CH}_2)\}(\eta^5\text{-C}_9\text{H}_7)\text{-}(\text{PMe}_2\text{Ph})_2][\text{PF}_6]$ ( <b>3b</b> )	21.46 s	5.43 d	5.54 t	2.2	6.77 m <sub>c</sub>	4.34 m	2.82 m	1.68 m	1.44 (vt, $^2J_{\text{HP}} + ^4J_{\text{HP}} = 8.1$ , $\text{PMe}_a + \text{PMe}_b$ ) 1.62 (vt, $^2J_{\text{HP}} + ^4J_{\text{HP}} = 8.2$ , $\text{PMe}_b + \text{PMe}_c$ ) 7.02–7.39 (m, PPh)	
$[\text{Ru}\{\text{C}(\text{OCH}_2(\text{CH}_2)_3\text{CH}_2)\}(\eta^5\text{-C}_9\text{H}_7)\text{-}(\text{PMe}_2\text{Ph})_2][\text{PF}_6]$ ( <b>5b</b> )	22.08 s	5.45 d	5.35 t	2.7	6.79 m 7.07 m	4.45 m	2.67 m	1.39 m	1.49 (vt, $^2J_{\text{HP}} + ^4J_{\text{HP}} = 8.8$ , $\text{PMe}_a + \text{PMe}_b$ ) 1.62 (vt, $^2J_{\text{HP}} + ^4J_{\text{HP}} = 9.0$ , $\text{PMe}_b + \text{PMe}_c$ ) 7.10–7.41 (m, PPh)	
$[\text{Ru}\{\text{C}(\text{OCH}_2\text{CH}_2\text{CH}_2)\}(\eta^5\text{-C}_9\text{H}_7)\text{-}(\text{dppm})][\text{PF}_6]$ ( <b>2c</b> )	15.14 s	5.76 d	5.56 t	2.6	6.86 m 7.09 m	3.28 m	3.28 m	1.46 m	4.91 (dt, $J_{\text{HH}} = 15.4$ , $J_{\text{HP}} = 12.1$ , $\text{PCH}_a\text{H}_b\text{P}$ ) 5.09 (dt, $J_{\text{HH}} = 15.4$ , $J_{\text{HP}} = 10.6$ , $\text{PCH}_a\text{H}_b\text{P}$ ) 7.21–7.41 (m, PPh <sub>2</sub> )	
$[\text{Ru}\{\text{C}(\text{OCH}_2(\text{CH}_2)_2\text{CH}_2)\}(\eta^5\text{-C}_9\text{H}_7)\text{-}(\text{dppm})][\text{PF}_6]$ ( <b>3c</b> )	15.35 s	5.56 d	5.47 t	2.4	6.83 m 7.00 m	3.02 t (6.8)	2.94 t (6.3)	0.80 m 1.21 m	4.95 (m, $\text{PCH}_2$ ) 7.07–7.40 (m, PPh <sub>2</sub> )	
$[\text{Ru}\{\text{C}(\text{OCH}_2(\text{CH}_2)_3\text{CH}_2)\}(\eta^5\text{-C}_9\text{H}_7)\text{-}(\text{dppm})][\text{PF}_6]$ ( <b>5c</b> )	15.56 s	5.64 d	5.34 t	2.5	7.00 m 7.17 m	3.20 m	2.87 m	0.36 m 1.21 m 1.60 m	4.95 (t, $J_{\text{HP}} = 11.4$ , $\text{PCH}_2\text{P}$ ) 7.21–7.40 (m, PPh <sub>2</sub> )	

Table 1 (Continued)

Compound	<sup>1</sup> H								
	$\eta^5\text{-C}_9\text{H}_7$ <sup>i</sup>								
	<sup>31</sup> P{ <sup>1</sup> H}	H-1,3	H-2	<i>J</i> <sub>HH</sub>	H-4,7, H-5,6	OCH <sub>2</sub> <sup>d</sup>	=CCH <sub>2</sub> <sup>d</sup>	-CH <sub>2</sub> -	Others
[Ru( $\eta^5\text{-COCH}_2\text{CH}_2\text{CH}_2\text{C}_9\text{H}_7$ )(PPh <sub>3</sub> )(PMe <sub>3</sub> )][PF <sub>6</sub> ] ( <b>2d</b> )	6.60 d <sup>e</sup> 54.50 d <sup>e</sup>	5.34 br 5.39 br	5.82 br	–	5.89 m, 5.90 m <sup>c</sup>	3.85 m 4.38 m	3.40 m	1.60 m 2.00 m	1.17 (d, <sup>2</sup> <i>J</i> <sub>HP</sub> = 9.4, PMe <sub>3</sub> ) 6.99–7.43 (m, PPh <sub>3</sub> )
[Ru( $\eta^5\text{-COCH}_2\text{CH}_2\text{CH}_2\text{C}_9\text{H}_7$ )(PPh <sub>3</sub> )(PMe <sub>3</sub> )][PF <sub>6</sub> ] ( <b>3d</b> )	6.43 d <sup>f</sup> 54.22 d <sup>f</sup>	5.33 br 5.34 br	5.70 br	–	5.76 m, 5.90 m, 7.17 m	3.66 m 4.40 m	3.09 m 3.19 m	1.62 m	1.50 (d, <sup>2</sup> <i>J</i> <sub>HP</sub> = 9.4, PMe <sub>3</sub> ) 6.94–7.42 (m, PPh <sub>3</sub> )
[Ru( $\eta^5\text{-COCH}_2\text{CH}_2\text{CH}_2\text{C}_9\text{H}_7$ )(PPh <sub>3</sub> )(PMe <sub>3</sub> )][PF <sub>6</sub> ] ( <b>5d</b> )	5.80 d <sup>g</sup> 55.30 d <sup>g</sup>	5.33 br 5.39 br	5.65 br	–	5.72 m, 6.86 m, 7.21 m <sup>c</sup>	<sup>h</sup>	<sup>h</sup>	1.61 m	1.21 (d, <sup>2</sup> <i>J</i> <sub>HP</sub> = 9.5, PMe <sub>3</sub> ) 7.00–7.44 (m, PPh <sub>3</sub> )

<sup>a</sup> Spectra recorded in CDCl<sub>3</sub>,  $\delta$  in ppm and *J* in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

<sup>b</sup> Overlapped by H-1,3 signal.

<sup>c</sup> Overlapped by aromatic signals.

<sup>d</sup> *J*<sub>HH</sub> in brackets.

<sup>e</sup> <sup>2</sup>*J*<sub>HP</sub> = 30.7 Hz.

<sup>f</sup> <sup>2</sup>*J*<sub>PP</sub> = 29.9 Hz.

<sup>g</sup> <sup>2</sup>*J*<sub>PP</sub> = 30.2 Hz.

<sup>h</sup> 2.88 (m, 1H), 3.63 (m, 2H), 4.00 (m, 1H), =CCH<sub>2</sub> and OCH<sub>2</sub>.

<sup>i</sup> Legend for protons:

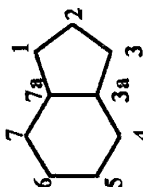


Table 2  
 $^{13}\text{C}\{^1\text{H}\}$ -NMR data for the oxacyclocarbene complexes

Compound	$\eta^5\text{-C}_9\text{H}_7$							Ru=C <sub>z</sub>	$J_{\text{CP}}$	OCH <sub>2</sub>	=CCH <sub>2</sub>	Others
	C-1,3	C-2	C-3a,7a	$\Delta\delta(\text{C-3a},7a)$ <sup>a</sup>	C-4,7, C-5,6							
<b>2a</b>	77.65	100.48	115.26	-15.34	123.48, 127.94	296.33 t	13.3	81.04	58.14	23.02 (s, CH <sub>2</sub> ), 128.10–135.48 (m, PPh <sub>3</sub> )		
<b>3a</b>	78.03	100.07	115.85	-14.85	123.17, 127.67	302.53 t	12.1	73.54	52.73	18.07, 21.42 (s, CH <sub>2</sub> ), 128.11–135.21 (m, PPh <sub>3</sub> )		
<b>5a</b>	78.90	98.80	116.00	-14.70	123.09, 127.82	306.84 t	12.4	78.14	57.24	22.55, 26.98, 28.25 (s, 3CH <sub>2</sub> ), 128.22–135.15 (m, PPh <sub>3</sub> )		
<b>2b</b>	78.03 vt <sup>b</sup>	99.00	112.62	-18.08	123.31, 127.37	295.06 t	13.0	80.77	56.06	17.72 (vt, $J_{\text{CP}}+^3J_{\text{CP}}/ = 32.3$ , PMe <sub>3</sub> +PMc <sub>6</sub> ), 20.20 (vt, $J_{\text{CP}}+^3J_{\text{CP}}/ = 34.1$ , PMe <sub>3</sub> +PMc <sub>6</sub> ), 23.26 (CH <sub>2</sub> ), 128.78–139.62 (m, PPh)		
<b>3b</b>	77.15	98.87	113.87	-16.83	122.81, 126.63	302.53 t	12.7	72.92	50.32	17.63 (vt, $J_{\text{CP}}+^3J_{\text{CP}}/ = 32.9$ , PMe <sub>3</sub> +PMc <sub>6</sub> ), 20.15 (vt, $J_{\text{CP}}+^3J_{\text{CP}}/ = 33.7$ , PMe <sub>3</sub> +PMc <sub>6</sub> ), 16.29, 20.65 (CH <sub>2</sub> ), 128.27–139.11 (m, PPh)		
<b>5b</b>	78.27	97.77	113.30	-17.40	122.60, 126.72	306.68 t	12.2	76.31	52.99	18.24 (vt, $J_{\text{CP}}+^3J_{\text{CP}}/ = 33.0$ , PMe <sub>3</sub> +PMc <sub>6</sub> ), 19.77 (vt, $J_{\text{CP}}+^3J_{\text{CP}}/ = 34.0$ , PMe <sub>3</sub> +PMc <sub>6</sub> ), 21.86, 27.78, 27.95 (CH <sub>2</sub> ), 128.78–139.62 (m, PPh)		
<b>2c</b>	76.34	95.44	109.66	-21.04	123.85, 126.38	300.30 t	12.0	80.53	57.50	22.37 (CH <sub>2</sub> ), 49.75 (t, $J_{\text{CP}} = 24.8$ , PCH <sub>2</sub> P), 128.22–134.89 (m, PPh <sub>2</sub> )		
<b>3c</b>	76.36	95.75	109.68	-21.02	123.72, 125.82	308.05 t	12.3	72.66	52.12	16.63, 20.14 (CH <sub>2</sub> ), 49.58 (t, $J_{\text{CP}} = 24.4$ , PCH <sub>2</sub> P), 127.90–135.90 (m, PPh <sub>2</sub> )		
<b>5c</b>	77.23	95.40	110.30	-20.40	123.60, 125.93	312.52 t	11.7	75.29	54.93	21.43, 26.23, 27.94 (CH <sub>2</sub> ), 48.90 (t, $J_{\text{CP}} = 25.8$ , PCH <sub>2</sub> P), 129.27–135.90 (m, PPh <sub>2</sub> )		
<b>2d</b>	75.74 d <sup>e</sup>	99.68	111.39	-17.71 (av.)	123.07, 123.90	296.75 t	13.5	80.85	57.38	20.15 (d, $J_{\text{CP}} = 32.3$ , PMe <sub>3</sub> ), 22.85 (CH <sub>2</sub> ), 128.21–134.07 (m, PPh <sub>3</sub> )		
	77.76 d <sup>e</sup>		114.58		126.83, 127.63		13.5					
<b>3d</b>	75.52 d <sup>d</sup>	99.49	111.60	-17.01 (av.)	122.68, 123.61	303.88 t	12.9	72.84	52.06	16.23, 20.42 (CH <sub>2</sub> ), 20.00 (d, $J_{\text{CP}} = 31.8$ , PMe <sub>3</sub> ), 127.99–134.01 (m, PPh <sub>3</sub> )		
	77.45 d <sup>d</sup>		115.78		126.32, 127.23		12.9					
<b>5d</b>	77.02 d <sup>e</sup>	100.01	111.84	-16.1 (av.)	122.89, 124.78	307.50 t	12.4	76.88	56.24	20.90 (d, $J_{\text{CP}} = 31.8$ , PMe <sub>3</sub> ), 22.72, 28.34, 28.63 (CH <sub>2</sub> ), 128.78–134.33 (m, PPh <sub>3</sub> )		
	79.88 d <sup>e</sup>		117.32		126.71, 128.16		12.4					

Spectra recorded in CDCl<sub>3</sub>;  $\delta$  in ppm and  $J$  in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; virtualtriplet.

<sup>a</sup>  $\Delta\delta(\text{C-3a}, 7a) = \delta(\text{C-3a}, 7a(\eta\text{-indenyl complex})) - \delta(\text{C-3a}, 7a(\eta\text{-sodium indenyl}))$ ;  $\delta(\text{C-3a}, 7a)$  for sodium indenyl 130.70 ppm.

<sup>b</sup>  $^2J_{\text{CP}} = ^2J_{\text{CP}} = 2.6$  Hz.

<sup>c</sup>  $^2J_{\text{CP}} = ^2J_{\text{CP}} = 6.3$  Hz.

<sup>d</sup>  $^2J_{\text{CP}} = 7.1$ ,  $^2J_{\text{CP}} = 7.2$  Hz.

<sup>e</sup>  $^2J_{\text{CP}} = 7.6$ ,  $^2J_{\text{CP}} = 7.1$  Hz.

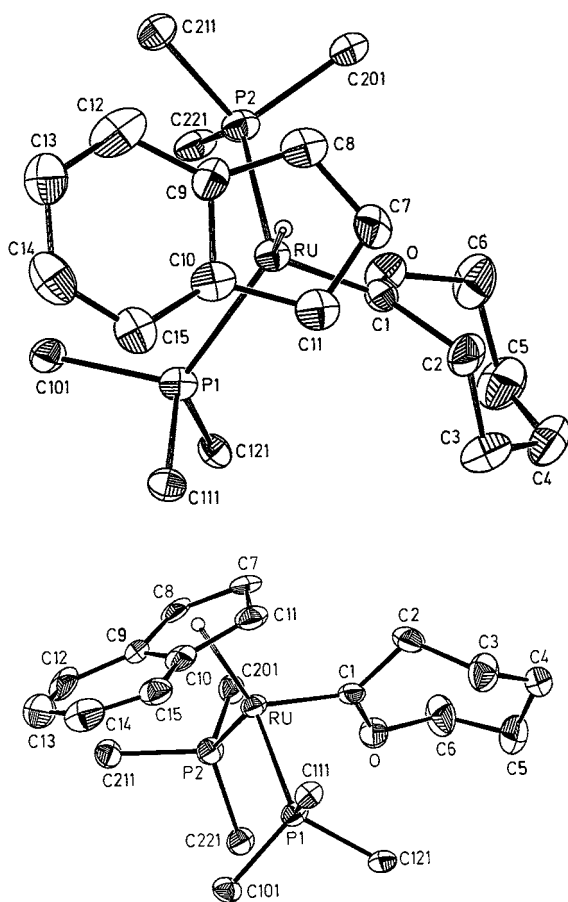


Fig. 1. ORTEP views of the molecular structure of the cationic complex  $[\text{Ru}\{\overline{\text{COCH}_2(\text{CH}_2)_3\text{CH}_2}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$  (**5a**), showing the conformation of the oxacycloheptylidene group. For clarity, only the *ipso* carbons of aryl groups of the triphenylphosphine ligands are depicted.

the hydroxybutylvinylidene complexes  $[\text{Ru}\{\overline{\text{C}=\text{C}(\text{H})-(\text{CH}_2)_3\text{CH}_2\text{OH}}\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}][\text{PF}_6]$  (**4a**);  $\text{L} = \text{L}' = \text{PPh}_3$  (**4a**);  $\text{L} = \text{L}' = \text{PMe}_2\text{Ph}$  (**4b**);  $\text{L} = \text{PPh}_3$ ,  $\text{L}' = \text{PMe}_3$  (**4d**) were formed in good yield (75–80%). Thermal cyclization into the thermodynamically more stable 2-oxacycloheptylidene complexes **5a**, **5b** and **5d** occurred when 5-hexyn-1-ol,  $\text{NaPF}_6$  and  $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)\text{LL}']$  were refluxed in ethanol for a longer time (2–3 h). In contrast, the complex **5c** ( $\text{LL}' = \text{dppm}$ ) is formed in a shorter time (1 h). This probably indicates the influence of the small-bite chelating *dppm* ligand which allows the intramolecular cyclization of  $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{dppm})]$  towards 5-hexyn-1-ol to be faster than that observed in all other cases. All attempts to prepare selectively the intermediate vinylidene failed, giving instead mixtures of the hydroxybutylvinylidene complex and the cyclic carbene complex **5c**.

The characterization of complexes **4a–d** and **5a–d** has been achieved by means of standard spectroscopic techniques (IR and  $^1\text{H}$ -,  $^{31}\text{P}\{^1\text{H}\}$ - and  $^{13}\text{C}\{^1\text{H}\}$ -NMR) and elemental analyses (details are given in the Section 4 and in Tables 1–4). Significant spectroscopic features

are: (a) Complexes **4a–d**: (i) in the  $^1\text{H}$ -NMR spectra, the resonance of the vinylidene hydrogen appears as a triplet in the range of  $\delta$  4.16–4.32 ( $J_{\text{HH}} = 7.3\text{--}7.9$  Hz); (ii) the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra display the characteristic low-field resonance for the carbenic  $\text{Ru}=\text{C}_\alpha$  atom, ca. 344 ppm ( $^2J_{\text{CP}} = 15.3\text{--}16.5$  Hz). The  $\text{C}_\beta$  resonance appears as a singlet in the range of  $\delta$  108.78–112.63. Four singlet carbon signals which are assigned to the  $\text{CH}_2$  carbon atoms of the  $\delta$ -hydroxybutyl substituent are observed. (b) Complexes **5a–d**: (i) the IR spectra exhibit the expected  $\nu(\text{COC})$  absorption at 1230–1240  $\text{cm}^{-1}$  and (ii) the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra show the low-field resonance of the carbene carbon  $\text{Ru}=\text{C}_\alpha$  as a triplet at  $\delta$  306.68–312.52 ( $^2J_{\text{CP}} = 11.7\text{--}12.7$  Hz) and five methylene resonances assigned to the  $\text{CH}_2$  groups of the 2-oxacycloheptylidene ligand.

It is worth mentioning that the intramolecular attack of the hydroxy group on the vinylidene group to generate the oxacyclo carbene complexes (**2a–d**, **3a–d**) takes place at a rate similar for 3-butyn-1-ol and 4-pentyn-1-ol (see above) and becomes increasingly disfavoured for 5-hexyn-1-ol, allowing the vinylidene intermediate complexes to be isolated (**4a–d**).

The solid-state structure of complex **5a** was determined by X-ray diffraction. Complex **5a** crystallizes, from a  $\text{CH}_2\text{Cl}_2$ –hexane solution, as the  $\text{CH}_2\text{Cl}_2$  solvate in a monoclinic system. ORTEP views of the cation complex are shown in Fig. 1. Selected bond distances, bond angles and indenyl distortion parameters, are listed in Table 5. The molecular structure shows the typical pseudooctahedral three-legged piano-stool geometry around the ruthenium atom, which is linked to the two phosphorus atoms of the triphenylphosphine ligands and to the  $\text{C}_\alpha$  of the oxacyclo carbene ligand. The values of the interligand angles  $\text{P1-Ru-P2}$ ,  $\text{C1-Ru-P1}$  and  $\text{C1-Ru-P2}$  as well as those between the centroid of five-carbon ring of the indenyl ligand and the legs are the ones expected for a pseudooctahedron. The distance  $\text{Ru-C1}$ , 1.89(1) Å, is similar to that found in  $[\text{Ru}\{\overline{\text{CO}(\text{CH}_2)_2\text{CH}_2}\}(\text{L}_{\text{OEt}})(\text{PPh}_3)_2]^+$  ( $\text{L}_{\text{OEt}} = (\eta^5\text{-C}_5\text{H}_5)\text{-Co}\{\text{P}(\text{O})(\text{OEt})_2\}_3$ ) (1.870(13) Å) [8c], and somewhat shorter than that found for other ruthenium(II) five- and six-membered oxacyclo carbene complexes  $[\text{Ru}\{\overline{\text{COCH}_2(\text{CH}_2)_n\text{CH}_2}\}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})]^+$  ( $n = 1$ , 1.92(1) and  $n = 2$ , 1.938(4) Å [8d],  $[\text{Ru}\{\overline{\text{CO}(\text{CH}_2)_2\text{CH}_2}\}(\eta^5\text{-C}_5\text{Me}_5)(\eta^3\text{-ADPP})]^+$  (ADPP = allyldiphenylphosphine) (1.956(4) Å) [8b],  $[\text{Ru}\{\overline{\text{CO}(\text{CH}_2)_2\text{CH}(\text{Ph})}\}(\eta^5\text{-C}_5\text{H}_5)\text{-CO}(\text{PPh}_3)]^+$  (1.946(8) Å) [8e]. The cyclic carbene ligand shows an appreciable deviation from the vertical orientation:  $\text{DA} = 29.7(5)^\circ$  versus  $\text{DA} = 0^\circ$  calculated by theoretical studies for carbene complexes [9]. The oxacycloheptylidene ring adopts a ‘pseudochair’ conformation. This is supported by the small torsion angle  $\text{C6-O1-C1-C2}$  ( $-13(2)^\circ$ ) and the similarity of the rest torsion angles (see Table 5).

Table 3  
 $^3\text{P}\{^1\text{H}\}$ - and  $^1\text{H}$ -NMR data for the hydroxybutyl/vinylidene complexes

Compound	$^3\text{P}\{^1\text{H}\}$ $^1\text{H}$							Others
	$\eta^5\text{-C}_9\text{H}_7$			$\text{CH}_2\text{OH}^a$				
	H-1,3	H-2	$J_{\text{HH}}$	H-4,7, H-5,6	$\text{C}_\beta\text{H}^a$	$-\text{CH}_2-$		
$[\text{Ru}\{\text{C}=\text{C}(\text{H})(\text{CH}_2)_3\text{CH}_2\text{OH}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ ( <b>4a</b> )	5.40 d	5.91 m	2.5	5.91 m <sub>b</sub>	4.32 t (7.8)	1.33 m 1.53 m 1.97 m	6.78–7.49 (m, PPh <sub>3</sub> )	
$[\text{Ru}\{\text{C}=\text{C}(\text{H})(\text{CH}_2)_3\text{CH}_2\text{OH}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PMe}_2\text{Ph})_2][\text{PF}_6]$ ( <b>4b</b> )	5.39 d	5.74 br	2.2	6.91 m <sub>b</sub>	4.31 t (7.9)	2.36 m 1.32 m 1.52 m 2.13 m	1.39–1.68 (m, PMe <sub>2</sub> Ph) 7.04–7.40 (m, PMe <sub>2</sub> Ph) 1.13 (d, $^2J_{\text{PP}}$ 10.2, PMe <sub>3</sub> ) 7.03–7.48 (m, PPh <sub>3</sub> )	
$[\text{Ru}\{\text{C}=\text{C}(\text{H})(\text{CH}_2)_3\text{CH}_2\text{OH}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)(\text{PMe}_3)][\text{PF}_6]$ ( <b>4d</b> )	5.63 br 5.67 br	5.83 br		6.09 m <sub>b</sub>	4.16 t (7.3)			
	47.16 d <sup>d</sup>							

Spectra recorded in  $\text{CDCl}_3$ .  $\delta$  in ppm and  $J$  in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

<sup>a</sup>  $J_{\text{HH}}$  in brackets.

<sup>b</sup> Overlapped by aromatic signals.

<sup>c</sup>  $\delta$  1.39–1.68 (m, 16H, 2CH<sub>2</sub>, 2PMe<sub>2</sub>Ph).

<sup>d</sup>  $^2J_{\text{PP}} = 28.6$  Hz.

Table 4  
 $^{13}\text{C}\{^1\text{H}\}$ -NMR data for the hydroxybutylvinylidene complexes

Compound	$\eta^5\text{-C}_9\text{H}_7$	C-1,3	C-2	C-3a,7a	$\Delta\delta(\text{C-3a,7a})^a$	C-4,7, C-5,6	Ru=C <sub>g</sub>	$^2J_{\text{CP}}$	HC <sub><math>\beta</math></sub>	CH <sub>2</sub> OH	Others
<b>4a</b>	82.94	98.95	114.98	-15.72	122.98 <sup>b</sup>	345.18 m	112.63	21.20, 27.52 (CH <sub>2</sub> ), 31.98 (=CCH <sub>2</sub> ), 128.10–133.99 (m, PPh)			
<b>4b</b>	79.25	98.09	112.84	-17.86	123.11, 128.07	343.92 t	16.4	108.78	62.32	62.11	16.68 (vt, $J_{\text{CP}} + ^3J_{\text{CP}} = 36.2$ , PMe <sub>a</sub> + PMe <sub>c</sub> ), 19.62 (vt, $J_{\text{CP}} + ^3J_{\text{CP}} = 36.2$ , PMe <sub>b</sub> + PMe <sub>d</sub> ), 21.10, 27.61 (CH <sub>2</sub> ), 31.10 (=CCH <sub>2</sub> ), 129.78–137.21 (m, PPh)
<b>4d</b>	78.33	98.69	113.09	-17.10	122.12, 123.38	343.80 dd	16.5	109.61	61.99		19.30 (d, $J_{\text{CP}} = 34.2$ , PMe <sub>3</sub> ), 20.35, 27.45 (CH <sub>2</sub> ), 31.65 (=CCH <sub>2</sub> ), 128.66–133.66 (m, PPh)
	80.37		114.11		b		15.3				

Spectra recorded in CDCl<sub>3</sub>;  $\delta$  in ppm and  $J$  in Hz. Abbreviations: d, doublet; t, triplet; m, multiplet; vt, virtualtriplet.

<sup>a</sup>  $\Delta\delta(\text{C-3a, 7a}) = \delta(\text{C-3a, 7a}(\eta\text{-indenyl complex})) - \delta(\text{C-3a, 7a}(\eta\text{-sodium indenyl}))$ ;  $\delta(\text{C-3a, 7a})$  for sodium indenyl 130.70 ppm.

<sup>b</sup> Overlapped by aromatic carbons.



The indenyl group is  $\eta^5$ -bonded to ruthenium with a distance between the metal atom and the centroid (C\*) of the five-membered ring of 1.99(9); this distance lies in the range 1.82–1.99 Å found for other ruthenium and osmium indenyl complexes [10]. The structure shows a slight distortion of the five-carbon ring from planarity with hinge angle (HA) and fold angle (FA) values of 6.0(1) and 11.0(1)°, respectively (Table 5). The characteristic displacement of the metal atom away from the C9–C10 ring junction in the indenyl ligand is also observed with a slip-fold ( $\Delta$ ) value of 0.22(5) Å, the highest one reported for  $\eta^5$ -indenyl complexes [10]. This distortion toward an  $\eta^3$  binding mode appears to be maintained in solution ( $\Delta\delta(\text{C-3a,7a}) = -14.70$  ppm) (see  $^{13}\text{C-NMR}$  data, Table 2). The preferred conformation of the indenyl ligand is such that the benzo ring is orientated nearly *trans* to the carbene group with a CA = 16.6(6)°. Further CA values for a series of  $\eta^5$ -indenyl ruthenium complexes have been reported [10].

Table 5

Selected bond distances, slip parameter  $\Delta^a$  (Å), bond, dihedral, FA<sup>b</sup>, HA<sup>c</sup>, DA<sup>d</sup>, and CA<sup>e</sup>, and torsion angles (°) for complex **5a**

Distances			
Ru–C*	1.99(9)	C2–C3	1.53(2)
Ru–C1	1.89(1)	C3–C4	1.55(3)
Ru–P1	2.358(4)	C4–C5	1.47(3)
Ru–P2	2.342(4)	C5–C6	1.50(3)
C1–C2	1.53(2)	C6–O1	1.49(2)
C1–O1	1.31(2)	$\Delta$	0.22(5)
Angles			
C*–Ru–C1	117.5(1)	C6–C5–C4	115(2)
C*–Ru–P1	123.2(1)	C5–C4–C3	114(2)
C*–Ru–P2	119.3(1)	C4–C3–C2	113(2)
P1–Ru–P2	103.4(1)	C3–C2–C1	116(1)
P1–Ru–C1	89.0(4)	Ru–C1–C2	124(1)
P2–Ru–C1	90.9(4)	Ru–C1–O1	122(1)
C2–C1–O1	114(1)	C1–O1–C6	126(1)
O1–C6–C5	116(2)	FA	11(1)
HA	6(1)	DA	29.7(5)
CA	16.6(6)		
Torsion angles			
C1–O1–C6–C5	74(2)	C2–C3–C4–C5	–64(2)
C6–O1–C1–C2	–13(2)	C3–C4–C5–C6	58(2)
O1–C1–C2–C3	–58(2)	C4–C5–C6–O1	–76(2)
C1–C2–C3–C4	84(2)		

<sup>a</sup>  $\Delta = d(\text{Ru–C9,C10}) - d(\text{Ru–C8,C11})$ .

<sup>b</sup> FA (fold angle) = angle between the planes defined by [C8, C7, C11] and [C10, C15, C14, C13, C12, C9].

<sup>c</sup> HA (hinge angle) = angle between the planes defined by [C8, C7, C11] and [C8, C11, C10, C9].

<sup>d</sup> DA (dihedral angle) = angle between the planes defined by [C\*, Ru, C1] and [Ru, C1, O1, C2].

<sup>e</sup> CA (conformational angle) = angle between the planes defined by [C\*\*, C\*, Ru] and [C\*, Ru, C1]. C\* = centroid of C8, C7, C11, C10, C9. C\*\* = centroid of C9, C10, C15, C14, C13, C12.

### 2.3. Reactivity of 2-oxacycloalkylidene complexes

As expected,  $\text{C}_\beta$ -hydrogen atoms of the oxacycloalkylidene complexes show acidity. Although no hydrogen–deuterium exchange processes have been observed in  $\text{CDCl}_3$ – $\text{D}_2\text{O}$  (excess), the treatment of oxacycloalkylidene compounds with an equimolar amount of  $\text{Li}^i\text{Bu}$  in THF gives rise to the formation of the oxacycloalkenyl complexes  $[\text{Ru}\{\overline{\text{C}=\text{CH}(\text{CH}_2)_n\text{CH}_2\text{O}}\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}']$  ( $\text{L} = \text{L}' = \text{PPh}_3$ ,  $n = 2$  (**7a**);  $\text{L} = \text{PPh}_3$ ,  $\text{L}' = \text{PMe}_3$ ,  $n = 1$  (**6d**),  $n = 2$  (**7d**),  $n = 3$  (**8d**) (55–60%). They have been isolated as very air and moisture-sensitive solids and characterized only by NMR spectroscopy (see Section 4). Significantly, the  $^1\text{H-NMR}$  spectra of alkenyl complexes show the  $=\text{CH}$  alkenyl proton as a broad singlet or a triplet in the  $\delta$  4.64–5.13 range. The complexes easily give back the oxacycloalkylidene precursors in the presence of traces of water. The treatment of a solution of oxacycloalkylidene complexes in  $\text{CDCl}_3$  with an excess of  $\text{Li}^i\text{Bu}$  leads to a double deprotonation of the  $\text{C}_\beta$ -hydrogens; the subsequent addition of  $\text{D}_2\text{O}$  produces deuterated complexes  $[\text{Ru}\{\overline{=\text{COCH}_2(\text{CH}_2)_n\text{CD}_2}\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}'][\text{PF}_6]$  as confirmed by the  $^1\text{H-NMR}$  spectra in which the  $\beta\text{-CH}_2$  resonance of the precursor complexes is no longer observed.

### 3. Conclusions

This study reports a general synthetic route for the preparation of oxacycloalkylidene complexes, containing the indenylruthenium(II) moiety  $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)\text{LL}']$ , starting from  $\omega$ -alkynols. Oxacycloalkylidene complexes  $[\text{Ru}\{\overline{=\text{C}=\text{C}(\text{H})(\text{CH}_2)_n\text{CH}_2\text{OH}}\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}'][\text{PF}_6]$  ( $\text{L} = \text{L}' = \text{PPh}_3$ ,  $n = 1$  (**2a**), 2 (**3a**), 3 (**5a**);  $\text{L} = \text{L}' = \text{PMe}_2\text{Ph}$ ,  $n = 1$  (**2b**), 2 (**3b**), 3 (**5b**);  $\text{LL}' = \text{dppm}$ ,  $n = 1$  (**2c**), 2 (**3c**), 3 (**5c**);  $\text{L} = \text{PPh}_3$ ,  $\text{L}' = \text{PMe}_3$ ,  $n = 1$  (**2d**), 2 (**3d**), 3 (**5d**)) are formed regardless of the separation between the triple bond and the hydroxy group in the starting alkynol. The formation of these complexes proceeds via intermediate hydroxyvinylidene complexes which have been isolated in the case of 5-hexyn-1-ol,  $[\text{Ru}\{\overline{=\text{C}=\text{C}(\text{H})(\text{CH}_2)_3\text{CH}_2\text{OH}}\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}'][\text{PF}_6]$  [ $\text{L} = \text{L}' = \text{PPh}_3$  (**4a**),  $\text{L} = \text{L}' = \text{PMe}_2\text{Ph}$  (**4b**),  $\text{L} = \text{PPh}_3$ ,  $\text{L}' = \text{PMe}_3$  (**4d**)]. The first ruthenium oxacycloheptylidene complexes (**5a–d**) are reported. In addition, the first crystallographic characterization of an 2-oxacycloheptylidene complex,  $[\text{Ru}\{\overline{=\text{COCH}_2(\text{CH}_2)_3\text{CH}_2}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$  **5a**, is also reported.

### 4. Experimental

The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by

standard methods and distilled under nitrogen before use. The complexes  $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)\text{LL}']$  ( $\text{L} = \text{L}' = \text{PPh}_3$ ,  $\text{PMe}_2\text{Ph}$ ;  $\text{LL}' = \text{dppm}$ ;  $\text{L} = \text{PPh}_3$ ,  $\text{L}' = \text{PMe}_3$ ) were prepared by literature methods [11,12]. Alkynols and  $\text{NaPF}_6$  were used as received from Aldrich Chemical Co.

Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature (r.t.), in ca.  $10^{-3}$  mol  $\text{dm}^{-3}$  acetone solutions, with a Jenway PCM3 conductimeter. The C, H and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer (uncompleted combustions were observed for **3a**, **2c** and **3d**). NMR spectra were recorded on a Bruker AC300 or AC200 instruments at 300 MHz ( $^1\text{H}$ ), 121.5 MHz ( $^{31}\text{P}$ ) or 75.4 MHz ( $^{13}\text{C}$ ) or 200 MHz ( $^1\text{H}$ ), 50.32 ( $^{13}\text{C}$ ) or 81.01 ( $^{31}\text{P}$ ), using  $\text{SiMe}_4$  or 85%  $\text{H}_3\text{PO}_4$  as standards.  $^1\text{H}$ -,  $^{13}\text{C}\{^1\text{H}\}$ - and  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopic data for the cyclic carbene and the hydroxybutylvinylidene complexes are collected in Tables 1–4.

#### 4.1. Synthesis of 2-oxacyclopentylidene and 2-oxacyclohexylidene complexes

$[\text{Ru}\{\overline{\text{COCH}_2(\text{CH}_2)_n\text{CH}_2}\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}'][\text{PF}_6]$ .  
 $\text{L} = \text{L}' = \text{PPh}_3$ ,  $n = 1$  (**2a**), 2 (**3a**);  $\text{L} = \text{L}' = \text{PMe}_2\text{Ph}$ ,  
 $n = 1$  (**2b**), 2 (**3b**);  $\text{LL}' = \text{dppm}$ ,  $n = 1$  (**2c**), 2 (**3c**);  
 $\text{L} = \text{PPh}_3$ ,  $\text{L}' = \text{PMe}_3$ ,  $n = 1$  (**2d**), 2 (**3d**)

##### 4.1.1. General procedure

A suspension of the complex  $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)\text{LL}']$  **1a–d** (1 mmol),  $\text{NaPF}_6$  (0.252 g, 1.5 mmol) and the corresponding alkynol (5 mmol) in 40 ml ethanol was refluxed until the colour of the solution changed from red to yellow. The resulting solution was then evaporated to dryness, and the solid residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (ca. 3 ml) and filtered into stirred  $\text{Et}_2\text{O}$  (ca. 100 ml) giving a light yellow precipitate of  $[\text{Ru}\{\overline{\text{COCH}_2(\text{CH}_2)_n\text{CH}_2}\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}'][\text{PF}_6]$ . Reaction time, yield (%), IR (KBr,  $\nu(\text{COC})$ ,  $\nu(\text{PF}_6^-)$ ,  $\text{cm}^{-1}$ ), analytical and conductivity (acetone, 20 °C,  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) data are as follows: for **2a**, 20 min; 80; 1181, 840; Anal. Calc. for  $\text{C}_{49}\text{H}_{43}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 61.57; H, 4.53. Found: C, 61.06; H, 5.06; 143%. For **3a**, 20 min; 85; 1253, 840; Anal. Calc. for  $\text{C}_{50}\text{H}_{45}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 61.92; H, 4.68. Found: C, 61.03; H, 4.71; 152%. For **2b**, 30 min; 70; 1168, 842; Anal. Calc. for  $\text{C}_{29}\text{H}_{35}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 49.23; H, 4.98. Found: C, 49.68; H, 4.97; 142%. For **3b**, 30 min; 60; 1239, 836; Anal. Calc. for  $\text{C}_{30}\text{H}_{37}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 49.93; H, 5.17. Found: C, 49.89; H, 5.16; 105%. For **2c**, 20 min; 60; 1167, 838; Anal. Calc. for  $\text{C}_{38}\text{H}_{35}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 55.96; H, 4.32. Found: C, 55.02; H, 4.38; 136%. For **3c**, 20 min; 60; 1243, 838; Anal. Calc. for  $\text{C}_{39}\text{H}_{37}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 56.46; H, 4.49. Found: C, 56.23; H, 4.69; 152%. For **2d**, 30 min; 90; 1168, 837;

Anal. Calc. for  $\text{RuC}_{34}\text{H}_{37}\text{F}_6\text{OP}_3$ ; C, 52.99; H, 4.84. Found: C, 53.14; H, 4.94; 139%. For **3d**, 30 min; 70; 1247, 838; Anal. Calc. for  $\text{C}_{35}\text{H}_{39}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 53.64; H, 5.01. Found: C, 52.73; H, 5.13; 155%.

#### 4.2. Synthesis of the hydroxybutylvinylidene complexes $[\text{Ru}\{\text{C}=\text{C}(\text{H})(\text{CH}_2)_3\text{CH}_2\text{OH}\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}'][\text{PF}_6]$ .

$\text{L} = \text{L}' = \text{PPh}_3$  (**4a**),  $\text{L} = \text{L}' = \text{PMe}_2\text{Ph}$  (**4b**);  $\text{L} = \text{PPh}_3$ ,  
 $\text{L}' = \text{PMe}_3$  (**4d**)

5-Hexyn-1-ol (0.54 ml, 5 mmol) was added to a refluxing solution of the complex  $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)\text{LL}']$  (1 mmol) and  $\text{NaPF}_6$  (0.330 g, 2 mmol) in 40 ml of ethanol. The resulting solution was refluxed (ca. 15 min) to give an orange solution. The solvent was then evaporated to dryness, and the solid residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (ca. 4 ml) and filtered into stirred  $\text{Et}_2\text{O}$  (ca. 100 ml) to give a precipitate. The resulting solid was washed with  $\text{Et}_2\text{O}$  ( $3 \times 20$  ml) and vacuum-dried. Yield (%), IR (KBr,  $\nu(\text{PF}_6^-)$ ,  $\text{cm}^{-1}$ ) and analytical data are as follows: For **4a**, 75; 839; Anal. Calc. for  $\text{C}_{51}\text{H}_{47}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 62.26; H, 4.81. Found: C, 61.50; H, 4.93%. For **4b**, 75; 840; Anal. Calc. for  $\text{C}_{31}\text{H}_{39}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 50.61; H, 5.34. Found: C, 50.79; H, 5.52%. For **4d**, 80; 839; Anal. Calc. for  $\text{C}_{36}\text{H}_{41}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 54.20; H, 5.18. Found: C, 54.61; H, 5.27%.

#### 4.3. Synthesis of the 2-oxacycloheptylidene complexes

$[\text{Ru}\{\overline{\text{COCH}_2(\text{CH}_2)_3\text{CH}_2}\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}'][\text{PF}_6]$ .  
 $\text{L} = \text{L}' = \text{PPh}_3$  (**5a**);  $\text{L} = \text{L}' = \text{PMe}_2\text{Ph}$  (**5b**);  
 $\text{LL}' = \text{dppm}$  (**5c**);  $\text{L} = \text{PPh}_3$ ,  $\text{L}' = \text{PMe}_3$  (**5d**)

##### 4.3.1. General procedure

A suspension of the complex  $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)\text{LL}']$  **1a–d** (1 mmol),  $\text{NaPF}_6$  (0.252 g, 1.5 mmol) and the corresponding alkynol (5 mmol) in 40 ml ethanol was refluxed until the colour of the solution changed from red to yellow. The resulting solution was then evaporated to dryness, and the solid residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (ca. 3 ml) and filtered into stirred  $\text{Et}_2\text{O}$  (ca. 100 ml) giving a light yellow precipitate of  $[\text{Ru}\{\overline{\text{COCH}_2(\text{CH}_2)_3\text{CH}_2}\}(\eta^5\text{-C}_9\text{H}_7)\text{LL}'][\text{PF}_6]$ . Reaction time, yield (%), IR (KBr,  $\nu(\text{COC})$ ,  $\nu(\text{PF}_6^-)$ ,  $\text{cm}^{-1}$ ), analytical and conductivity (acetone, 20 °C,  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) data are as follows: For **5a**, 3 h; 75; 1241, 840; Anal. Calc. for  $\text{C}_{51}\text{H}_{47}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 62.26; H, 4.81. Found: C, 61.34; H, 5.69; 127%. For **5b**, 3 h; 65; 1240, 838; Anal. Calc. for  $\text{C}_{31}\text{H}_{39}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 50.61; H, 5.34. Found: C, 50.21; H, 5.46; 161%. For **5c**, 1 h; 60; 1230, 837; Anal. Calc. for  $\text{C}_{40}\text{H}_{39}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 56.94; H, 4.66. Found: C, 57.45; H, 4.80; 111%. For **5d**, 2h; 65; 1243, 837; Anal. Calc. for  $\text{C}_{36}\text{H}_{41}\text{F}_6\text{OP}_3\text{Ru}$ ; C, 54.20; H, 5.18. Found: C, 53.71; H, 5.21; 125%.

Table 6  
Crystallographic data for  $C_{51}H_{47}F_6OP_3Ru \cdot CH_2Cl_2$

Formula	$C_{51}H_{47}F_6OP_3Ru \cdot CH_2Cl_2$
<i>a</i> (Å)	12.087(2)
<i>b</i> (Å)	17.752(6)
<i>c</i> (Å)	24.413(8)
$\beta$ (°)	92.97(4)
Molecular weight	1068.84
<i>V</i> (Å <sup>3</sup> )	5232(3)
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.36
<i>F</i> (000)	2184
Wavelength (Å)	0.7107
Temperature (K)	293
Radiation	Mo-K $\alpha$
Monochromator	Graphite crystal
Space group	$P2_1/n$
Crystal system	Monoclinic
Crystal size (mm)	0.18, 0.28, 0.21
$\mu$ (mm <sup>-1</sup> )	0.55
Range of abs	0.84–1.18
Diffraction geom	$\omega$ -2 $\theta$
$\theta$ Range (°)	2–22
Index ranges for data collection	$-13 \leq h \leq 13$ , $0 \leq k \leq 20$ , $0 \leq l \leq 26$
Number of contrib. reflections	4808
Number of variables	586
Final <i>R</i> factors $R(I > 3\sigma(I))$	$R = 0.080$ , $R_w = 0.084$

#### 4.4. Oxacycloalkenyl complexes

$[Ru\{\overline{C=CH(CH_2)_nCH_2O}\}(\eta^5-C_9H_7)LL']$ .

$L = L' = PPh_3$ ,  $n = 2$  (**7a**);  $L = PPh_3$ ,  $L' = PMe_3$ ,  $n = 1$  (**6d**), **2** (**7d**), **3** (**8d**)

Li<sup>t</sup>Bu (60  $\mu$ l of a 1.7 M solution, 0.1 mmol) was added to a suspension of  $[Ru\{\overline{COCH_2(CH_2)_nCH_2}\}(\eta^5-C_9H_7)LL'] [PF_6]$  (0.1 mmol) in THF at  $-20$  °C to give an orange solution. After stirring at r.t. for 15 min, the solvent was evaporated under vacuum and the solid residue was extracted with Et<sub>2</sub>O. The evaporation of the Et<sub>2</sub>O gave an orange, air- and moisture-sensitive solid of  $[Ru\{\overline{C=CH(CH_2)_nCH_2O}\}(\eta^5-C_9H_7)LL']$ . Yield (%), and NMR spectroscopic data are as follows: For **7a**, 60;  $^{31}P\{^1H\}(C_6D_6)$   $\delta$ : 50.77;  $^1H(C_6D_6)$   $\delta$ : 2.30 (m, 2H, CH<sub>2</sub>), 2.98 (m, 2H, =CCH<sub>2</sub>), 3.68 (m, 2H, OCH<sub>2</sub>), 4.96 (d, 2H,  $J_{HH} = 2.2$  Hz, H-1,3), 5.13 (s br, 1H, =CH), 5.63 (m, 2H, Ind), 5.87 (s br, 1H, H-2), 6.86–7.15 (m, 32H, PPh<sub>3</sub>, Ind). For **6d**, 55;  $^{31}P\{^1H\}(C_6D_6)$   $\delta$ : 7.75 (d,  $^2J_{PP'} = 33.4$  Hz, PMe<sub>3</sub>), 56.45 (d,  $^2J_{PP'} = 33.4$  Hz, PPh<sub>3</sub>).  $^1H(C_6D_6)$   $\delta$ : 1.22 (d, 9H,  $J_{HP} = 8.7$  Hz, PMe<sub>3</sub>), 2.94 (m, 2H, =CCH<sub>2</sub>), 4.27 (t, 2H,  $J_{HH} = 9.0$  Hz, OCH<sub>2</sub>), 4.89 (t, 1H,  $J_{HH} = 1.9$  Hz, =CH), 5.11 and 5.12 (s br, 1H each, H-1 and H-3), 5.79 (s br, 1H, H-2), 6.52 (m, 1H, Ind), 7.00–7.62 (m, 18H, PPh<sub>3</sub>, Ind). For **7d**, 60;  $^{31}P\{^1H\}(C_6D_6)$   $\delta$ : 7.80 (d,  $^2J_{PP'} = 34.2$  Hz, PMe<sub>3</sub>), 57.10 (d,  $^2J_{PP'} = 34.2$  Hz, PPh<sub>3</sub>).  $^1H(C_6D_6)$   $\delta$ : 0.94 (d, 9H,  $J_{HP} = 8.5$  Hz, PMe<sub>3</sub>), 1.71 (m, 2H, CH<sub>2</sub>), 2.26 (m, 2H, =CCH<sub>2</sub>), 3.66 (m, 2H, OCH<sub>2</sub>), 4.64 (t, 1H,  $J_{HH} = 3.5$  Hz, =CH), 4.85 and 4.89 (s br, 1H each, H-1 and H-3),

5.66 (s br, 1H, H-2), 6.33 (m, 1H, Ind), 6.76–7.50 (m, 18H, PPh<sub>3</sub>, Ind). For **8d**, 55;  $^{31}P\{^1H\}(C_6D_6)$   $\delta$ : 6.20 (d,  $^2J_{PP'} = 34.7$  Hz, PMe<sub>3</sub>), 57.20 (d,  $^2J_{PP'} = 34.7$  Hz, PPh<sub>3</sub>).  $^1H(C_6D_6)$   $\delta$ : 0.98 (d, 9H,  $J_{HP} = 8.4$  Hz, PMe<sub>3</sub>), 1.74 (m, 4H, 2CH<sub>2</sub>), 2.29 (m, 2H, =CCH<sub>2</sub>), 3.84 (m, 2H, OCH<sub>2</sub>), 4.90 (m, 2H, =CH and Ind), 5.03 (s br, 1H, Ind), 5.85 (s br, 1H, H-2), 6.48 (m, 1H, Ind), 6.85–7.38 (m, 18H, PPh<sub>3</sub>, Ind).

#### 4.5. X-ray structure determination

A summary of the fundamental crystal data is given in Table 6. Data were collected from a single crystal on a PW1100 diffractometer, using graphite-monochromated Mo-K $\alpha$ . A total of 6484 independent reflections were measured, of which 4808 were considered observed according to the criterion  $I > 3\sigma(I)$ . Scattering factors and dispersion corrections were taken from International Tables for Crystallography [13]. The structure was solved by Patterson methods and Fourier synthesis and most of the calculations were performed by using XRAY80 [14] and DIRDIF [15]. The structure was refined by least-squares methods using unit weights and anisotropic thermal parameters for all non-hydrogen atoms. The positions of the H atoms were calculated geometrically and were fixed during the least-squares refinement. No extinction correction was applied but three low angle reflections which were observed much smaller than calculated were not used. At the end of the isotropic refinement, an empirical absorption correction was carried out using DIFABS [16].

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