

# Synthesis and solid-state structure of $[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Ru}(\eta^3\text{-C}_3\text{H}_5)]$

Aurora Castro\*, Michael L. Turner\*, Peter M. Maitlis

*Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK*

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## Abstract

Treatment of the tetramethylfulvene-Ru(II) complex  $[(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{RuCl}_2]_2$  with allylmagnesium chloride leads to the allyl ruthenium complex  $[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Ru}(\eta^3\text{-C}_3\text{H}_5)]$ , which has been characterized spectroscopically and by a single crystal X-ray determination.

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*Keywords:* Ruthenium complexes; Functionalized cyclopentadienyl ligand; Olefin chelate; Crystal structures

## 1. Introduction

Pentamethylcyclopentadienyl (Cp\*) has been widely used as a ligand in organometallic chemistry [1] as it can stabilize reactive metal complexes not accessible using the cyclopentadienyl ligand. The steric shielding afforded by the five methyl groups significantly decreases the reactivity of the ring-metal bond and it has been found that the Cp\* ligand can stabilize complexes in a wide variety of oxidation states. In recent years attention has been focused on the synthesis of functionalized cyclopentadienyl ligands  $\text{C}_5\text{Me}_4\text{X}$  [2–6], where X is a pendant arm bearing a functionality which can act as a hand to grasp, orient, and hold potential reactants; alternatively, X can chelate to the metal center.

We have recently described syntheses of a number of ring-substituted tetramethylcyclopentadienyl complexes of ruthenium(II) [3] and the solid-state structures of several of these complexes  $[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{O}(\text{CH}_2)_n\text{CH}=\text{CH}_2)\text{Ru}(\text{CO})_2][\text{BF}_4]$  ( $n = 1$ , **1a**;  $n = 2$ , **1b**) have been studied by single crystal X-ray diffraction [3j].

We now report the synthesis, characterization, and crystal structure of a new chelate ruthenium(II) com-

pound made in a one-pot reaction from  $[(\eta^6\text{-C}_5\text{Me}_4\text{-CH}_2)\text{RuCl}_2]_2$  and allyl Grignard.

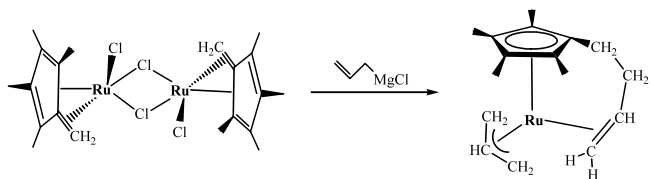
## 2. Results and discussion

Reaction of the tetramethylfulvene complex  $[(\eta^6\text{-C}_5\text{Me}_4\text{-CH}_2)\text{RuCl}_2]_2$  [3i] with four equivalents of allylmagnesium chloride gave the chelate compound  $[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Ru}(\eta^3\text{-C}_3\text{H}_5)]$  in which allyl moieties have added to the fulvene methylene carbon and to the ruthenium center (Scheme 1). In reactions with stoichiometric amounts of allyl Grignard, no intermediate metal complexes were observed by NMR spectroscopy.

The new complex is stable to air and was characterized by NMR spectroscopy, including  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^1\text{H}\text{-}^1\text{H}$  COSY-2D, and  $^1\text{H}\text{-}^{13}\text{C}$  HETCOR-2D spectra, elemental analysis, and by a single crystal X-ray structure determination. The NMR spectra (Table 1) show the presence of a 70:30 mixture of two isomers, neither of which has a plane of symmetry, as the methyl groups and the ring carbons in  $\text{C}_5\text{Me}_4$  are all non-equivalent. The protons in the bridging  $\text{CH}_2$  groups are non-equivalent and the chemical shift of the alkenyl protons are consistent with the coordination of the double bond to the metal and with the coordinated

\* Corresponding authors. Tel.: +44-114-222-9505; fax: +44-114-273-8673.

E-mail addresses: [a.castro@sheffield.ac.uk](mailto:a.castro@sheffield.ac.uk) (A. Castro), [m.l.turner@sheffield.ac.uk](mailto:m.l.turner@sheffield.ac.uk) (M.L. Turner).



Scheme 1.

alkenyl group being oriented parallel to the cyclopentadienyl ring.

Similar coordination modes have been observed for the ruthenium complexes  $[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{O}(\text{CH}_2)_n\text{-CH}=\text{CH}_2)\text{Ru}(\text{CO})_2][\text{BF}_4]$  [3] and for the hexamethylbenzene-chromium complexes  $[(\eta^6:\eta^2\text{-C}_6\text{Me}_5(\text{CH}_2)_n\text{-CH}=\text{CH}_2)\text{Cr}(\text{CO})_2]$  [7,8].

Single crystals of  $[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Ru}(\eta^3\text{-C}_3\text{H}_5)]$  were grown by cooling of an *n*-pentane solution and the solid-state structure was determined by X-ray crystallography (see Fig. 1). The

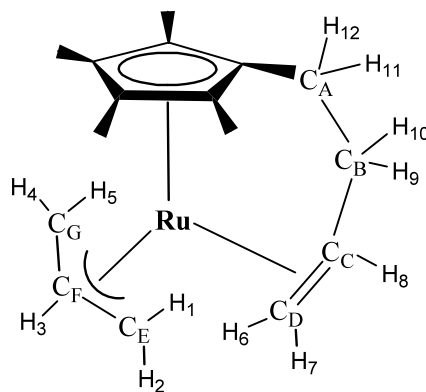
ruthenium atom is bonded  $\eta^2$  to a 3-butenyl ligand (Ru–C(8), 2.167 Å; Ru–C(9), 2.161 Å),  $\eta^5$  to the five-membered ring (distances from Ru to C(1)–C(5) range between 2.154 and 2.264 Å), and  $\eta^3$  to an allyl ligand. The  $\eta^3$ -bonded allyl ligand is disordered, giving two orientations (*exo* and *endo*) with respect to the ring. The root mean square (r.m.s.) deviation of the C<sub>5</sub>-ring is 0.009 Å, with a perpendicular distance of the ruthenium atom from the mean plane of 1.852 Å; the methyl carbons are displaced between 0.011 and 0.049 Å above the ring, while the CH<sub>2</sub> carbon lies at a distance of 0.061 Å below the ring.

Structural data on similar chelate complexes with two, three, and four atoms (either all carbons or carbons and one oxygen) linking the ring and the coordinated double bond have been reported and selected data are collected in Table 2. The available data suggest that variations in the metal atom and the ring size of the chelate have little effect on the overall structure. Thus, the twist angle ( $\alpha$ )

Table 1

<sup>1</sup>H- and <sup>13</sup>C{<sup>1</sup>H}-NMR spectra for the two isomers of complex  $[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Ru}(\eta^3\text{-C}_3\text{H}_5)]$  in C<sub>6</sub>D<sub>6</sub> ( $\delta$  in ppm, *J* in Hertz)

	Major isomer		Minor isomer	
	<sup>1</sup> H ( $\delta$ )	<sup>13</sup> C{ <sup>1</sup> H} ( $\delta$ )	<sup>1</sup> H ( $\delta$ )	<sup>13</sup> C{ <sup>1</sup> H} ( $\delta$ )
C <sub>5</sub> Me <sub>4</sub>	1.22 s, 1.28 s 1.87 s, 2.01 s	8.4, 9.0 10.0, 11.5	1.22 s, 1.58 s 1.87 s, 2.11 s	8.6, 10.3 10.8, 12.7
C <sub>5</sub> Me <sub>4</sub>		90.9, 92, 92.8 93.1, 107.8		89, 91.8, 92.1 104, 107
CH <sub>2</sub>	1.85 <sup>a</sup> (m, H <sub>11,12</sub> )	21.3 (C <sub>A</sub> )	1.67 (m, H <sub>11,12</sub> )	19.5 (C <sub>A</sub> )
CH <sub>2</sub>	3.10–3.00 (m, H <sub>9</sub> ) 2.86–2.77 (m, H <sub>10</sub> )	41.1 (C <sub>B</sub> )	2.75–2.65 (m, H <sub>9</sub> ) 2.50 (d, H <sub>10</sub> , <i>J</i> = 7)	41.2 (C <sub>B</sub> )
–CH=	3.37 (m, H <sub>8</sub> )	65.4 (C <sub>C</sub> )	1.85 <sup>a</sup> (m, H <sub>8</sub> )	58.3 (C <sub>C</sub> )
=CH <sub>2</sub>	2.86–2.77 (m, H <sub>7</sub> ) 0.91 (brd, H <sub>6</sub> , <i>J</i> <sub>H<sub>6,8</sub></sub> = 8)	44.2 (C <sub>D</sub> )	1.49 (m, H <sub>7</sub> ) 0.71 (d, H <sub>6</sub> , <i>J</i> <sub>H<sub>6,8</sub></sub> = 7.5)	36.5 (C <sub>D</sub> )
C <sub>3</sub> H <sub>5</sub>	1.17 (d, H <sub>4</sub> , <i>J</i> <sub>H<sub>4,3</sub></sub> = 6) 2.46 (d, H <sub>5</sub> , <i>J</i> <sub>H<sub>5,3</sub></sub> = 10)	44.1 (C <sub>E</sub> )	2.86–2.77 (m, H <sub>4</sub> ) 1.15 (d, H <sub>5</sub> , <i>J</i> <sub>H<sub>5,3</sub></sub> = 10)	44.7 (C <sub>E</sub> )
C <sub>3</sub> H <sub>5</sub>	3.10–3.00 (m, H <sub>3</sub> )	80.6 (C <sub>F</sub> )	1.85 <sup>a</sup> (m, H <sub>3</sub> )	91.0 (C <sub>F</sub> )
C <sub>3</sub> H <sub>5</sub>	2.86–2.77 (m, H <sub>2</sub> ) –0.28 (d, H <sub>1</sub> , <i>J</i> <sub>H<sub>1,3</sub></sub> = 10)	44.3 (C <sub>G</sub> )	2.86–2.77 (m, H <sub>2</sub> ) 0.80 (d, H <sub>1</sub> , <i>J</i> <sub>H<sub>1,3</sub></sub> = 10)	41.3 (C <sub>G</sub> )



<sup>a</sup> Partially obscured by other signals.

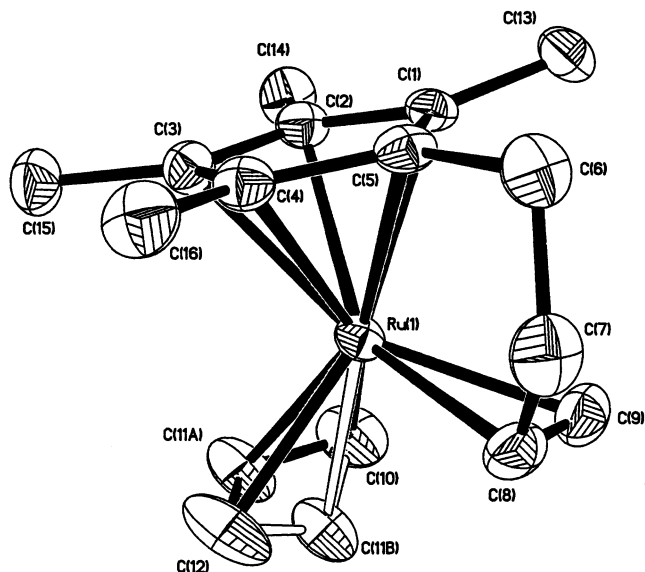


Fig. 1. ORTEP plot of  $[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Ru}(\eta^3\text{-C}_3\text{H}_5)]$ . Selected bond lengths (Å): Ru–C(10) = 2.188(4), Ru–C(11A) = 2.121(5), Ru–C(11B) = 2.123(6), Ru–C(12) = 2.165(5), Ru–C(8) = 2.167(4), Ru–C(9) = 2.161(4), C(5)–C(6) = 1.514(5), C(6)–C(7) = 1.542(6), C(7)–C(8) = 1.531(6), C(8)–C(9) = 1.411(5). Selected bond angles (°): C(9)–Ru–C(8) = 38.06(14), C(5)–C(6)–C(7) = 109.7(3), C(6)–C(7)–C(8) = 112.1(3), C(7)–C(8)–C(9) = 123.4(4), C(12)–C(11A)–C(10) = 129.1(5).

between the ring and the bridge varies between  $108.3^\circ$  and  $119.2^\circ$ , consistent with  $sp^3$  and  $sp^2$  hybridization, respectively. The variation in the second twist angle ( $\beta$ ) between the coordinated double bond and the bridge is smaller ( $111.5\text{--}115^\circ$ ). The distance of the metal to the

coordinated double bond, metal–C(A) or metal–C(B), reflects the variation in size of the 3d metals, Ni(II) and Co(II), and Ru(II). The distances observed in the new complex are slightly shorter than those previously reported and this may indicate a stronger bonding. We suggest that the conformations shown by all of these structures are close to energy minima.

### 3. Experimental

All reactions were carried out under nitrogen using carefully dried and purified solvents. Allylmagnesium chloride (2 M solution in tetrahydrofuran) was obtained from Aldrich and  $[(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{RuCl}_2]_2$  was prepared by literature procedures [3i]. NMR spectra were recorded on a Bruker WH-400 spectrometer, TOF mass spectra were recorded on a Micromass Prospec, and elemental analyses were performed by the University of Sheffield Microanalytical Service.

#### 3.1. Preparation of $[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{-CH}_2\text{CH}_2\text{CHCH}_2)\text{Ru}(\eta^3\text{-C}_3\text{H}_5)]$

Allylmagnesium chloride (2 M solution in THF; 0.32 ml, 0.64 mmol) was added to a freshly prepared solution of  $[(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{RuCl}_2]_2$  (100 mg, 0.16 mmol) in dry tetrahydrofuran (30 ml) at  $-78^\circ\text{C}$  and the reaction was left to warm to room temperature with stirring over 1 h. The solvent was removed under reduced pressure and the residue extracted with *n*-pentane ( $3 \times 5$  ml) to leave

Table 2  
Selected bond angles (°) and bond lengths (Å) for some  $\text{C}_5\text{Me}_4\text{R}$ -chelate compounds

Complex	$\alpha$ (°)	$\beta$ (°)	M–C(A)	M–C(B)
$[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CHCH}_2)\text{Ru}(\eta^3\text{-C}_3\text{H}_5)]$	109.7(3)	112.1(3)	2.167(4)	2.161(4)
$[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CHCH}_2)\text{Co}(\text{Me}_3\text{SiCCSiMe}_3)]$ [9]	108.27	111.5(2)	2.036(2)	2.023(2)
$[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2(\text{CH}_2)_2\text{CHCH}_2)\text{NiBr}]$ [10]	114.1(6)	111.9(8)	2.054(8)	2.029(7)
$[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{OCH}_2\text{CHCH}_2)\text{Ru}(\text{CO})_2]^+$ [3j]	119.2(2)	115(2)	2.20(2)	2.26(2)
$[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{O}(\text{CH}_2)_2\text{CHCH}_2)\text{Ru}(\text{CO})_2]^+$ [3j]	112.8(5)	115.1(5)	2.333(6)	2.257(6)
$[(\eta^2:\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{OCH}_2\text{CHCH}_2)\text{Ru}(\text{CO})(\text{COOMe})]$ [3k]	–	–	2.206	2.204

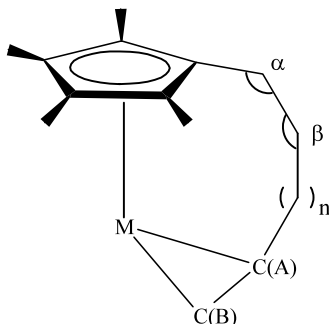


Table 3  
Crystallographic data for C<sub>16</sub>H<sub>24</sub>Ru

Formula weight	317.42
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Unit cell dimensions	
<i>a</i> (Å)	8.162(2)
<i>b</i> (Å)	22.295(6)
<i>c</i> (Å)	8.565(2)
α (°)	90
β (°)	116.627(4)
γ (°)	90
Volume (Å <sup>3</sup> )	1393.3(6)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	1.513
Absorption coefficient (mm <sup>-1</sup> )	1.102
<i>F</i> (0 0 0)	656
Crystal size (mm <sup>3</sup> )	0.35 × 0.19 × 0.09
Theta range for data collection (°)	1.83–28.33
Index ranges	–10 ≤ <i>h</i> ≤ 10, –29 ≤ <i>k</i> ≤ 27, –10 ≤ <i>l</i> ≤ 11
Reflections collected	8702
Independent reflections	3354 [ <i>R</i> <sub>int</sub> = 0.0599]
Completeness to θ = 28.33° (%)	96.7
Absorption correction	Semi-empirical
Max/min transmission	0.9073, 0.6990
Data/restraints/parameters	3354/9/164
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.948
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0401, <i>wR</i> <sub>2</sub> = 0.0882
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0624, <i>wR</i> <sub>2</sub> = 0.0954
Largest difference peak and hole (e Å <sup>-3</sup> )	1.357 and –0.794

yellow crystals after evaporation of the solvent to 5 ml and cooling to –20 °C. Yield: 0.057 g (55%). Anal. Calc. for C<sub>16</sub>H<sub>24</sub>Ru: C, 60.54; H, 7.62. Found: C, 60.72; H, 7.84%. Mass spectra (TOF–MS–ES<sup>+</sup>): 317 M<sup>+</sup>. Spectroscopy data are summarized in Table 1.

### 3.2. X-ray structure determination

Crystal data for C<sub>16</sub>H<sub>24</sub>Ru are summarized in Table 3. Data were collected on a Bruker Smart CCD area detector with Oxford Cryosystems low-temperature system. Reflections were measured from a hemisphere of data collected of frames each covering 0.3° in omega. The measured reflections were corrected for Lorentz and polarization effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections; 2422 independent reflections exceeded the significance level ( $|F|/\sigma(|F|) > 4.0$ ). The structure was solved by direct methods and refined by full-matrix least-squares methods on *F*<sup>2</sup>. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with *U*<sub>iso</sub> constrained to be 1.2 (1.5 for methyl groups) times *U*<sub>eq</sub> of the carrier atom. All of the non-hydrogen

atoms were refined anisotropically. Carbon C11 was found to be disordered and refined with a 67:33% occupancy. A weighting scheme  $w = 1/[\sigma^2 F_o^2 + (0.0456 \times P)^2 + 0.00 \times P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ , was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL [11] as implemented on the Viglen Pentium computer.

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