22. A Variable-Pressure 2D ^{1}H-NMR Study of the Mechanism of Trimethyl Phosphate Intermolecular Exchange and *cis/trans*-Isomerisation of Tetrachlorobis(trimethyl phosphate)zirconium(IV)[1]

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In chloroform, $[ZrCl_4 \cdot 2(MeO)_3PO]$ exists in both *cis*- and *trans*-isomeric forms. Three reactions can be envisaged in the presence of excess $(MeO)_3PO = L$: (*1*) *cis*-$[ZrCl_4 \cdot 2L] + {}^*L \leftrightharpoons$ *cis*-$[ZrCl_4 \cdot L{}^*L] + L$; (*2*) *trans*-$[ZrCl_4 \cdot 2L] + {}^*L \leftrightharpoons$ *trans*-$[ZrCl_4 \cdot L{}^*L] + L$; (*3*) *cis*-$[ZrCl_4 \cdot 2L] \leftrightharpoons$ *trans*-$[ZrCl_4 \cdot 2L]$. To distinguish between these possible reaction pathways, we have used 2D ^{1}H-NMR spectroscopy. For the first time, variable-pressure 2D exchange spectra were used for mechanistic assignments. *cis/trans*-Isomerisation was found to be the fastest reaction (in $CHCl_3/CDCl_3$), with a small acceleration at higher pressure: it is concluded to be an intramolecular process with a slightly contracted six-coordinate transition state. The intermolecular $(MeO)_3PO$ exchange on the *cis*- and *trans*-isomer are second-order processes and are strongly accelerated by increased pressure: I_a mechanisms are suggested without ruling out limiting *A* mechanisms.

Introduction. – Spectroscopic studies have shown that octahedral $[MX_4 \cdot 2L]$ complexes (M = Ti [2], Sn [3] [4], Zr, and Hf [5]; X = halide; L = neutral *Lewis* base) exist in general as either the *cis*- or the *trans*-form in the solid, but that coexistence of both isomers in solution is not uncommon. NMR line-broadening and magnetization-transfer kinetic studies have furnished the most detailed information to date on the exchange reactions of $[MX_4 \cdot 2L]$ complexes (M = Ti [6], Sn [7–9]) and show that, in the presence of excess ligand, three potential reaction pathways are possible. The first pathway involves the exchange of a free ligand with a coordinated ligand on the *cis*-isomer:

$$cis\text{-}[MX_4 \cdot 2L] + {}^*L \overset{k_c}{\leftrightharpoons} cis\text{-}[MX_4 \cdot L{}^*L] + L \qquad (1)$$

The second pathway is the analogous reaction on the *trans*-isomer:

$$trans\text{-}[MX_4 \cdot 2L] + {}^*L \overset{k_t}{\leftrightharpoons} trans\text{-}[MX_4 \cdot L{}^*L] + L \qquad (2)$$

And the third pathway is an isomerisation between *cis*- and *trans*-isomers:

$$cis\text{-}[MX_4 \cdot 2L] \overset{k_i}{\leftrightharpoons} trans\text{-}[MX_4 \cdot 2L] \qquad (3)$$

In the previous studies on the $3d^0$ Ti(IV) and $4d^{10}$ Sn(IV) complexes, only reactions (*1*) and (*3*) were observed. The fastest reaction was the intermolecular exchange on the *cis*-isomer. Both reactions have first-order rate laws and positive $\Delta S^{\neq}$ and $\Delta V^{\neq}$ values. *D* mechanisms with five-coordinate intermediates were assigned to the intermolecular *cis*-substitutions. Intramolecular mechanisms with expanded six-coordinate transition

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[1] Part 45 of the series 'High-Pressure NMR Kinetics'; for part 44, see [1].

[2] Taken, in part, from the Ph.D. thesis of *U. F.*

states were assigned to the isomerisations on the basis of smaller, but still positive activation volumes.

Zr^{4+} (r = 80 pm) is a much larger ion than Ti^{4+} (68 pm) and Sn^{4+} (71 pm); one may thus expect large differences in the mechanistic behaviour of their $[MX_4 \cdot 2L]$ complexes. To demonstrate these possible differences and to distinguish between the three possible reaction pathways, we have used 2D ^{1}H-NMR spectroscopy. For the first time, variable-pressure 2D NMR exchange spectra were used for mechanistic assignments.

Experimental. – Sample solns. were prepared by mixing appropriate quantities (given as *m* [mol/kg] of solvent) of $ZrCl_4$ (*Merck, puriss.* 99.9%), trimethyl phosphate $(MeO)_3PO$, and a mixture $CHCl_3/CDCl_3$ 1:1 (purified by passing through a column containing basic Al_2O_3; stored over molecular sieves). Sample manipulations were carried out in a dry glove box (less than 2 ppm of H_2O).

^{1}H-NMR spectra were obtained at 400 MHz on a *Bruker-AM-400* spectrometer. The variable-pressure spectra were measured with a homebuilt high-pressure probe [10]. Two-dimensional ^{1}H-EXCSY spectra were obtained using the pulse sequence $90° (\phi_1)-t_1-90° (\phi_2)-\tau_m-90°-t_2$ with a mixing time τ_m of 0.1 s. The first pulse creates magnetization which evolves with a characteristic frequency during the interval t_1. The second pulse creates longitudinal magnetization which can undergo interconversion by chemical exchange during the mixing time. Finally, the third pulse reconverts the longitudinal magnetization into observable transverse magnetization, and the resultant free induction decay is acquired during t_2. If exchange is occurring between two spins *A* and *X* on a time scale comparable with τ_m, the frequency spectrum obtained by FT with respect to t_1 and t_2 will contain crosspeaks which have the frequency Ω_A in f_1 and Ω_X in f_2, and *vice versa*. The spectra were obtained with 1024 complex points in f_2 over a total spectral width of 400 Hz and 8 scans for each of 256 points in f_1, which was zero-filled to 1024 x 512 and weighted by a *Lorentz-Gauss* transformation in both dimensions before complex *Fourier* transform to obtain a phase-sensitive spectrum. The phases ϕ_1–ϕ_3 were cycled so as to select populations during τ_m and to suppress axial peaks. The choice of τ_m was a compromise: it was chosen large enough to show up all crosspeaks, but small enough to fulfill the condition of initial rate ($\tau_m < 1/k_{max}$), where k_{max} is the largest exchange rate. Moreover, τ_m is at least by a factor 30 smaller than the spin-lattice relaxation time T_1 (3.4, 3.2, and 4.0 s for the ^{1}H of the *cis*-isomer, *trans*-isomer, and free $(MeO)_3PO$, resp., at 249 K) and, therefore, does not affect the intensities of both the autopeaks and the crosspeaks [11]. Exchange rates were obtained using the D2DNMR program [12].

Results and Discussion. – *Fig. 1* shows the ^{1}H-NMR spectrum of a 0.1 *m* $[ZrCl_4 \cdot 2(MeO)_3PO]$ and 0.2 *m* $(MeO)_3PO$ solution in $CHCl_3/CDCl_3$ at 236 K. The spectrum contains 3 *d*, each *d* due to $^3J(^1H,^{31}P)$ splitting. The *d* at 3.78 ppm (^3J = 14.0 Hz) is due to free $(MeO)_3PO$ and the other two, at 4.08 (11.7 Hz) and 4.17 ppm (11.8 Hz), to $(MeO)_3PO$ in the *cis*- and *trans*-isomers, respectively [5]. The isomerisation constant $K_{iso} = [trans]/[cis]$ is 2.04. As the temperature is raised, the *d*'s of the *trans*- and *cis*-isomers broaden and eventually coalesce, indicating that the *cis*/*trans*-isomerisation occurs first (this observation differs fundamentally from those made on the $[TiX_4 \cdot 2L]$ and $[SnX_4 \cdot 2L]$ complexes where the reaction of *Eqn. 1* is the fastest). At slightly higher temperature, the free-ligand *d* broadens also and coalesces with the signal of the *cis*/*trans*-isomers. The source of this second broadening could be a ligand-exchange reaction between the free ligand and the *cis*- and/or *trans*-isomer. In this case, NMR line-broadening simulation can hardly quantify the individual contribution of the three exchange reactions to the observed spectra.

Fig. 2a shows the ambient-pressure 2D ^{1}H-NMR exchange spectra of a $[ZrCl_4 \cdot 2(MeO)_3PO]$ solution in $CDCl_3/CHCl_3$ at 256 K, with excess $(MeO)_3PO$. Under these conditions, the most intense crosspeaks relate the *d*'s of the *cis*- and *trans*-isomers, confirming that the isomerisation *(Eqn. 3)* is the fastest process. The crosspeaks for the intermolecular ligand exchange on the *trans*-isomer *(Eqn. 2)* are smaller, and finally the crosspeaks for the exchange reaction on the *cis*-isomers *(Eqn. 1)* are just observable. The

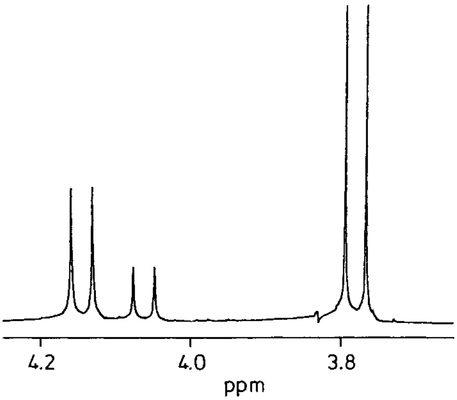

Fig. 1. *400-MHz* ^{1}*H-NMR spectrum of* cis- *and* trans-*[*$ZrCl_4 \cdot 2(MeO)_3PO$*] in the presence of excess* $(MeO)_3PO$. In $CHCl_3/CDCl_3$ at 236 K. Assignments, see text.

corresponding calculated rate constants are reported in the *Table*. *Fig. 2b*, obtained at 198 MPa, shows the effect of pressure on the three observed reactions.

The isomerisation is only slightly accelerated at higher pressure, leading to a small negative volume of activation $\Delta V_{\mathrm{i}}^{\ddagger}$. It can be interpreted as an intramolecular rearrangement *via* a slighthly contracted six-coordinated transition state. This behaviour contrasts

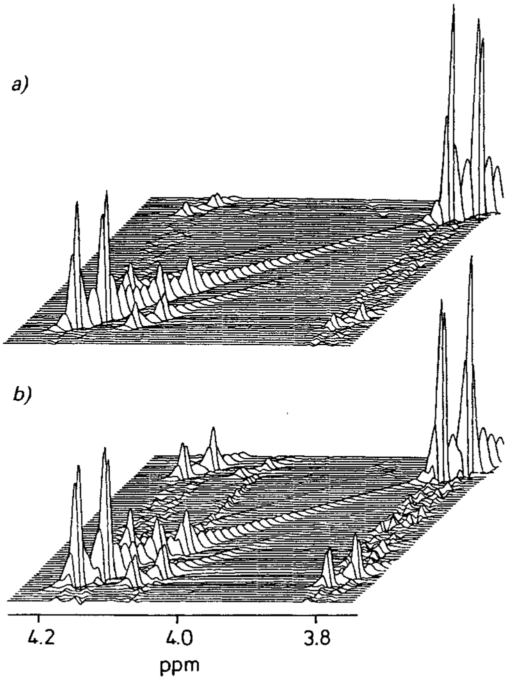

Fig. 2. *400-MHz 2D* ^{1}*H-NMR exchange correlation spectra* a) *at 0.1 MPa and* b) *at 198 MPa for the intermolecular exchanges between free* $(MeO)_3PO$ *and both* cis- *and* trans-*coordinated ligand in [*$ZrCl_4 \cdot 2(MeO)_3PO$*] and for the intramolecular* cis/trans-*isomerisation.* In $CHCl_3/CDCl_3$ at 256 K. [$ZrCl_4 \cdot 2(MeO)_3PO$] = 0.108 *m*, $(MeO)_3PO$ = 0.107 *m*.

Table. *Effect of Pressure on the Rate Constants* $k^r_{c\text{-free}}$ *and* $k^r_{t\text{-free}}$ *for Intermolecular Exchange of Free (MeO)₃PO on* cis *and* trans-*[ZrCl₄·2(MeO)₃PO], Respectively, and on the Rate Constant* k^r_i *for* cis/trans-*Isomerisation*[a])[b]) (CHCl₃ solutions at 256 K)

P [MPa]	$k^r_{c\text{-free}}$ [s^{-1}]	$k^r_{t\text{-free}}$ [s^{-1}]	k^r_i [s^{-1}]
0.1	$0.1_5 \pm 0.1$	0.5 ± 0.1	5.2 ± 0.5
198	0.4 ± 0.1	1.7 ± 0.1	7.1 ± 1.0

a) $k^r = 1/\tau_r$ where τ_r is the mean residence time of (MeO)₃PO in the corresponding site.

b) Reported errors represent one standard deviation. k^r is the mean value of the rate constants obtained from the four crosspeaks corresponding to one particular exchange process.

with that of [$TiCl_4 \cdot 2(MeO)_3PO$] ($\Delta V_i^{+} = +6.2$ cm^3 mol^{-1} [6]) and [$SnCl_4 \cdot 2Me_2S$] (+9.0 cm^3 mol^{-1} [9]) for which this process is characterised by a clearly positive activation volume that was also interpreted in terms of an intramolecular mechanism, but this time with an expanded six-coordinate transition state.

On the contrary, the intermolecular (MeO)₃PO exchange on both *cis*- and *trans*-[$ZrCl_4 \cdot 2(MeO)_3PO$] is strongly accelerated at higher pressure. Both processes also obey a second order rate law: first order in complex and first order in (MeO)₃PO. Together, these observations are taken as evidence for associative interchange mechanisms I_a, without ruling out possible limiting *A* mechanisms. This result contrasts sharply with the *D* mechanism assigned to the intermolecular exchange on the *cis*-[$TiX_4 \cdot 2L$] and *cis*-[$SnX_4 \cdot 2L$] complexes on the basis of very positive volumes of activation (+17.5 to + 38.4 cm^3 mol^{-1} [6] [9]) and first-order rate laws.

The striking differences in reaction mechanism for [$ZrX_4 \cdot 2L$] as, compared to [$TiX_4 \cdot 2L$] and [$SnX_4 \cdot 2L$] are due to the increase in ionic radius which favours the changeover from a dissociative to an associative activation mode.

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