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Adducts of Titanium Tetrahalides with Neutral Lewis Bases. Part II. Kinetics and Reaction Mechanism: a Variable Temperature and Variable Pressure Proton NMR Study*

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Abstract

The ligand exchange reaction *cis*-$TiX_4 \cdot 2L + {}^*L \rightleftarrows$ *cis*-$TiX_4 \cdot L^*L + L$ has been studied for a series of *cis*-$TiX_4 \cdot 2L$ adducts (X = Cl, Br; L = Lewis base) in CH_2Cl_2 and $CHCl_3$ by variable temperature and variable pressure proton NMR. The exchange reactions are characterized by large, positive values of ΔH^* (50.2–61.5 kJ/mol), ΔS^* (9.2–103 J/mol K) and ΔV^* (17.5–26.1 cm^3/mol) and by first order rate laws. For this series of adducts, ΔG^* (213 K) for ligand exchange decreases as the stability of the adduct decreases. It was concluded that this ligand exchange process occurs via a dissociative, D, mechanism. The *cis*/*trans* isomerization of $TiCl_4 \cdot 2TMPA$ in $CHCl_3$ was also investigated. In view of the small but positive ΔV^*_{iso} (6.2 cm^3/mol), it was concluded that the isomerization process occurs via an intramolecular twist mechanism with an expanded six-coordinate transition state.

Introduction

As discussed in our previous paper [2], $TiX_4 \cdot 2L$ adducts (X = F, Cl, Br; L = Lewis base) in inert solvents and in the presence of excess free ligand exist primarily as *cis* isomers except when the adducts contain Lewis base ligands having a strong electron donating ability or a large amount of steric bulk, for which case an equilibrium between *cis* and *trans* isomers is observed. The absence of *trans* isomers in solutions of $TiX_4 \cdot 2L$ adducts with weak electron donating Lewis base ligands is not observed for solutions of the analogous $SnX_4 \cdot 2L$ complexes where an equilibrium between *cis* and *trans* isomers is observed for most Lewis base ligands. It has been determined that $p_\pi - d_\pi$ halogen–metal bonding is important in the formation of d^0 $TiX_4 \cdot 2L$ adducts but that such bonding is unimportant in the formation of d^{10} $SnX_4 \cdot 2L$ species. Although $TiCl_4$ and $SnCl_4$ have similar radii, electronic effects influence the formation of their Lewis base adducts differently.

For exchange reactions involving the $TiX_4 \cdot 2L$ and $SnX_4 \cdot 2L$ adducts, three reaction pathways can be envisaged. The first pathway involves the exchange of a free ligand with a coordinated ligand on the *cis* isomer:

$$cis\text{-}MX_4 \cdot 2L + L^* \overset{k_{cis}}{\rightleftharpoons} cis\text{-}MX_4 \cdot L \cdot L^* + L \qquad (1)$$

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

$$trans\text{-}MX_4 \cdot 2L + L^* \overset{k_{trans}}{\rightleftharpoons} trans\text{-}MX_4 \cdot L \cdot L^* + L \qquad (2)$$

And the third pathway is an isomerization reaction between *cis* and *trans* isomers:

$$cis\text{-}MX_4 \cdot 2L \overset{k_{iso}}{\rightleftharpoons} trans\text{-}MX_4 \cdot 2L \qquad (3)$$

For the $SnX_4 \cdot 2L$ system [3], ligand exchange between *cis* and free sites was observed and the mechanism for the exchange was found to involve the dissociation of the *cis*-$SnX_4 \cdot 2L$ adduct into a five coordinate intermediate and a free ligand. No ligand exchange reaction was observed for the *trans* isomer, but an intramolecular isomerization reaction between *cis* and *trans* isomers was found to be important. The mechanism for the *cis*–*trans* isomerization did not involve the dissociation of a ligand from the adduct as with the *cis*-free ligand exchange, but did seem to involve an intramolecular twisting motion of the adduct with an expansion of the Sn–X and Sn–L bond lengths. In contrast to the $SnX_4 \cdot 2L$ adducts, the $TiX_4 \cdot 2L$ complexes have empty t_{2g} orbitals so ligand exchange reactions with these species can be expected [4, 5] to occur via a pathway where association between a free ligand and the adduct to form a seven coordinate intermediate takes place.

Since electronic effects influence the formation of $TiX_4 \cdot 2L$ and $SnX_4 \cdot 2L$ isomers differently and since these effects have the potential to alter the mechanism

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for exchange reactions, we undertook a kinetic study of the $TiX_4 \cdot 2L$ adducts. This paper reports the results of that study and is concerned with the ligand exchange behavior of several *cis*-$TiX_4 \cdot 2L$ adducts in inert solvents and also the kinetic behavior of $TiCl_4 \cdot 2TMPA$, which exists as an equilibrium between *cis* and *trans* isomers.

Experimental

The preparation of the $TiX_4 \cdot 2L$ adducts was described in the previous report [2]. For the rate law determination studies a TiX_4 concentration of 0.10 m (m = mol kg^{-1}) was used and the total concentration of added ligand varied from 0.270 to 0.869 m. The temperature and pressure dependence work was done with solutions containing 0.10 m TiX_4 and 0.40 m added ligand (except for *cis*-$TiCl_4 \cdot 2Cl(MeO)_2PO$ where $[TiCl_4] = 0.067$ m and $[Cl(MeO)_2PO] = 0.268$ m) giving a $TiX_4 \cdot 2L$ to free ligand ratio of 1:2.

The ambient pressure ^1H NMR measurements were made with either Bruker WP-60 or CXP-200 instruments operating at 60 and 200 MHz, respectively. For the variable pressure ^1H NMR measurements a Bruker CXP-200 instrument equipped as described previously [6] was used. The temperature was measured with a platinum resistor for both ambient [7] and variable pressure measurements.

The rate constants were measured by ^1H NMR. For exchange in the slow exchange region the rate constants were determined from the peak width at half-height. For fast and intermediate exchange the experimental data were least-squares fitted to the theoretical spectrum using a program derived from EXCNG [8]. Any linewidth variations due to field inhomogeneity and instability were accounted for by measuring the linewidth of the solvent and TMS peaks. These variations were typically 0.2–1.0 Hz for the ambient pressure measurements and 2–5 Hz for the variable pressure measurements. The exchange matrices used in the computer program included spin–spin coupling when it was present, *i.e.* $^2J(^1H-^{77}Se)$ in $TiX_4 \cdot 2Me_2Se$ and $^3J(^1H-^{31}P)$ in $TiCl_4 \cdot 2TMPA$ and $TiCl_4 \cdot 2Cl(MeO)_2PO$.

The choice of temperature for the variable pressure measurements was made so that a small change in the exchange rate resulted in a significant change in the NMR spectrum. This temperature is at the point where the NMR signals of the exchanging species are just coalescing at 0.1 MPa. The pressure dependent kinetic data for the *cis–trans* isomerization of $TiCl_4 \cdot 2TMPA$ was collected at a lower temperature than the coalescent temperature due to rapid decomposition of the adduct at a high temperature.

Results

For the $TiX_4 \cdot 2L$ adducts investigated in this report, the $TiCl_4 \cdot 2L$ adducts with L = Me_2O, Me_2S, Et_2S, Me_2Se, MeCN, Me_2CO and $Cl(MeO)_2PO$ and the $TiBr_4 \cdot 2L$ adducts with Me_2S and Me_2Se were found to exist only as *cis* isomers in inert solvents. For $TiCl_4 \cdot 2TMPA$, an equilibrium between *cis* and *trans* isomers was observed with an isomerization constant, K_{iso} (= [*trans*]/[*cis*]), of 0.36 at 277 K. The low temperature ^1H NMR spectra of the above *cis* adducts in the presence of an excess of L show two peaks or two sets of peaks (when spin–spin coupling between ^1H and other nuclei is present) which can be assigned to both forms of the Lewis base ligands. As the temperature is increased both the coordinated and the free peaks broaden and eventually coalesce, indicating that the Lewis base ligand is exchanging between the two sites. Figure 1 shows the ^1H NMR spectrum of $TiCl_4 \cdot 2TMPA$ in $CHCl_3$ at several temperatures. At low temperature in the absence of exchange, three doublets are observed due to *trans*, *cis* and free TMPA. As the temperature is increased, the *cis* and free ligand peaks broaden and coalesce. A further increase in temperature results in the broadening of the *trans* peaks and the coalesced *cis*/

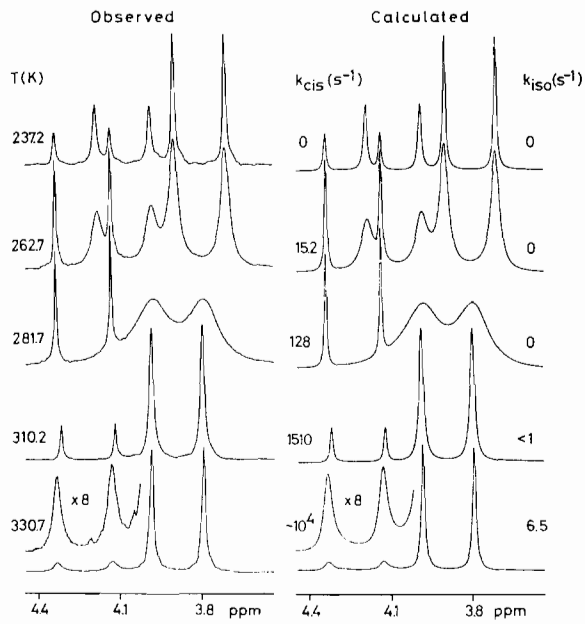

Fig. 1. Variable temperature 60 MHz ^1H NMR spectra of *cis*- and *trans*-$TiCl_4 \cdot 2TMPA$ in $CHCl_3$ showing ligand exchange between free and *cis* coordinated sites and broadening of the *trans* and coalesced *cis*/free signals. The spectra to the right were calculated using least-squares fitting. At 237.2 K, in the absence of exchange, the peak assignments are (center of doublets): *trans* (4.25 ppm), *cis* (4.11 ppm) and free (3.84 ppm). The $TiCl_4 \cdot 2TMPA$ and free TMPA concentrations were 0.10 m and 0.20 m, respectively.

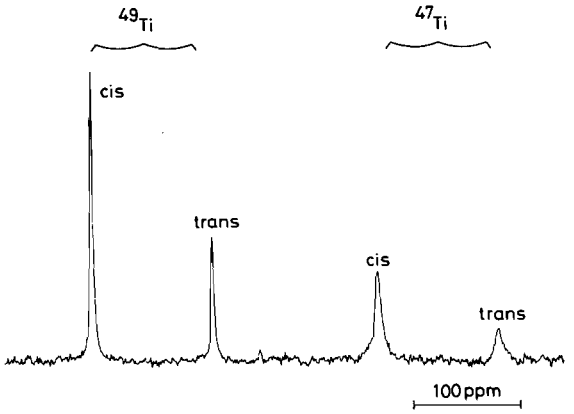

Fig. 2. ^{47,49}Ti NMR spectrum at 325.9 K of 0.1 m $TiCl_4$·2TMPA (total concentration of *cis* and *trans* isomer) and 0.2 m TMPA solution in $CDCl_3$. 3000 scans of 4 k data points (29 400 Hz sweep widths; pulse length: 20 μs) were accumulated. An exponential filter of 15 Hz was used before Fourier transformation.

free peaks. The source of the second broadening could be a ligand exchange reaction between a coordinated *trans* site and a free ligand site, or an isomerization reaction between the *cis* and *trans* isomers: ^{1}H NMR does not permit the identification of the reaction process.

To assist in the determination of the reaction process occurring with the *trans*-$TiCl_4$·2TMPA isomer, we attempted to observe the ^{49}Ti NMR spectrum of *cis* and *trans*-$TiCl_4$·2TMPA. If the reaction process is a *cis–trans* isomerization, then exchange effects will be observed in the individual *cis* and *trans* ^{49}Ti NMR signals because the two sites are magnetically inequivalent. However, if the reaction process is an exchange between coordinated *trans* and free ligand sites, then no exchange effects will be observed in the ^{49}Ti NMR spectrum. At a frequency of 22.56 MHz (9.4 Tesla) at 325.9 K, using a 0.1 m $TiCl_4$·2TMPA and 0.2 m TMPA chloroform solution, we observed four NMR peaks (Fig. 2). The two narrower higher frequency peaks are due to the ^{49}Ti NMR spectrum ($I = 7/2$; natural abundance = 5.51%; magnetogyric ratio $\gamma = -1.5083 \times 10^7$ rad T^{-1} s^{-1}; quadrupole moment $Q = +0.24 \times 10^{-28}$ m^2), while the two broader lower frequencies are from the ^{47}Ti NMR spectrum ($I = 5/2$; 7.28%; $\gamma = -1.5079 \times 10^7$ rad T^{-1} s^{-1}; $Q = +0.29 \times 10^{-28}$ m^2) [9]. The chemical shift of the titanium nuclei in the two chemical environments are referred to external neat $TiCl_4$: −351 ppm for *cis*-$TiCl_4$·2TMPA and −463 ppm for *trans*-$TiCl_4$·2TMPA. This assignment yields a K_{iso} value of 0.4 similar to that obtained by ^{1}H NMR ($K_{iso} \sim 0.33$ at 325.9 K) [2]. The linewidths even of the ^{49}Ti signals are unfortunately too broad (>50 Hz; due to quadrupolar and ^{49}Ti–^{35,37}Cl scalar interaction) to extract kinetic information in this case. From ^{1}H NMR it appears that at this temperature the exchange broadening is less than 3 Hz. The strong quadrupolar interaction, acting not only on spin–spin relaxation (T_2) but also on spin lattice relaxation (T_1), made it impossible to use the magnetization transfer technique as used in the case of the analogue tin(IV) adduct (^{119}Sn has a spin 1/2, therefore no quadrupole moment) [10, 3]. In conclusion titanium NMR cannot help to distinguish between intramolecular *cis–trans* isomerization and intermolecular ligand exchange on the *trans* adduct.

The exchange of a ligand molecule between free and coordinated sites on TiX_4·2L adducts could involve a mechanism with a dissociative, associative or interchange pathway and a major portion of this work was to determine the mechanism of the ligand exchange process. To assist in this determination, the rate law and the activation parameters (ΔH^*, ΔS^* and ΔV^*) were determined for several ligand exchange reactions using the procedures described below.

The rate law for ligand exchange between free and coordinated sites (pathways (1) and (2) in 'Introduction') has different forms depending on the reaction mechanism. In the case of a first order reaction, *i.e.* zero order in ligand and first order in complex, the mean lifetime τ_C of the complex is defined by:

$$1/\tau_C = -d[TiX_4 \cdot 2L]/[TiX_4 \cdot 2L]dt = k_1$$

The mean lifetime τ_C is related to the NMR determined residence time τ_C^r by the relationship: $1/\tau_C = 2/\tau_C^r = k_1$. The factor of 2 in the expression for $1/\tau_C$ is due to the fact that the observed ^{1}H NMR spectrum is the result of two Lewis base ligands but only one ligand is exchanging at any given time. The above equations apply for a dissociative mechanism where the $TiCl_4$·2L forms a five coordinate intermediate and a free ligand. One may also define the kinetic equations for a second order rate law which apply for an associative mechanism, in this case $1/\tau_C = k_2[L]$. For a *cis–trans* isomerization reaction, the mean lifetime of the *trans* isomer ($1/\tau_C = k_{iso}$) is equal to the residence time of the ligand on that isomer.

We have determined the rate laws for the exchange reactions of the adducts by measuring the residence time of the ligand as a function of free ligand concentration. For all the adducts studied no change was observed in $1/\tau_C^r$ over the ligand concentration range used. Figure 3 shows a plot of k (k refers to both k_{cis} and k_{iso}) *versus* free ligand concentration for the adducts *cis*-$TiCl_4$·2TMPA, *cis*-$TiCl_4$·2Me_2Se and *trans*-$TiCl_4$·2TMPA. Table I contains the results of a ligand exchange study involving the *cis*-TiF_4·2Me_2O adduct in SO_2 for which a second order rate law was measured [11].

To determine the activation enthalpy and entropy, ΔH^* and ΔS^*, the dependence of the exchange rate *versus* temperature was measured and the results were

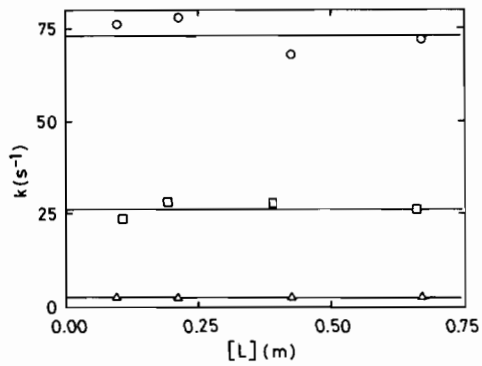

Fig. 3. Rate constants, k, as a function of free ligand, L, concentrations for the *i*-$TiCl_4 \cdot 2L$ adducts: ○, *i* = *cis*, L = TMPA, at 277.2 K in $CHCl_3$; □, *i* = *cis*, L = Me_2Se, at 207.2 K in CH_2Cl_2; △, *i* = *cis/trans*, L = TMPA, at 323.2 K in $CHCl_3$. The $TiCl_4 \cdot 2L$ concentration was 0.10 m in all three cases.

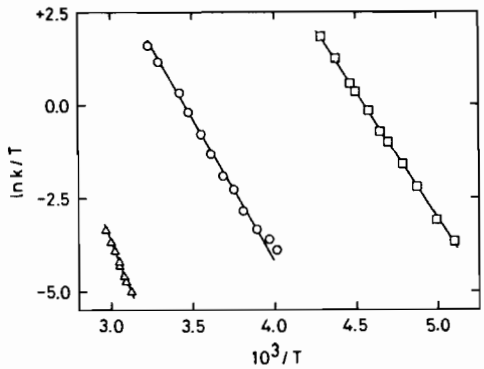

Fig. 4. Eyring plots for the ligand exchange reaction on *cis*-$TiCl_4 \cdot 2L$: □, L = Me_2Se in CH_2Cl_2; ○, L = TMPA in $CHCl_3$; and for the *cis/trans* isomerization reaction of $TiCl_4 \cdot 2TMPA$ in $CHCl_3$ (△). The $TiCl_4 \cdot 2L$ and free ligand concentrations were 0.10 m and 0.20 m in all three cases.

fitted to the Eyring equation. Linear plots of ln k/T *versus* $1/T$ were obtained for all the systems studied. Figure 4 shows the Eyring plots for the adducts *cis*-$TiCl_4 \cdot 2TMPA$, *cis*-$TiCl_4 \cdot 2Me_2Se$ and *trans*-$TiCl_4 \cdot 2TMPA$. The values obtained for ΔH^*, ΔS^* and ΔG^* (at 213 K) are reported in Table I, as are the temperature ranges (ΔT) over which the measurements were made. Only ΔG^* was determined for the adducts *cis*-$TiCl_4 \cdot 2Et_2S$, *cis*-$TiCl_4 \cdot 2MeCN$ and *cis*-$TiCl_4 \cdot 2Me_2CO$. The accuracy of ΔS^* and ΔH^* is dependent on the temperature range of the experiment. Therefore, for systems where only a small ΔT could be used, such as for *trans*-$TiCl_4 \cdot 2TMPA$, the error in ΔS^* is certainly greater than the statistical error reported in Table I. The activation parameters for *cis*-$TiF_4 \cdot 2Me_2O$, as calculated from the values of A and E_a given in ref. 11, are also listed in Table I. In general, large positive values were obtained for ΔH^* and ΔS^*.

The volume of activation, ΔV^*, was determined for the exchange of a ligand between free and

TABLE I. Reaction Orders and Activation Parameters for Ligand Exchange on *cis*-$TiX_4 \cdot 2L$ in CH_2Cl_2 and for *cis–trans* Isomerization of $TiCl_4 \cdot 2TMPA$ (reported errors are ±1σ)

Adduct	Reaction order	ΔH^* (kJ/mol)	ΔS^* (J/mol K)	ΔG^* (213 K) (kJ/mol)	ΔV^* (cm^3/mol)	$\Delta\beta^*$ (10^2 cm^3/mol MPa)
cis-$TiF_4 \cdot 2Me_2O$[b]	2	52.3 ± 2.1	30.5 ± 10.5	45.8 ± 0.4 (205–240)[a]		
cis-$TiCl_4 \cdot 2Me_2O$	1	61.3 ± 1.9	103.1 ± 9.2	39.3 ± 0.1 (187–223)		
cis-$TiCl_4 \cdot 2Me_2S$	1	56.9 ± 2.8	71.1 ± 13.3	41.8 ± 0.2 (191–229)	24.4 ± 1.0 (218.1)[a]	7.0 ± 0.9
cis-$TiCl_4 \cdot 2Et_2S$				39.2 ± 0.2		
cis-$TiCl_4 \cdot 2Me_2Se$	1	56.1 ± 1.2	57.1 ± 5.6	43.9 ± 0.1 (196–240)	26.1 ± 1.2 (228.1)	8.5 ± 0.9
cis-$TiCl_4 \cdot 2MeCN$				42.8 ± 0.3		
cis-$TiCl_4 \cdot 2Me_2CO$				41.7 ± 0.2		
cis-$TiCl_4 \cdot 2Cl(MeO)_2PO$[c]	1	56.6 ± 1.8	35.7 ± 7.7	49.0 ± 0.2 (212–261)		
cis-$TiCl_4 \cdot 2TMPA$[c]	1	60.1 ± 3.1	9.3 ± 11.3	58.2 ± 0.7 (249–310)	17.5 ± 1.2 (285.3)	2.6 ± 1.1
cis-$TiBr_4 \cdot 2Me_2S$	1	50.2 ± 2.5	45.4 ± 12.5	40.6 ± 0.2 (187–229)		
cis-$TiBr_4 \cdot 2Me_2Se$	1	53.8 ± 1.3	47.7 ± 6.2	43.6 ± 0.1 (200–231)		
cis/trans-$TiCl_4 \cdot 2TMPA$[c]	1	92.4 ± 2.3	49.0 ± 7.1	81.9 ± 1.6 (320–337)	6.2 ± 1.8 (340.7)	

[a]The temperature range (in the case of ΔH^*, ΔS^* and ΔG^*) or temperature (in the case of ΔV^*) at which the measurements were made is given in parentheses. [b]Data from ref. 11. [c]In $CHCl_3$.

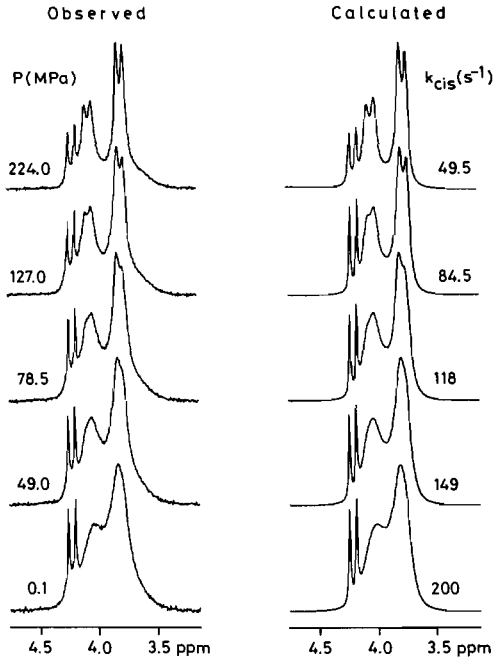

Fig. 5. Observed and calculated 200 MHz ^{1}H NMR spectra of *cis*- and *trans*-$TiCl_4$·2TMPA as a function of pressure at 285.3 K showing the decrease in the exchange rate between *cis* and free ligand sites as the pressure is increased. Exchange effects involving the *trans* isomer peaks are negligible at this temperature. The $TiCl_4$·2L and free TMPA concentrations, in CH_2Cl_2, were 0.10 m and 0.20 m, respectively.

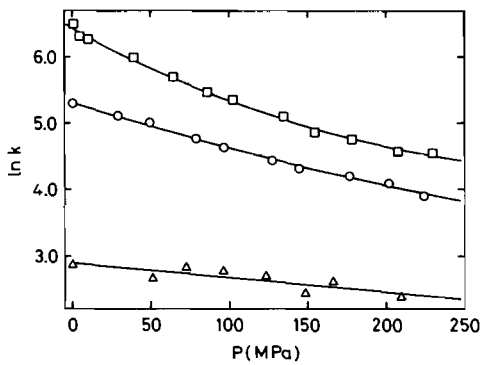

Fig. 6. Plot of ln *k versus* pressure for the ligand exchange reaction on *cis*-$TiCl_4$·2L: □, L = Me_2Se in CH_2Cl_2 at 228.1 K; ○, L = TMPA in $CHCl_3$ at 285.3 K; and for the *cis*/*trans* isomerization reaction of $TiCl_4$·2TMPA in $CHCl_3$ at 340.7 K (△). The $TiCl_4$·2L and free ligand concentrations were 0.1 m and 0.2 m, respectively.

coordinated sites on *cis*-$TiCl_4$·2Me_2S, *cis*-$TiCl_4$·2Me_2Se and *cis*-$TiCl_4$·2TMPA and also for the reaction involving the *trans*-$TiCl_4$·2TMPA isomer. To determine ΔV^*, the pressure dependence of the exchange rate was measured from 0.1 to *ca.* 225 MPa at constant temperature. The effect of pressure on the ^{1}H NMR spectra was significant for the systems involving ligand exchange between free and *cis* positions. Figure 5 shows the NMR spectrum of *cis*- and *trans*-$TiCl_4$·2TMPA at several pressures. The pressure effect is great enough to change the spectrum from a state in which the *cis* and free ligand peaks are nearly coalesced to a state in which $^3J(^1H-^{31}P)$ can be easily resolved in the individual peaks. The effect on the *trans* peaks is very small since no reaction on the *trans* ligands occurs at this temperature. The pressure dependences of the exchange rate constant for *cis*-$TiCl_4$·2Me_2Se, *cis*-$TiCl_4$·2TMPA and *trans*-$TiCl_4$·2TMPA are shown in Fig. 6. For the *cis* adduct systems, the plots are characterized by large negative slopes with significant curvature, and by a lesser negative slope with no curvature for the *trans*-$TiCl_4$·2TMPA system. To calculate ΔV^* for the systems with significant curvature, the data were fit to the quadratic equation [12]:

$$\ln k = \ln k_0 - \frac{\Delta V^*}{RT} P + \frac{\Delta \beta^*}{2RT} P^2$$

where k is the measured rate constant at pressure P, k_0 is the rate constant at zero pressure, R is the gas constant, T is the absolute temperature and $\Delta\beta^*$ is the compressibility coefficient of activation. For the *trans*-$TiCl_4$·2TMPA system where no curvature was observed in the pressure dependence, the data were fitted to the above equation with the $\Delta\beta^*$ term set equal to zero. The values obtained for ΔV^* are listed in Table I. For the ligand exchange reactions between free and coordinated *cis* sites, large positive values of ΔV^* were obtained and the magnitude of $\Delta\beta^*$ increased with increasing ΔV^*. For the exchange reaction involving the *trans*-$TiCl_4$·2TMPA isomer, a much smaller, but positive value of ΔV^* was obtained.

Discussion

Ligand Exchange on the cis-$TiCl_4$·2L Adducts

The exchange of a ligand between free and coordinated sites on *cis*-$TiCl_4$·2L and *cis*-$TiBr_4$·2L adducts is characterized by first order rate laws and large positive values for ΔH^*, ΔS^* and ΔV^*. A reaction having these characteristics can safely be assumed to occur via a dissociative pathway. To support the assignment of a dissociative mechanism to the *cis*-$TiCl_4$·2L and *cis*-$TiBr_4$·2L systems, other kinetic characteristics indicative of a dissociative rate determining step can be considered. Since a dissociative reaction mechanism involves the breaking of a M–L bond in forming the five-coordinate intermediate, the rate of the reaction should increase as the strength of the M–L bond decreases. The strength of the M–L bond is reflected in the stability of the complex. The relative stabilities of the adducts used in this work were determined in the previous paper [2] and the order of increasing stability was found to

be: $Me_2O \sim MeCN < Me_2CO < Me_2S < Me_2Se \ll Cl(MeO)_2PO \ll TMPA$.

Examination of the ΔG^* values in Table I shows that the labilities of the adducts decrease in the order: $Me_2O < Me_2CO \sim Me_2S < MeCN < Me_2Se \ll Cl(MeO)_2PO \ll TMPA$. These data show that there is a good qualitative agreement between thermodynamic stability and kinetic lability of the adducts except for the adduct with the Lewis base MeCN. Langford and Gray [13] predicted for limiting dissociative, D, mechanisms that a linear free energy relationship (LFER) should exist between the free energy of activation, ΔG^*, and the free energy of formation, ΔG_f, and that the slope of a plot of ΔG^* *versus* ΔG_f should be -1. LFERs have been observed for the dissociative ligand exchange reactions involving MX_5L (M = Nb [14] and Sb [15]) adducts as the plotted data gave slopes near -1. Such a LFER is not strictly observed for the *cis*-$TiCl_4 \cdot 2L$ adducts. This may be due to the fact that the five-coordinate intermediate formed when *cis*-$TiCl_4 \cdot 2L$ dissociates into $TiCl_4 \cdot L$ and L contains a different Lewis base ligand for each adduct. This leads to the formation of a different activated complex in the transition state which may mask any sequential energy differences that may be due to the breaking of progressively stronger M–L bonds. The $MX_5 \cdot L$ complexes all have the same five-coordinated activated complex in the transition state independent of the Lewis base ligand.

The breaking of a M–L bond during a dissociative reaction can be facilitated if the geometry of the ligand is such that steric interactions interfere with the strength of the M–L bond. Ligands with bulky substituents are, therefore, more easily removed than smaller, less hindered ligands. When looking for steric effects it is important to consider ligands of the same type, preferably those that differ in only an R group, since the donating ability of the ligand also affects the M–L bond strength. The best adducts to use for making this comparison in this study are the $TiCl_4$ adducts with Me_2S and Et_2S. The adduct with Et_2S is about 4 times more labile at 213 K than the Me_2S adduct. Since the major difference in these two adducts is the bulkiness of the ligands, the difference in reaction rate gives support to the assignment of a dissociative mechanism to the *cis*-$TiCl_4 \cdot 2L$ system. An acceleration in the reaction rate has been observed for the dissociative ligand exchange reaction on $TaCl_5 \cdot L$ adducts when Me_2O is replaced with Et_2O, whereas a deceleration has been observed for the associative ligand exchange reaction on the same adducts when Me_2S is replaced by Et_2S [14].

Similarly, it has been shown previously that the D mechanism ligand exchange rates on $MX_5 \cdot Me_2O$ (M = Nb, Ta) do increase on going from pentachlorides to pentabromides, with ΔG^* differences of the order of 8 kJ/mol [14]. The same observation has been made for the adducts *cis*-$SnX_4 \cdot 2L$ (L = Me_2S, Me_2Se, TMPA, HMPA), with differences of the order of 8 to 11 kJ/mol [16]. Two explanations were suggested: either steric effect (the larger bromides do favour the dissociation), or electronic effects (the metal charge is smaller in the case of the less electronegative bromide, favouring dissociation), or both of them. Astonishingly, this effect is small for *cis*-$TiX_4 \cdot 2Me_2S$ (1.2 kJ/mol), and even less marked for *cis*-$TiX_4 \cdot 2Me_2Se$ (0.3 kJ/mol) (see Table I).

In view of the kinetic information collected for the *cis*-$TiX_4 \cdot 2L$ adducts: first order rate laws, large positive values of ΔH^*, ΔS^* and ΔV^*, a qualitative correlation between the thermodynamic stability of the adducts and their kinetic lability, and an increase in the ligand exchange rate with increased ligand bulk, the evidence strongly supports the conclusion that ligand exchange between free and coordinated sites on *cis*-$TiX_4 \cdot 2L$ adducts occurs via a dissociative, D, mechanism. Such a mechanistic assignment needs to be made in view of the data available for other ligand exchange systems. Ligand exchange on the analogous *cis*-$SnCl_4 \cdot 2L$ adducts has been investigated [3] and the results also support the assignment of a dissociative rate determining step in the reaction mechanism. The assignment was strongly supported by the huge value of ΔV^*, +38.4 cm^3/mol, for Me_2S exchange on *cis*-$SnCl_4 \cdot 2Me_2S$. Although the value of ΔV^* for Me_2S exchange on *cis*-$TiCl_4 \cdot 2Me_2S$ is large, it is not as large as for the $SnCl_4$ analogue. In comparing ΔV^* values for ligand exchange in different systems, all factors influencing ΔV^* must be considered. One such factor is the bond length changes that occur during the formation of the transition state. For the five-coordinate intermediate, the remaining five metal–ligand bond lengths may be smaller than those in the six-coordinate adduct because of the decrease in the ionic radii of Sn^{4+} and Ti^{4+} when the number of coordinated ligands decreases from six to five [17]. For the d^{10} $SnX_4 \cdot 2L$ adducts, electronic repulsion between the filled t_{2g} orbitals and the ligands may prevent the metal–ligand bond lengths from decreasing to the same extent as for the d^0 $TiX_4 \cdot 2L$ adducts. The greater negative volume change for the formation of the $TiX_4 \cdot L$ intermediate would result in a smaller ΔV^* for ligand exchange.

The value of ΔV^* for ligand exchange on *cis*-$TiCl_4 \cdot 2L$ adducts increases in the order TMPA < Me_2S < Me_2Se. This is the order expected for a dissociative mechanism since ΔV^* has been shown to be influenced by the volume of the ligand in the inner coordination sphere of the adduct [18]. Since the TMPA ligand essentially has only a linear P=O group within the inner sphere of the adduct, ΔV^* is expected to be smaller than for the bent Me_2S and Me_2Se molecules. Also, the sulfur atom in Me_2S is roughly 8% smaller than the selenium atom in Me_2Se, so ΔV^* for ligand exchange is likely to be smaller for Me_2S than for Me_2Se.

The operation of a dissociative mechanism for the d^0 $TiX_4 \cdot 2L$ adducts is not entirely expected. From a theoretical point of view both Taube [4] and Orgel [5] concluded that nucleophilic attack on octahedral metal complexes should be facilitated when an empty t_{2g} orbital exists. Indeed, a dissociative–associative crossover in the ligand exchange mechanism was observed for the d^0 $NbX_5 \cdot L$ and $TaX_5 \cdot L$ adducts when L is changed from Me_2O to Me_2S, Me_2Se and Me_2Te [18]. Although a dissociative mechanism is observed for ligand exchange on the *cis*-$TiCl_4 \cdot 2L$ and the *cis*-$TiBr_4 \cdot 2L$ adducts, the second order rate law observed for Me_2O exchange on *cis*-$TiF_4 \cdot 2Me_2O$ in SO_2 suggests an associative interchange mechanism for this system [11]. Since the magnitude and sign of ΔS^* indicates a dissociative pathway, the measurement of ΔV^* for this reaction would greatly facilitate the mechanistic assignment.

cis to trans Isomerization of $TiCl_4 \cdot 2TMPA$

As noted in 'Results', the *trans*-$TiCl_4 \cdot 2TMPA$ ^1H NMR signals showed evidence of exchange with the coalesced NMR signals of *cis*-$TiCl_4 \cdot 2TMPA$ and free TMPA. ^1H NMR cannot distinguish whether the exchange reaction is between the *trans* and the free ligand, the *trans* and the *cis* adduct, or a combination of both. In a similar study involving *cis*- and *trans*-$SnCl_4 \cdot 2Me_2S$, ^{119}Sn NMR was used to conclusively show that the reaction involving the *trans* isomer is an isomerization reaction with the *cis* isomer, and that any exchange between *trans* and free ligands is too slow to be measured [3]. Since the ΔV^* for *cis–trans* $SnCl_4 \cdot 2Me_2S$ isomerization was only 32% of the value for *cis*-free exchange, the mechanism for isomerization could not involve the dissociation of a ligand from the adduct to form a five-coordinate intermediate. The value of ΔV^*_{iso} was positive, however, so the isomerization reaction was assigned as occurring via a mechanism involving a twisting motion of the adduct with significant expansion of the six-coordinate transition state due to lengthening of the Sn–X and Sn–L bonds. The analogous experiment for *cis*/*trans*-$TiCl_4 \cdot 2TMPA$ using ^{47}Ti or ^{49}Ti NMR is not possible due to the quadrupolar properties of the ^{47}Ti and ^{49}Ti nuclei. However, since ΔV^*_{iso} is 35% of ΔV^* for *cis*–free exchange (almost the same percentage as for the $SnCl_4 \cdot 2Me_2S$ system), it is likely that a mechanism similar to the one in operation for *cis–trans* isomerization of $SnCl_4 \cdot 2Me_2S$ is in operation for the isomerization of $TiCl_4 \cdot 2TMPA$.

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