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Preliminary communication

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^{1}H NMR STUDY OF THE FLUXIONAL BEHAVIOUR OF TETRAALLYLHAFNIUM AND CYCLOOCTATETRAENEDIALLYLZIRCONIUM

R. BENN* and E.G. HOFFMANN

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-433 Mülheim a.d. Ruhr (B.R.D.)

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Summary

The thermodynamic data for the *syn—anti* rearrangement in tetra-η^3-allylhafnium and cyclooctatetraenedi-η^3-allylzirconium have been calculated by line shape analysis of the temperature dependent ^{1}H NMR spectra.

The structure and fluxional nature of the allyl group in allylmetal compounds has been widely investigated by means of nuclear magnetic resonance [1]. From a ^{1}H NMR point of view two broad types of metal—allyl bonding may be distinguished, namely those in which the allyl groups give AM_2X_2 spectral patterns (η^3-allyl systems or ionic species $M^+[C_3H_5]^-$) and those in which they give $ABCX_2$ patterns (η^1-allyl systems). In many cases, however, (e.g. Li(allyl) [2], Mg(allyl)$_2$ [3], Zn(allyl)$_2$ [1, 4], Hf(allyl)$_4$ [5], Zr(allyl)$_4$ [1, 5]) simple AX_4 spectra are observed at room temperature, these originating either from equilibrated *syn*- and *anti*-protons or from methylene and terminal olefinic protons. The true nature of the metal—allyl bonding can be revealed only if a slow rate of exchange (on the ^{1}H NMR time-scale) can be achieved at lower temperatures. In the case of Li-[2], Zn- [1, 4], and Zr-allyl systems [5] ^{1}H NMR spectra with slow exchange ($k \leqslant 40$ s^{-1}) can be observed at sufficiently low temperatures.

Diallylmagnesium [3], tetraallylhafnium (I) [5] as well as cyclooctatetraenediallylzirconium (II) [5, 6] are examples of systems which give AX_4 spectra even at $-80°$C (100 MHz), and it has been suggested that the free activation energy for the equilibration of the protons must be very small. Use of high-field NMR spectrometers of up to 400 MHz permits study of exchange processes with small free activation energies (down to 5 kcal/mol), and therefore the spectra of I and II have been examined at 400 and 270 MHz. Complexes I and II may also serve as models for related cyclooctatetraene (COT) complexes such as [(COT)-1,2,3,6-η-2-hexenediyl]metal, [(COT)-1,2,3,6,7,8-η-2,6-octadienediyl]-metal and [(COT)-1,2,3,4-η-butadiene]metal (metal = Zr, Hf), which have also been shown to be fluxional by line shape analysis and magnetisation transfer*.

Complex I (dissolved in pentane-d_{10}, a solvent without any donor capability) shows in the 400 MHz spectra at —70°C the well known AX_4 pattern (δ_A 5.39 ppm, δ_X 2.74 ppm, J_{AX} 12.6 Hz). At lower temperatures the resonance of the doublet broadens, and at —123°C two broad resonances at δ 3.25 ppm (half width $\Delta \sim 52$ Hz) and δ 2.01 ppm ($\Delta \sim 80$ Hz) appear. Coalescence is observed at —110°C (400 MHz). The broader (smaller) resonances at δ 2.01 ppm (δ 3.25 ppm) are assigned to the *anti* (*syn*) protons due to the larger (smaller) vicinal coupling of the *anti* (*syn*) protons with the *meso* proton. The low temperature spectrum indicates four equivalent symmetrically bonded η^3-allyl groups. The activation parameters resulting from a preliminary line shape analysis (with complete neglect of the spin coupling constants) are listed in Table 1. In this analysis the permutation scheme (mutual exchange of the terminal protons) due to the π—σ—π exchange mechanism was used. This process has been shown to account for the fluxional behaviour of tetra-η^3-allylzirconium (III) [1, 5, 7], whose activation parameters are also listed in Table 1. These parameters result from a reinvestigation of the temperature dependent spectra of III dissolved in toluene-d_8. A complete line shape analysis including the vicinal coupling constants was performed: the activation parameters (cf. Table 1) are in line with earlier results [5] and the accuracy of the measurements allow the entropy of activation to be determined.

TABLE 1

ACTIVATION PARAMETERS FOR I, II, III AND IV. (E_a results from an Arrhenius plot, whereas $\Delta H^\ddagger$ and $\Delta S^\ddagger$ result from the corresponding Eyring diagram. In III and IV the vicinal couplings were included in the line shape analysis)

	$Hf(\eta^3\text{-all})_4$ (I)	$Zr(\eta^3\text{-all})_4$ (III)	$COT\text{-}Zr(\eta^3\text{-all})_2$ (II)	$COT\text{-}Hf(\eta^1\text{-all})_2THF$ (IV)
E_a (kcal/mol)	6.5 ± 0.5	15.2 ± 0.5	9.1 ± 0.5	11.4 ± 0.5
$\Delta H^\ddagger$ (kcal/mol)	6.1 ± 0.5	14.7 ± 0.5	8.7 ± 0.5	10.9 ± 0.5
$\Delta S^\ddagger$ (e.u.)	—5.6 ± 4	+19.4 ± 3	+3.3 ± 3	+8.1 ± 3

Furthermore, COT-diallylzirconium (II) (dissolved in toluene-d_8) was studied between —60° and —105°C at 270 MHz (cf. Fig. 1). At temperatures below —100°C two broadened signals are observed at δ 2.94 ppm ($\Delta \sim 54$ Hz) and δ 2.14 ppm ($\Delta \sim 35$ Hz); these resonances are assigned to the *anti* and *syn* protons of II. Again the assignment is based on the correlation of the halfwidth of the resonances with the larger (smaller) vicinal coupling of the *anti* (*syn*) protons with the *meso* proton. Normally in η^3-allylmetal complexes the relationship $\delta(syn) > \delta(anti)$ holds. However, for related COT-allylzirconium compounds chemical shifts similar to those in II have been observed**. The proce-

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*These compounds were prepared by L. Stehling and G. Wilke (1977, unpublished results); a comprehensive study of DNMR in these and related compounds is in progress (R. Benn to be published).

**For [(COT)-η^3-allyl-*O*-t-butyl]zirconium the chemical shifts of the allyl protons are: δ(*meso*) 6.10; δ(*syn*) 2.24 ppm, ^3J 10.0 Hz; δ(*anti*) 2.92 ppm, ^3J 15.5 Hz; toluene-d_8, —50°C; cf. ref. 8; [(COT)-1,2,3,6,7,8-η-2,6-octadienediyl]zirconium: δ(*syn*) 3.38 ppm, δ(*anti*) 3.75 ppm [6].

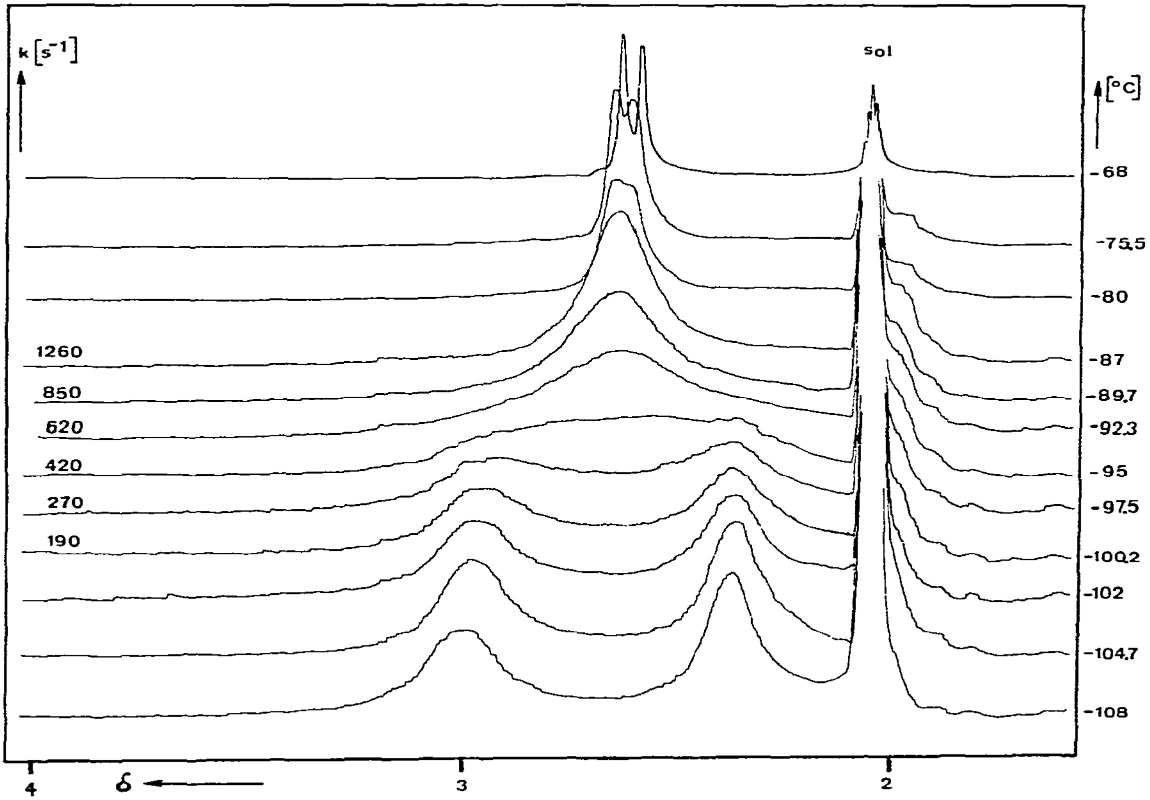

Fig. 1. 270 MHz spectra of II (solvent ≡ sol:toluene-d_8) at temperatures between −68 and −108°C, k denotes the rate constants resulting from the line shape analysis by complete neflect of the coupling constants (k = 1600 s^{-1} at −84.5°C). The *meso*- and the COT-absorptions are omitted for clarity.

dure for the line shape analysis was the same as for I, and the estimated exchange rate constants are noted in Figure 1. The thermodynamic data for the π—σ—π rearrangements are also listed in the Table.

The thermodynamic data reveal different properties for I, II and III. The CIDNP experiments also reveal significant differences in behaviour between I and II on the one hand and III on the other hand [9]. If the π—σ—π exchange mechanism [1] which has been shown to be dominant for III [5, 7] also accounts for the fluxional behaviour of I and II an appreciably higher participation of an η^1-allyl like species in the transition state may be postulated for I and II than for III, in accord with the large differences in the activation energies. This is in line with results of IR investigation of these compounds [5], where in the range of C=C valence vibrations no indications of η^1-allyl absorptions could be observed for III in contrast to I and II. Interestingly, in COT-diallylhafnium (IV) the allyl groups are η^1 bonded to metal, when IV is dissolved in a donor solvent such as THF [5]*. The 270 MHz low temperature spectra of IV confirm the influence of the donor solvent: the methylene pro-

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*For COT-di-η^1-allylhafnium (IV) in THF-d_8, −99°C, 270 MHz. ^{1}H NMR δ 6.15 ppm. δ(*trans*) 4.00 ppm, ^3J 15.4 Hz, δ(*cis*) 3.95 ppm, ^3J 10.3 Hz, δ_A (methylene) 0.30 ppm, δ_B (methylene) 0.42 ppm, $^2J_{A,B}$ 8.8 Hz. Preliminary results indicate that in non-donor solvents such as pentane or toluene IV has η^3-bonded allyl groups.

tons become diastereotopic, clearly indicating that the solvent THF acts as ligand and may induce the η^1-coordination of the allyl group. The large changes in $\Delta S^\ddagger$ for the homologous compounds I and III are noteworthy. They may be caused by differences in the reaction paths (a first order reaction has been found for III [5, 10], whereas for I higher order may operate) thus leading to lower activation entropies. The lower activation parameters for II (compared with III) may result from the fact that COT in II has a dianion type of bonding.

References

1 G. Wilke et al., Angew. Chem., 78 (1966) 157: K. Vrieze in Dynamic Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1975, p. 441.
2 P. West, J.I. Purmont and S.V. McKinley, J. Amer. Chem. Soc., 90 (1968) 797.
3 H.E. Ziegler and J.D. Roberts, J. Org. Chem., 34 (1969) 1976.
4 R. Benn, E.G. Hoffmann, H. Lehmkuhl and H. Nehl, J. Organometal. Chem., 146 (1978) 103.
5 E.G. Hoffmann, R. Kallweit, G. Schroth, K. Seevogel, W. Stempfle and G. Wilke, J. Organometal. Chem., 97 (1975) 183.
6 H.J. Kablitz and G. Wilke, J. Organometal. Chem., 51 (1973) 241.
7 J.K. Krieger, J.M. Deutsch and G.M. Whitesides, Inorg. Chem., 12 (1973) 1535.
8 R. Kallweit, Ph.D. Thesis, Ruhr-Universität Bochum, B.R.D. 1974, p. 111.
9 R. Benn and G. Wilke, J. Organometal. Chem., 174 (1979) C38.
10 J.K. Becconsall. B.E. Job and S.O. Brien, J. Chem. Soc. (A), (1966) 423.