

Note

# Formation and structural study of a mixed ene/enyl ligand on reaction of $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ with 1,3-cyclononadiene

Rehan Basta, Atta M. Arif, Richard D. Ernst \*

Department of Chemistry, University of Utah, 315 S. 1400 E., Salt Lake City, UT 84112-0850, USA

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## Abstract

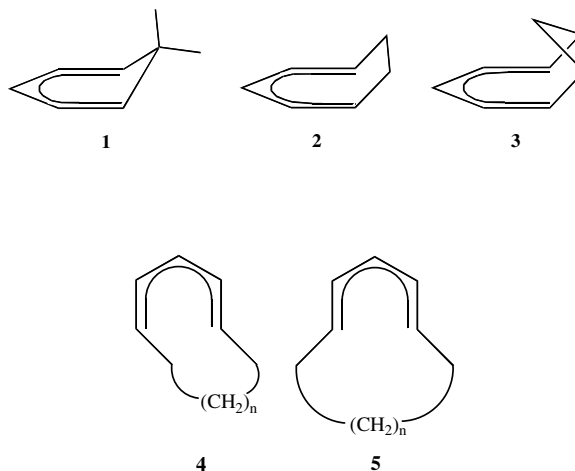
The reaction of  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$  with an excess of 1,3-cyclononadiene in the presence of metallic zinc leads to  $\text{Ru}(\text{C}_5\text{Me}_5)(1,2,3,6,7-\eta^5\text{-C}_9\text{H}_{13})$ , in which the nine-membered ring provides both allyl and olefin coordinations, linked together on each side by  $\text{C}_2\text{H}_4$  bridges. The complex has been characterized analytically, spectroscopically, and structurally.  
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**Keywords:** Cyclononadienyl; Ruthenium; Pentamethylcyclopentadienyl

## 1. Introduction

A large number of edge-bridged  $\eta^5$ -dienyl complexes are known in which the dienyl fragment is incorporated into a ring system, as in cyclohexadienyl, cycloheptadienyl, and cyclooctadienyl ligands [1]. Related species are also well known for other polyene and enyl ligands. It is, however, far less common for such species to be incorporated in nine-membered or larger ring systems. Whether this represents an instability of such species, or simply a lack of effort to prepare them, is unclear. However, for the edge-bridged  $\eta^5$ -dienyl ligands, one observes a significant increase in the girth of the ligand, as reflected by the separation of the dienyl termini (C1, C5), as the length of the bridge increases. Thus, for example, this separation increases from 2.305 Å in  $\text{Fe}(\text{6,6-dmch})_2$  ([2], 6,6-dmch (**1**)) to 2.715 Å in  $\text{Fe}(c\text{-C}_7\text{H}_9)_2$  ([3],  $c\text{-C}_7\text{H}_9$  (**2**)) to 2.947 Å in  $\text{Fe}(c\text{-C}_8\text{H}_{11})_2$  ([4],  $c\text{-C}_8\text{H}_{11}$  (**3**)). As this increase has been correlated with a decrease in metal–ligand overlap, one could easily understand how complexes with even larger ring systems might tend to be unstable, although it would be possible for alter-

native orientations of the edge-bridges to result, as in **4** or **5**. In order to begin addressing the issue of stability of  $\eta^5$ -dienyl coordination by larger rings, we have examined the reaction of  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$  with 1,3-cyclononadiene. Perhaps in part due to strain or poor orbital overlap that might result for an  $\eta^5$ -cyclononadienyl complex, an alternative product has been isolated, in which  $\eta^5$  coordination is achieved through isolated allyl and olefin components.



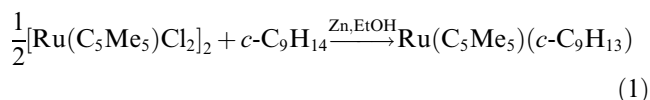
\* Corresponding author. Tel.: +1-801-581-6681; fax: +1-801-581-8433.

E-mail address: [ernst@chem.utah.edu](mailto:ernst@chem.utah.edu) (R.D. Ernst).

## 2. Results and discussion

### 2.1. Synthetic and spectroscopic data

The reactions of  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}]_4$  or  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$  with a variety of acyclic 1,3-pentadienes have generally been found to lead straightforwardly to the desired, yellow  $\text{Ru}(\text{C}_5\text{Me}_5)(\text{Pdl})$  (Pdl = pentadienyl or substituted pentadienyl ligand) complexes [5]. A similar yellow product can also be isolated from the analogous reaction involving 1,3-cyclononadiene.



The  $^1\text{H}$  NMR spectrum of the product revealed that coordination of the nine-membered ring system was not provided by a contiguous diene fragment. In particular, despite substantial complication of the  $^1\text{H}$  NMR spectrum due to extensive couplings, there was clearly a lack of coupling between the resonances for the unsaturated H(1,3) and H(6,7) atoms, together with couplings for these four atoms to both saturated  $\text{CH}_2$  fragments, signifying the presence of two isolated unsaturated systems. The formal mirror plane symmetry evident from the NMR spectra would only be consistent with the presence of two  $\text{C}_2\text{H}_4$  bridges located between the two isolated systems.

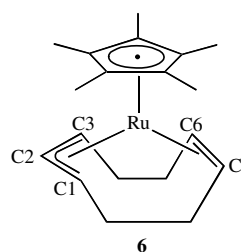
A single crystal X-ray diffraction study (Tables 1 and 2, Fig. 1) revealed that  $\eta^5$  coordination by the nine-membered ring involved allyl and olefin coordinations,

Table 1  
Crystallographic parameters for  $\text{Ru}(\text{C}_5\text{Me}_5)(1,2,3,6,7\text{-}\eta^5\text{-C}_9\text{H}_{13})$

Formula	$\text{C}_{19}\text{H}_{28}\text{Ru}$
Formula weight	357.48
Temperature (K)	200(1)
$\lambda$ (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
$a$ (Å)	8.5704(2)
$b$ (Å)	9.3097(2)
$c$ (Å)	20.0448(3)
$\beta$ (°)	95.5393(13)
Volume (Å <sup>3</sup> ); $Z$	1591.86(6); 4
$D_{\text{calc}}$	1.492
Absorption coefficient (cm <sup>-1</sup> )	9.74
$\theta$ range (°)	3.7–27.5
Limiting indices	$-11 \leq h \leq 11$ , $-12 \leq k \leq 11$ , $-25 \leq l \leq 26$
Reflections collected	5970
Independent reflections; $n: I > n\sigma(I)$	3631; 2
$R(F)$	0.0220
$R_w(F^2)$	0.0510
Maximum/minimum difference Fourier peak (e Å <sup>-3</sup> )	0.50/–0.55

Table 2  
Selected bond distances (Å) and angles (°) for  $\text{Ru}(\text{C}_5\text{Me}_5)(1,2,3,6,7\text{-}\eta^5\text{-C}_9\text{H}_{13})$

Bond distances (Å)			
Ru–C1	2.178(2)	Ru–C10	2.241(2)
Ru–C2	2.122(2)	Ru–C11	2.221(2)
Ru–C3	2.173(2)	Ru–C12	2.252(2)
Ru–C6	2.172(2)	Ru–C13	2.251(2)
Ru–C7	2.172(2)	Ru–C14	2.244(2)
C1–C2	1.424(3)	C10–C14	1.421(2)
C2–C3	1.411(3)	C11–C12	1.436(2)
C6–C7	1.416(3)	C12–C13	1.419(3)
C10–C11	1.434(3)	C13–C14	1.440(3)
Bond angles (°)			
C1–C2–C3	123.7(2)	C6–C7–C8	122.8(2)
C2–C3–C4	125.1(2)	C7–C8–C9	112.4(2)
C3–C4–C5	109.7(2)	C8–C9–C1	114.2(2)
C4–C5–C6	111.1(2)	C9–C1–C2	129.3(2)
C5–C6–C7	123.6(2)		



with  $\text{C}_2\text{H}_4$  groups separating their termini, as in **6**. The idealized mirror plane symmetry of this arrangement is consistent with the relatively simple  $^1\text{H}$  and  $^{13}\text{C}$

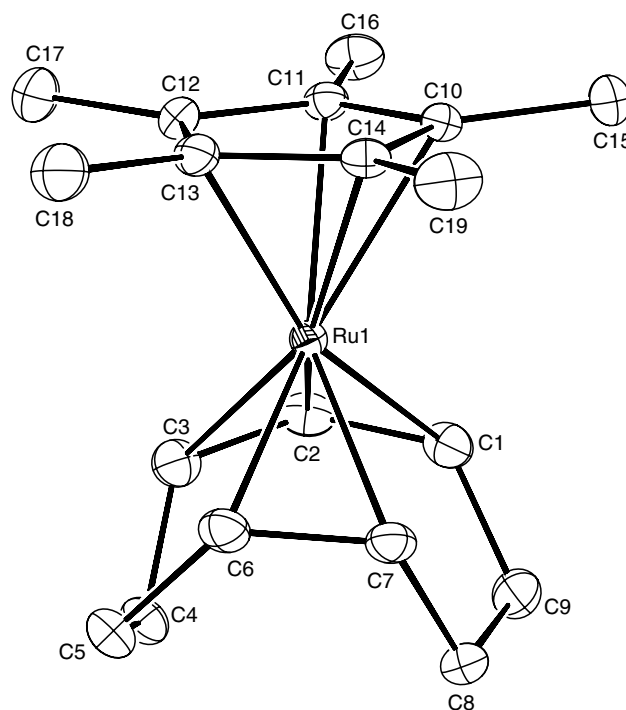


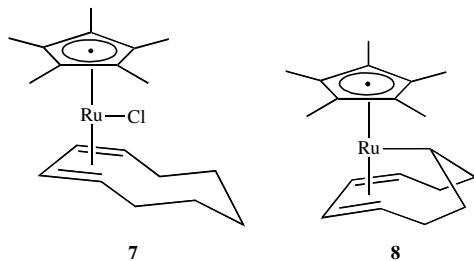
Fig. 1. Solid state structure of  $\text{Ru}(\text{C}_5\text{Me}_5)(1,2,3,6,7\text{-}\eta^5\text{-C}_9\text{H}_{13})$ .

NMR spectra. The  $C_5Me_5$  coordination is similar to that observed in  $Ru(C_5Me_5)(\eta^5\text{-dienyl})$  complexes, with Ru–C distances ranging from 2.221(2) to 2.252(2) Å, C–C distances ranging from 1.419(3) to 1.440(3) Å, and displacements of the methyl groups out of the C10–C14 plane by 0.091–0.121 Å (3.4–4.6°, avg. 4.0°), away from the ruthenium center. The ruthenium center lies 1.883 Å out of this plane.

The Ru–C distances for the non-aromatic allyl and olefin ligands are significantly shorter, being 2.122(2) for C2 and averaging 2.172(1) and 2.175(2) Å, respectively, for C(6,7) and C(1,3). For comparison, in  $Ru(C_5Me_5)(\eta^5\text{-dienyl})$  complexes, the Ru–C distances for the open dienyl ligands tend to be slightly shorter than those for the  $C_5Me_5$  ligand. Hence, as  $\pi$  ligands experience greater stabilization through delocalization, their subsequent interactions with a metal center become diminished, as both their donor and acceptor capabilities decrease.

The incorporation of the allyl and olefin groups in the nine-membered ring does not appear to lead to significant distortion, which can readily be seen from the relatively normal tilts experienced by the allyl group's substituents. For H(1–3), C(4), and C(9), these tilts are 15°, 19°, 17°, 37.5°, and 36.8°, respectively, or, alternatively, 48.1(3)° and 50.7(3)° for the latter two based on torsion angles. In contrast, ruthenium complexes in which separate allyl and olefin fragments are incorporated into eight-membered rings, although much more common [6], appear to experience substantially greater strain.

The formation of the observed product from 1,3-cyclononadiene is reminiscent of the long known, related isomerizations of various dienes to their 1,3 isomers for iron complexes [7], but to 1,5 isomers for rhodium [8], and also of the general facility of the activations of C–H bonds in saturated bridges across coordinated  $\pi$  systems [9]. In this case, subsequent to the presumed initial formation of diene complex **7**, coordination and activation of a C–H bond, concomitant with either ionization of the chloride ion or a ligand slip process, could lead to a complex such as **8**. A subsequent 1,3 hydrogen shift, made possible via either an  $\eta^5\text{-}\eta^3\text{-}C_5Me_5$  slip or  $\eta^4\text{-}\eta^2\text{-diene}$  slip, would then lead to the observed, presumably thermodynamic, product **6**.



The scarcity of 1,2,3,6,7- $\eta^5$ -nonadienyl coordination appears general, as only one other monocyclic ana-

logue, prepared by the coupling of a diene to  $Mn(2,4-C_7H_{11})(CO)_3$  ( $C_7H_{11}$  = dimethylpentadienyl), appears to have been structurally characterized [10]. This scarcity must be attributed to the much greater accessibility of the eight-membered starting materials. However, bicyclic analogues are more common, some having been proposed to be something of “doubly opened” Cp ligands [11], containing (like **6**) electronically separated allyl and olefin coordinations.

### 3. Conclusions

Although the approach taken here did not lead to a fully conjugated  $\eta^5$ -cyclononadienyl complex, it is possible that such species could still be isolated, perhaps for smaller metal centers, for which widely separated allyl and olefin coordination might be unfavorable. Such species can be expected to be subject to electrocyclization reactions, as can even occur for cyclooctadienyl ligands [12]. Additionally, other modes of  $\eta^5$  coordination (e.g.,  $\eta^{1,4}$ ) could also be adopted.

### 4. Experimental

All reactions were carried out in Schlenk apparatus under a nitrogen atmosphere. Organic solvents were dried and deoxygenated by distillation from benzophenone ketyl under a nitrogen atmosphere. Ethanol was distilled from calcium hydride. 1,3-cyclononadiene [13,14] and  $[Ru(C_5Me_5)Cl_2]_2$  [15] were prepared following published procedures. Elemental analysis results were obtained from Desert Analytics.

#### 4.1. (1,2,3,6,7- $\eta^5$ -cyclononadienyl)(pentamethylcyclopentadienyl)ruthenium, $Ru(C_5Me_5)(C_9H_{13})$

To a slurry of  $[Ru(C_5Me_5)Cl_2]_2$  (0.400 g, 0.651 mmol) in 20 ml of freshly distilled ethanol was added 1,3-cyclononadiene (2.57 g, 21.1 mmol) which resulted in the formation of a red-orange solution. The mixture was stirred for an hour, after which zinc dust (0.300 g, 4.59 mmol) was added and the reaction mixture was allowed to stir overnight, leading to the formation of a yellow-colored solution. The solvent was removed in vacuo. The residue was extracted with ca. 80 ml of hexanes and filtered through a Celite pad on a frit. Concentration in vacuo of the yellow filtrate to ca. 15 ml and cooling to  $-20^\circ C$  for 2 h gave 0.126 g (27%) of yellow crystals (m.p., 190–192°).

$^1H$  NMR ( $C_6D_6$ ):  $\delta$  1.45 (s, 15H, Cp\*), 1.93 (m, 2H, methylenes), 2.18 (m, 2H, methylenes), 2.54 (br, m, 5H, H<sub>2</sub> and methylenes), 3.47 (m, 2H, H<sub>1,3</sub>), 4.08 (m, 2H, H<sub>6,7</sub>).

$^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  8.7 (5C,  $\text{Cp}^*\text{Me}$ ), 36.4 (2C,  $\text{C}_{4,9}$ ), 37.1 (2C,  $\text{C}_{5,8}$ ), 71.8 (2C,  $\text{C}_{1,3}$ ), 75.6 (2C,  $\text{C}_{6,7}$ ), 79.9 (1C,  $\text{C}_2$ ), 92.0 (5C,  $\text{Cp}^*$  ring).

MS (EI, 70 eV)  $m/z$  (relative intensity): 230 (10), 231 (12), 231 (12), 233 (14), 281 (17), 315 (14), 326 (11), 327 (15), 328 (17), 329 (16), 335 (12), 337 (12), 338 (27), 339 (35), 340 (40), 341 (80), 342 (21), 343 (50), 352 (27), 353 (25), 354 (30), 355 (81), 356 (64), 357 (77), 358 (100), 359 (22), 360 (46).

Anal. Calc. for  $\text{C}_{19}\text{H}_{28}\text{Ru}$ : C, 63.83; H, 7.89. Found: C, 63.56; H, 7.85%.

#### 4.2. X-ray diffraction studies

Crystal, data collection, and refinement parameters are contained in Table 1. Suitable crystals of the compound were examined under Paratone oil, and a suitable crystal was then selected and transferred to a Nonius Kappa CCD diffractometer, where it was immediately cooled with a nitrogen stream. The structure was solved using direct methods and difference Fourier maps. Subsequent least-squares refinements were carried out with anisotropic thermal parameters for the nonhydrogen atoms, while the hydrogen atoms were successfully refined isotropically. Pertinent bonding parameters are presented in Table 2.

#### 5. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 212687. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ [FAX +44(1223)336-033] or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

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#### References

- [1] (a) R.D. Ernst, Chem. Rev. 88 (1988) 1255;  
(b) R.D. Ernst, Comm. Inorg. Chem. 21 (1999) 285.
- [2] R. LeSuer, R. Basta, A.M. Arif, W.E. Geiger, R.D. Ernst, Organometallics 22 (2003) 1487.
- [3] R. Basta, D.R. Wilson, H. Ma, A.M. Arif, R.H. Herber, R.D. Ernst, J. Organomet. Chem. 637–639 (2001) 172.
- [4] V. Kulsomphob, R. Tomaszewski, G.P.A. Yap, L.M. Liable-Sands, A.L. Rheingold, R.D. Ernst, J. Chem. Soc., Dalton Trans. (1999) 3995.
- [5] (a) S.D. Loren, B.K. Campion, R.H. Heyn, T.D. Tilley, B.E. Bursten, K.W. Luth, J. Am. Chem. Soc. 111 (1989) 4712;  
(b) U. Koelle, M.H. Wang, G. Raabe, Organometallics 10 (1991) 2573;  
(c) H.W. Bosch, H.-U. Hund, D. Nietlispach, A. Salzer, Organometallics 11 (1992) 2087;  
(d) W. Trakarnpruk, A.M. Arif, R.D. Ernst, Organometallics 11 (1992) 1686;  
(e) F. Urbanos, M.A. Halcrow, J. Fernandez-Baeza, F. Dahan, D. Labroue, B. Chaudret, J. Am. Chem. Soc. 115 (1993) 3484;  
(f) W. Trakarnpruk, A.L. Rheingold, B.S. Haggerty, R.D. Ernst, Organometallics 13 (1994) 3914;  
(g) V. Kulsomphob, K.A. Ernst, K.-C. Lam, A.L. Rheingold, R.D. Ernst, Inorg. Chim. Acta 296 (1999) 170;  
(h) V. Kulsomphob, G.C. Turpin, K.-C. Lam, C. Youngkin, W. Trakarnpruk, P. Carroll, A.L. Rheingold, R.D. Ernst, J. Chem. Soc., Dalton Trans. (2000) 3086.
- [6] (a) T.V. Ashworth, M.J. Nolte, R.H. Reinmann, E. Singleton, J. Chem. Soc., Chem. Commun. (1977) 937;  
(b) V. Ashworth, A.A. Chalmers, D.C. Liles, E. Meintjies, E. Singleton, Organometallics 6 (1987) 1543;  
(c) J.A. Wiles, C.E. Lee, R. McDonald, S.H. Bergens, Organometallics 15 (1996) 3782;  
(d) J.W. Steed, D.A. Tocher, R.D. Rogers, J. Chem. Soc., Chem. Commun. (1996) 1589;  
(e) M.A. Bennett, A.C. Willis, L.Y. Goh, W. Chen, Polyhedron 15 (1996) 3559;  
(f) C.C. McComas, J.W. Ziller, D.L.V. Vranken, Organometallics 19 (2000) 2853;  
(g) P. Alvarez, J. Gimeno, E. Lastra, S. García-Granda, J.F.V. der Maelen, M. Bassetti, Organometallics 20 (2001) 3762.
- [7] (a) R.B. King, T.A. Manuel, F.G.A. Stone, J. Inorg. Nucl. Chem. 16 (1961) 233;  
(b) J.E. Arnet, R. Pettit, J. Am. Chem. Soc. 83 (1961) 2954.
- [8] R.E. Rinehart, J.S. Lasky, J. Am. Chem. Soc. 86 (1964) 2516.
- [9] R. Basta, A.M. Arif, R.D. Ernst, Organometallics 22 (2003) 812.
- [10] C.G. Kreiter, K. Lehr, M. Leyendecker, W.S. Sheldrick, R. Exner, Chem. Ber. 124 (1991) 3.
- [11] (a) A.V. Rivera, G.M. Sheldrick, Acta Crystallogr., Sect. B 34 (1978) 1716;  
(b) J. Blümel, F.H. Köhler, G. Müller, J. Am. Chem. Soc. 110 (1988) 4846;  
(c) J. Blümel, F.H. Köhler, G. Müller, D.L. Wilkinson, Angew. Chem., Intl. Ed. 27 (1988) 977;  
(d) J. Blümel, N. Hertkorn, B. Kanellakopulos, F.H. Köhler, J. Lachmann, G. Müller, F.E. Wagner, Organometallics 12 (1993) 3896;  
(e) I.T. Chizhevskii, T.V. Zinevich, P.V. Petrovskii, V.I. Bregadze, F.M. Dolgushin, A.I. Yanovskii, Yu.T. Struchkov, Izv. Akd. Nauk SSSR (1995) 776;  
(f) H.-J. Chung, J.B. Sheridan, M.L. Coté, R.A. Lalancette, Organometallics 15 (1996) 4575.
- [12] (a) B.E. Mann, P.W. Manning, C.M. Spencer, J. Organomet. Chem. 312 (1986) C64;  
(b) R.U. Kirss, Organometallics 11 (1992) 497;  
(c) R.U. Kirss, A. Quazi, C.H. Lake, M.R. Churchill, Organometallics 12 (1993) 4145;  
(d) K.K. Joshi, R.H.B. Mais, F. Nyman, P.G. Owston, A.M. Wood, J. Chem. Soc. A (1968) 318;  
(e) H. Lehmkuhl, W. Leuchte, E. Janssen, J. Organomet. Chem. 30 (1971) 407;  
(f) G. Alibrandi, B.E. Mann, J. Chem. Soc., Dalton Trans. (1994) 951.
- [13] L. Skattebøl, S. Solomon, Org. Syn. 49 (1969) 35.
- [14] R. Vaidyanathaswamy, D. Devaprabhaka Ra, Ind. J. Chem. 13 (1975) 873.
- [15] U. Koelle, J. Kossakowski, Inorg. Syn. 29 (1992) 225.