CHEMISTRY LETTERS, pp. 1979-1982, 1982. © The Chemical Society of Japan

MOLECULAR STRUCTURE OF $[(\eta^5\text{-}C_5H_5)_2\overline{Zr(CH_2=C(CH_3)=CH\text{-}CH_2)\text{—}C(CH_3)=C}(CH_3)]$ PREPARED BY REGIOSELECTIVE INSERTION OF 2-BUTYNE TO $Zr(\eta^5\text{-}C_5H_5)_2$(ISOPRENE)

Yasushi KAI, Nobuko KANEHISA, Kunio MIKI, Nobutami KASAI*,
Kazushi MASHIMA†, Kinya NAGASUNA†, Hajime YASUDA†, and Akira NAKAMURA†*
Department of Applied Chemistry, Faculty of Engineering, Osaka
University, Suita, Osaka 565, and †Department of Macromolecular
Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560

The X-ray structure analysis revealed a unique 1–3-η;6–η-(2E,5Z)-2,5-dimethyl-2,5-heptadien-1,6-diyl ligand bound to $Zr(\eta^5\text{-}C_5H_5)_2$ species.

The 1,3-diene complexes of Group IVA metals (Ti, Zr, Hf) are known to have reactive metal-carbon bonds, which insert compounds with unsaturated C-O, C-C and C-N bonds into the metal-carbon bond to lead to regioselective carbon-carbon bond formations.[1,2] $ZrCp_2$(isoprene)(Cp=cyclopentadienyl), thus, inserts ketones or aldehydes at an unusual position [Zr-C(1) bond] to give a sterically hindered product, while the corresponding magnesium-diene complexes and allylic zirconium complexes generally react with ketones or aldehydes at the Zr-C(3) bond.[1,3] In contrast to the reaction of carbonyl compounds, insertion of olefins, dienes or alkynes occurred into the Zr-C(4) bond regioselectively.[2a]

The determination of the molecular structures of these complexes provides us clear evidences for the regioselective C-C bond formation. The X-ray structure analysis of the insertion product obtained from $Zr(\eta^5\text{-}C_5Me_5)_2$(isoprene) and diisopropyl ketone showed a 7-membered ring oxametallacyclic structure where the ketone is inserted into the Zr-C(1) bond.[4] Here we report the molecular structure of a novel regioselective insertion product of 2-butyne with $ZrCp_2$(isoprene), determined by the X-ray crystal structure analysis.

Crystal Data: $C_{19}H_{24}Zr$, M=343.6, orthorhombic, $P2_12_12_1$, a=21.828(6), b=8.280(2), c=8.842(2) Å, U=1598.1(7) $Å^3$, Z=4, Dc=1.428 g cm^{-3}, μ(Mo$K\alpha$)=6.66 cm^{-1}.
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 air-sensitive, the crystal was sealed in a thin-wall glass capillary tube under an atmosphere of argon. A total of 3402 independent reflections was collected up to 2θ=66° by the θ-2θ scan method, of which 2734 were non-zero reflections.
The crystal structure was solved by the conventional heavy atom method and refined by the block-diagonal least-squares (*HBLS*-V)$^{5)}$, (non-hydrogen atoms anisotropically, hydrogen atoms isotropically except methyl hydrogens which could not be located from the D-Fourier map) to the *R* index of 0.067. The molecular structure obtained is shown in Fig. 1.

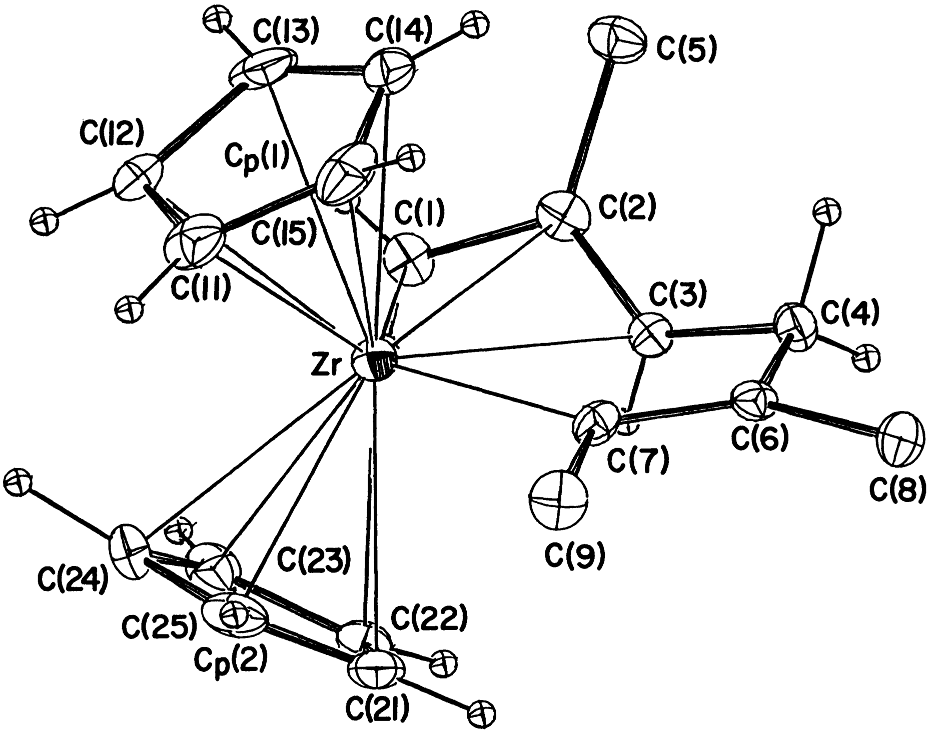

Fig. 1. Molecular structure of the regioselective insertion product of 2-butyne with $ZrCp_2$(isoprene). Thermal ellipsoids are drawn at the 20% probability level.

Note that the 2-butyne molecule was inserted into the Zr-C(4) bond of $ZrCp_2$(isoprene) making bonds between Zr and C(7) [2.367(7) Å], and C(6) and C(4) [1.511(11) Å]. The C(6)-C(7) bond distance of 1.347(10) Å agrees with the normal double bond distance of 1.337±6 Å.6) The 2-butyne moiety [C(6), C(7), C(8) and C(9)] locates roughly on the plane composed of Zr, C(1) and C(4) with the maximum atomic deviation of 0.23 Å.

The most important feature of this molecule is in the structure of the isoprene moiety. The Zr-C(1), Zr-C(2) and Zr-C(3) distances are 2.427(8), 2.595(8) and 2.522(7) Å, respectively, while Zr-C(4) distance of 3.466(9) Å is far from the bonding distance. The C(1)-C(2), C(2)-C(3) and C(3)-C(4) distances are 1.421(11), 1.361(11) and 1.485(11) Å, respectively. These distances indicate a π-allyl type coordination of the isoprene moiety to the Zr atom. The present complex takes a π-allylic structure also in solution.7) The structure of the starting material, $ZrCp_2$(isoprene), has been reported to have the conventional *s-cis* structure in an benzene solution.8) Thus, the (*s-cis*-η^4-diene)metal or metallacyclo-3-pentene structures changed to the (π-allyl)metal structure. Because of this structural change, the conformation of the isoprene moiety changed from *s-cis* to *s-trans*, the torsional angle around C(2)-C(3) bond, C(1)-C(2)-C(3)-C(4), being 166.4°. The dihedral angle between the planes defined by Zr, C(1) and C(3), and by C(1), C(2), C(3) and C(5) is 114.1°.

The bond distances between the Zr atom and carbon atoms of Cp(1) [C(11) to C(15)] and Cp(2) [C(21) to C(25)] range from 2.507(10) to 2.565(9) Å [av. 2.538 Å], and 2.530(10) to 2.584(9) Å [av. 2.559 Å], respectively. The Cp(1)centroid-Zr-Cp(2)centroid angle is 128.1°, which is similar to those in $ZrCp_2$(*s-cis*-2,3-dimethylbutadiene) [124°]9) and $ZrCp_2$(*s-trans*-1,4-diphenylbutadiene) [125.0 and 129.4°].10)

Similar structures to the present complex have been deduced from the ^{1}H-NMR spectra for a series of olefin insertion products, $(\eta^5\text{-}C_5H_5)_2\overline{Zr(CH_2 \doteq C(CH_3) \doteq CH\text{-}CH_2)\text{-}CRR'CH_2}$ where R, R' are H, CH_3, C_2H_5, C_3H_7 or C_4H_9.11)

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7) The previously reported ^{1}H-NMR data (Ref. 2a) are better understood by the 1–3-η;6–η-2,5-dimethyl-2,5-heptadien-1,6-diyl structure based on the present X-ray work.

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11) For example, ^{1}H-NMR data for isobutene insertion product (toluene-d_8 at 30°C); δ 1.39(d,H_1(*anti*),J_{gem}=4.6Hz), 1.98(d,H_1(*syn*)), 3.55(d of d,H_3,$J_{3,4}$=10.2, $J_{3,4'}$=4.0Hz), 1.90(d,H_4,J_{gem}=12.0Hz), 2.06(d,$H_{4'}$), 1.56(s,CH_3 of isoprene unit), 1.20 and 1.41(s,CH_3 of isobutene unit), 5.01 and 5.36(s,C_5H_5), 0.87(s,CH_2, Zr-CH_2).

(Received October 12, 1982)