

## X-Ray Evidence for a Mononuclear *s-trans*- $\eta^4$ -1,3-Diene Complex; Molecular Structure of $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2(\text{s-trans-PhCH=CH-CH=CHPh})$

Yasushi Kai,<sup>a</sup> Nobuko Kanehisa,<sup>a</sup> Kunio Miki,<sup>a</sup> Nobutami Kasai,<sup>\*a</sup> Kazushi Mashima,<sup>b</sup> Kinya Nagasuna,<sup>b</sup> Hajime Yasuda,<sup>b</sup> and Akira Nakamura<sup>\*b</sup>

<sup>a</sup> Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

<sup>b</sup> Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Novel *s-trans*- $\eta^4$ -co-ordination of butadiene to a single metal atom was confirmed by the X-ray crystal structure analysis of thermally stable  $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2(\text{PhCH=CH-CH=CHPh})$ ; this agrees with the solution structure determined by <sup>1</sup>H n.m.r. spectroscopy.

A series of 1,3-diene complexes of Zr of the type  $\text{Zr}(\text{cp})_2(1,3\text{-diene})$  (cp = cyclopentadienyl) was recently prepared by (a) reaction of  $\text{ZrCl}_2\text{cp}_2$  with enediylmagnesium<sup>1</sup> and (b) photolysis of  $\text{Zr}(\text{cp})_2(\text{aryl})_2$  in the presence of 1,3-dienes.<sup>2</sup> In the case of butadiene, the first method gave the conventional *s-cis*-1,3-diene complex exclusively while the second method provided the thermally less stable *s-trans*-1,3-diene complex (the ratio *s-cis*/*s-trans* at 25 °C being 55/45). The recent X-ray work on  $\text{Zr}(\text{cp})_2(\text{s-trans-but-1,3-diene})$  remains equivocal about the conformation of the diene group because of the positional ambiguity of its two central carbon atoms.<sup>2</sup> We present here an X-ray structure analysis of  $\text{Zr}(\text{cp})_2(1,4\text{-diphenylbuta-1,3-diene})$ . In solution, this complex, prepared by method (a), is assigned the *s-trans*- $\eta^4$ -1,3-diene conformation from the coupling constants;  $J(\text{H}^2\text{H}^3)$  (*s*-vicinal) 15.0 Hz and  $J(\text{H}^1\text{H}^2) = J(\text{H}^3\text{H}^4)$  (vicinal) 15.8 Hz, determined by simulation of the <sup>1</sup>H n.m.r. spectrum.

Crystal data:  $\text{C}_{26}\text{H}_{24}\text{Zr}$ ,  $M = 427.7$ , orthorhombic,  $P2_12_12_1$ ,  $a = 8.481(1)$ ,  $b = 21.803(3)$ ,  $c = 21.667(5)$  Å,  $U = 4006.4(11)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.418$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 5.49$  cm<sup>-1</sup>. The X-ray diffraction data were collected on a Rigaku automated four-circle diffractometer with Zr-filtered Mo-K $\alpha$  radiation.

As the compound is very unstable in air, the crystal was sealed in a thin-walled glass capillary tube in argon. 4001 reflections were collected up to  $2\theta = 50^\circ$  by the  $\theta$ - $2\theta$  scan method, of which 3302 were considered significant [ $|F_o| > 3\sigma(F_o)$ ] and were used for the structure refinement. The crystal structure was solved by the conventional heavy atom method and refined by block-diagonal least-squares (HBLS-V),<sup>3</sup> (cp carbon atoms isotropic, other non-hydrogen atoms anisotropic) to an  $R$  index of 0.076.†

The crystal structure obtained includes two crystallographically independent molecules (I) and (II), which make an enantiomorphic pair related by a pseudo-local centre of symmetry and have essentially the same molecular structures, one of which<sup>4</sup> is shown in Figure 1. The most important features of the molecular structure are as follows. (i) The molecule has approximate  $C_2$  symmetry.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

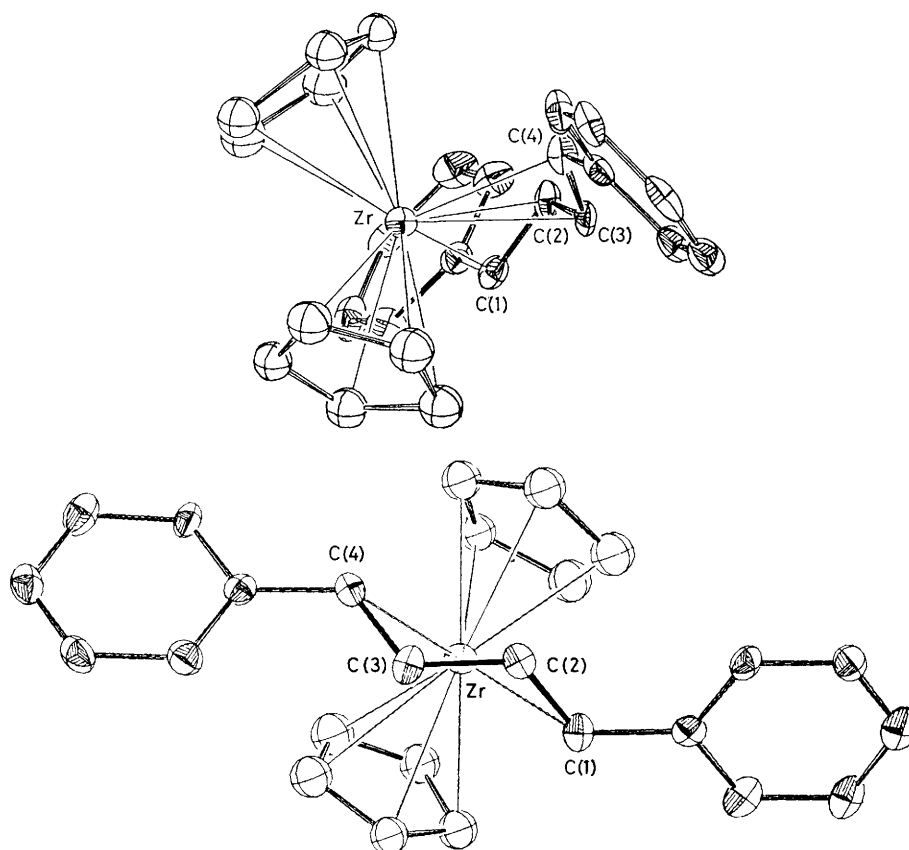


Figure 1. Molecular structure of  $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2(\text{s-trans-1,4-diphenylbuta-1,3-diene})$ .

(ii) The Zr atom is co-ordinated pseudotetrahedrally to two  $\eta^5$ -cp rings [cp-Zr-cp;  $125.0^\circ$  in (I) and  $129.4^\circ$  in (II)] and the diene double bonds. (iii) The torsional angles around the C(2)-C(3) bond are  $126.8^\circ$  in (I) and  $125.5^\circ$  in (II). (iv) The bond distances of Zr-C(1) [2.509 Å in (I) and 2.483 Å in (II)] and Zr-C(4) (2.503 and 2.502 Å) are longer than those of Zr-C(2) (2.391 and 2.359 Å) and Zr-C(3) (2.399 and 2.382 Å). (v) The bond distances C(1)-C(2) [1.435 Å in (I) and 1.371 Å in (II)] and C(3)-C(4) (1.403 and 1.387 Å) are shorter than C(2)-C(3) (1.467 and 1.485 Å). The e.s.d's of the Zr-C and C-C bond distances lie between 0.015 and 0.019, and 0.021 and 0.027 Å, respectively. The rather low accuracy of the molecular structure results from the partial rotational disorder of the cp rings.

These observations show the conformation of 1,4-diphenylbuta-1,3-diene to be *s-trans*. This is the first clear evidence for *s-trans* diene co-ordination to a single metal atom obtained

by X-ray work; some binuclear and trinuclear *s-trans*-1,3-dienes have been reported previously.<sup>5</sup>

Received, 9th October 1981; Com. 1198

### References

- 1 H. Yasuda, Y. Kajihara, K. Mashima, K. Lee, and A. Nakamura, *Chem. Lett.*, 1981, 519.
- 2 G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich, and C. Krüger, *J. Am. Chem. Soc.*, 1980, **102**, 6346.
- 3 T. Ashida, The Universal Crystallographic Computing System—Osaka, The Computation Center, Osaka University, 1979, pp. 53–59.
- 4 C. K. Johnson, ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.
- 5 H. E. Sasse and M. L. Ziegler, *Z. Anorg. Allg. Chem.*, 1972, **392**, 167; C. G. Pierpont, *Inorg. Chem.*, 1978, **17**, 1976.