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^{1}H-NMR EVIDENCE FOR η^4-DIENE COORDINATION STRUCTURE OF $ZrCp_2(C_4H_6)$ AND HAFNACYCLO-3-PENTENE STRUCTURE OF $HfCp_2(C_4H_6)$ IN SOLUTION

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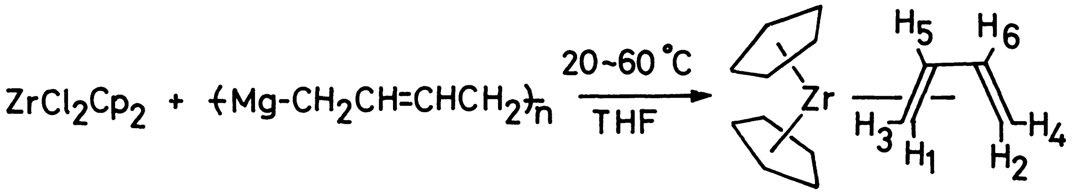
The temperature-variant ^{1}H-NMR study of a 1,3-diene complex, $ZrCp_2(CH_2CHCHCH_2)$, in toluene-d_8 showed the η^4-diene coordination structure below -40 °C, while the corresponding Hf complex assumed the metallacyclo-3-pentene structure in the wide temperature range of -90 $\sim$ 80 °C.

Previously we have orally reported a novel method for preparation of a variety of 1,3-diene complexes of type $ZrCp_2$(diene) by the reaction of enediylmagnesium with zirconacene chloride.$^{1)}$ Very recently these Zr complexes were synthesized through entirely different photochemical method and the X-ray structures were communicated.$^{2)}$ Here we present a clear difference in solution structure between $ZrCp_2$(diene) and $HfCp_2$(diene) complexes as observed in the variable temperature ^{1}H-NMR spectra.

The 1:1 reaction of enediylmagnesium $(MgCHR_1\text{-}CR_2{=}CR_3\text{-}CHR_1)_n$ with zirconacene chloride in THF gave $ZrCp_2(CHR_1{=}CR_2\text{-}CR_3{=}CHR_1)$ in 85-95% yield, where R_1,R_2,R_3= H,H,H; R_1,R_2,R_3=H,CH_3,CH_3 or R_1,R_2,R_3=Ph,H,H. These complexes were isolated as air-sensitive orange crystals by recrystallization from THF-hexane and characterized by chemical analysis of the metal, gas chromatographic analysis of the hydrolysis products and the ^{1}H-NMR spectroscopic method. All the complexes exist as



monomeric form in benzene as revealed by the cryoscopic method. As a typical example, the analytical data of $ZrCp_2(CH_2{=}CH{-}CH{=}CH_2)$ 1 were given here; mp. 73 °C; Zr content, 33% by oxidation method (Calcd. 33.1%); hydrolysis product, 1-butene 0.95 mol/mol (Calcd. 1.0 mol/mol); Cp/diene ratio, 2.0 mol/mol by ^1H-NMR (Calcd. 2.0 mol/mol; mol.wt 291 (Calcd. 296).

The ^1H-NMR spectra of the complex 1 were temperature-dependent with limiting η^4-C_4H_6 structure below -40 °C as shown in Figure 1. The computer simulation of the pattern assignable to the C_4H_6 ligand revealed the following parameters; δ= -0.69($H_{1\sim2}$), 3.45($H_{3\sim4}$), 4.78 ppm($H_{5\sim6}$); $J_{15}=J_{26}=10.5$, $J_{35}=J_{46}=9.5$, $J_{13}=J_{24}=-10.0$, $J_{56}=8.0$, $J_{12}=0.5$, $J_{34}=0.2$, $J_{16}=J_{25}=-0.8$, $J_{36}=J_{45}=-1.5$ Hz. When 1 was heated, the proton signal coalesced at -20 ∿ 10 °C and the equilibration of syn- and anti-protons at the diene termini has been reached at 60 °C to show the time-averaged chemical shift values of $H_{1\sim4}$ and $H_{5\sim6}$ at 1.43 and 4.74 ppm, respectively. The solution structure of the complex 1 obtained by the present method was thus determined to be $ZrCp_2(\eta^4$-s-cis-1,3-butadiene) in accord with the crystalline structure

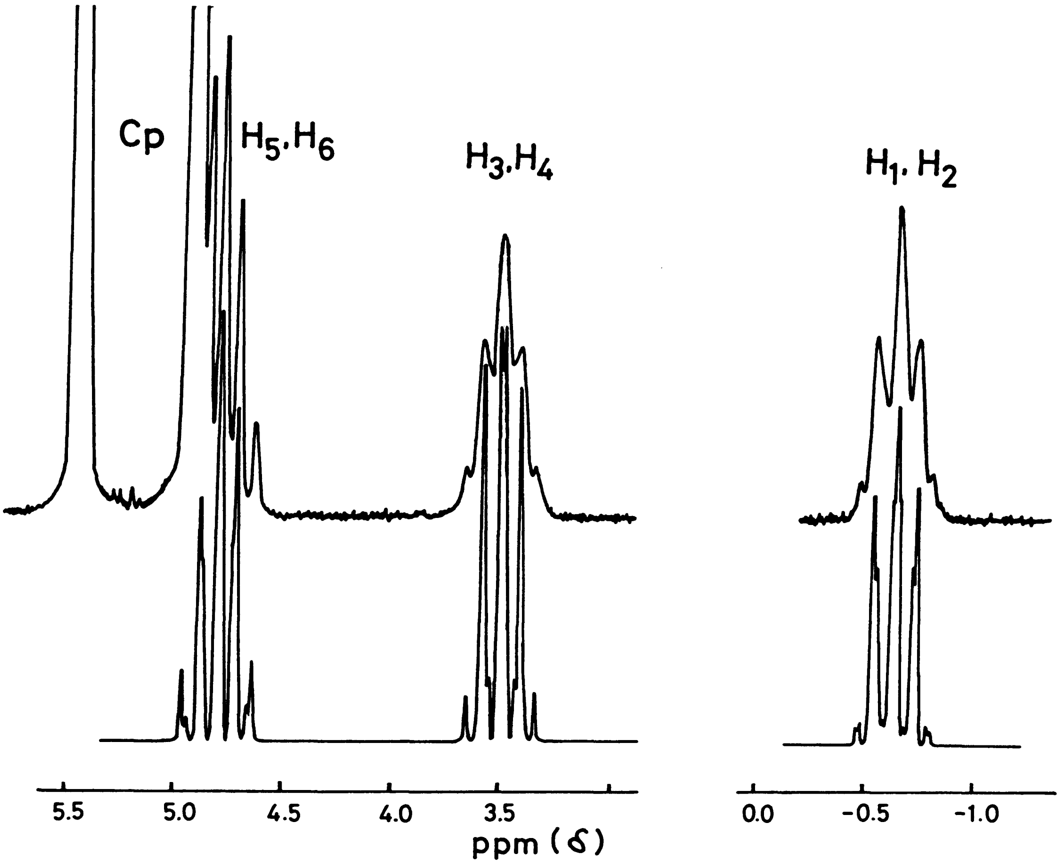
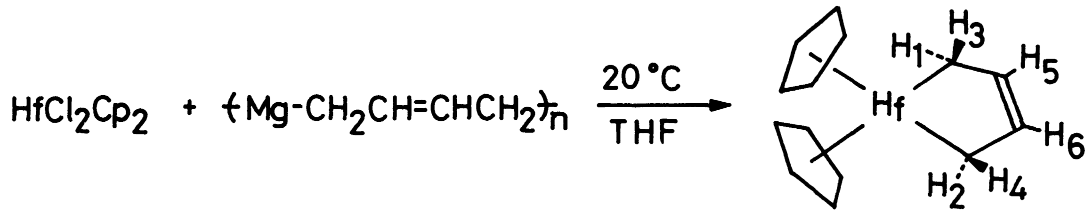


Fig. 1. ^1H-NMR(100 MHz) spectrum of $ZrCp_2(CH_2CHCHCH_2)$ in toluene-d_8 at -40 °C (above) and the simulated spectrum (below).

reported by Krüger.$^{2)}$ The formation of ZrCp$_2$(s-trans-1,3-butadiene) was suppressed in this case. The chemical shift difference between the syn- and anti-protons of the coordinated diene was very large (ca. 4.0 ppm) compared to those in η^4-s-cis-diene complexes of group VIII element (ca. 1.4 ∿ 2.1 ppm) presumably due to the anisotropic magnetic shielding effect of the Cp rings.

The corresponding HfCp$_2$(CHR$_1$-CR$_2$=CR$_3$-CHR$_1$) where R$_1$,R$_2$,R$_3$=H,H,H; R$_1$,R$_2$,R$_3$= H,CH$_3$,H or R$_1$,R$_2$,R$_3$=H,CH$_3$,CH$_3$ could also be prepared in essentially the same method as ZrCp$_2$(diene) and were isolated as air-sensitive yellow crystals. All the complexes were monomeric in benzene. The structure of these complexes was determined



by the same method as described for the zirconium complexes. For example, HfCp$_2$-(CH$_2$-CH=CH-CH$_2$) 2 showed the following data; mp. 78 °C; Hf 49% (Calcd. 49.2%); hydrolysis product, 1-butene 1.0 mol/mol (Calcd. 1.0 mol/mol); Cp/diene ratio by ^{1}H-NMR, 2.1 mol/mol (Calcd. 2.0 mol/mol). The spectroscopic behavior of the Hf-butadiene complex 2 was distinctly different from that of Zr-complex 1 and was essentially temperature independent from 80 °C to a temperature as low as -90 °C in toluene-d_8. Since the spectrum of 2 cannot be analyzed at hand by the first-order analysis, the parameters were obtained by simulation; δ=1.14(H$_{1\sim4}$), 5.04 ppm (H$_{5\sim6}$); J_{15},J_{35},J_{26},J_{46}=10.1, J_{12},J_{34}=1.4, J_{16},J_{25},J_{36},J_{45}=-0.3, J_{56}=11.1 Hz. Such spectroscopic difference between 1 and 2 is worthy of remark since Zr and Hf are known to have the similar electonegativities and atomic or ionic radii due to the Lanthanide contraction. Based upon the following reasons, the present ^{1}H-NMR data of 2 can be interpreted by the hafnacyclo-3-pentene structure where only the terminal carbons of the diene are covalently bound to Hf. 1) The recently reported X-ray structure of ZrCp$_2$(2,3-dimethyl-1,3-butadiene) shows stronger bonding between the metal and terminal carbons of the diene moiety. 2) The chemical shift of the protons at diene termini in 2 appeared at higher field by 0.29 ppm from the time-averaged chemical shift of the Zr analogue 1. 3) The preference of 1-4-η^2-diene coordination for Hf and η^4-diene coordination for Zr are in accord with the general trend that the metal-hydrogen or metal-carbon σ-bond is stronger and less fluxional for the 3rd row transition metals than the corresponding bond in the 2nd row metals

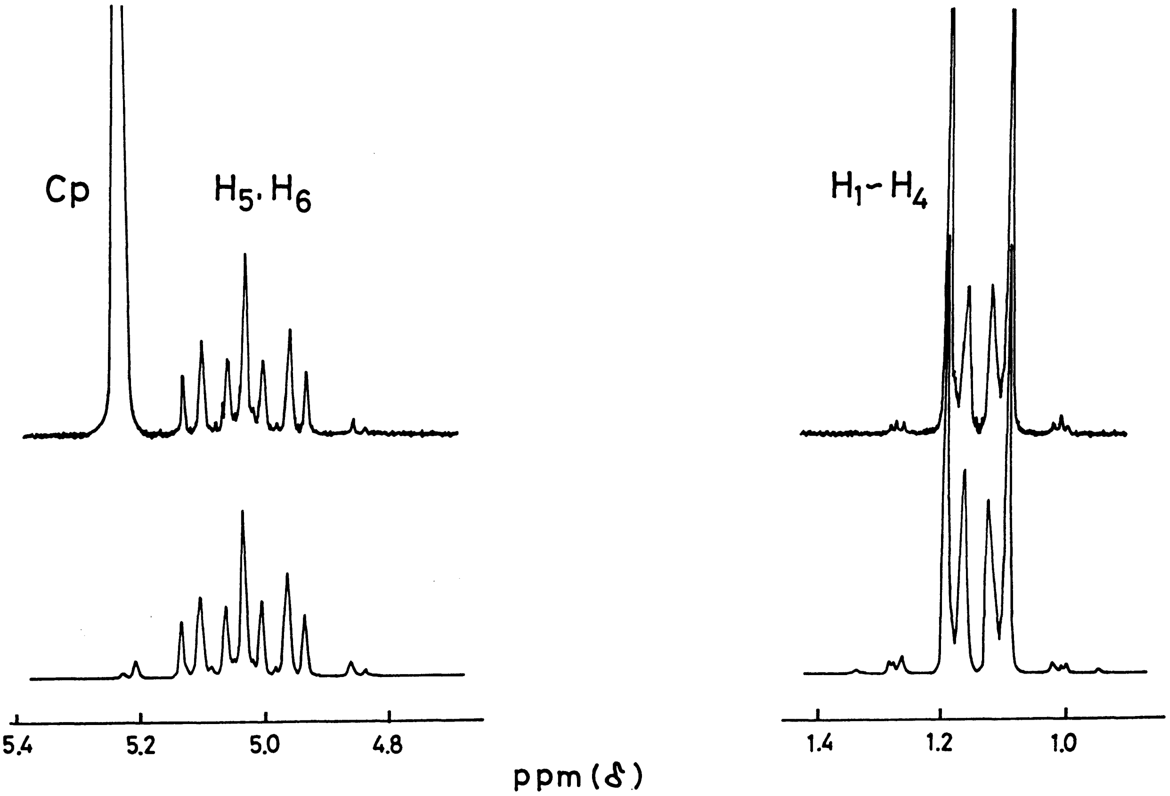


Fig. 2. ^{1}H-NMR(100 MHz) spectrum of $HfCp_2(CH_2CHCHCH_2)$ 2 in toluene-d_8 at -40 °C and the simulated spectrum.

when the isostructural complexes are compared. 4) Although there are many olefin- or diolefin-complexes having the fluxional structure in solution, quite few are *known to be highly fluxional even at -90 °C.*

Thus, very little difference existing between isostructural Zr and Hf complexes, which is not discernible by the usual chemical method, could be detected in the organometallic complexes bearing η-cyclopentadienyl and multicenter-carbon ligands.

References

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