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THE INVERSION BARRIER OF THE TiS_5 RING IN DI(η^5-CYCLOPENTADIENYL)TITANIUM PENTASULPHIDE *

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Summary

Accurate NMR band shape fittings applied to the temperature-variable spectra of $(\eta^5\text{-}C_5H_5)_2TiS_5$ have yielded the following activation parameters for the 6-membered TiS_5 ring inversion process: $E_a = 69.1 \pm 2.3$ kJ mol^{-1}, $\Delta H^{\ddagger} = 66.2 \pm 2.3$ kJ mol^{-1}, $\Delta G^{\ddagger} = 76.3 \pm 4.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -33.9 \pm 6.4$ J K^{-1} mol^{-1}.

Introduction

As part of our studies of the inversion process about sulphur when it is bonded to metals [1—5] we were interested in the phenomenon of sulphur-containing metallacycles. The complex $(\eta^5\text{-}C_5H_5)_2TiS_5$ [6,7] has been shown to have the TiS_5 six-membered ring in the chair form in the solid state [8] and to have a temperature dependent ^1H NMR spectrum which shows at ambient temperature two sharp signals. On warming the sample these two signals coalesce around 90°C and become a sharp single line at 120°C [7].

For the NMR experiment, rotation about the $\eta^5\text{-}C_5H_5$—Ti bond is very rapid over all temperatures studied herein, averaging all protons on individual cyclopentadienyl rings. The high temperature averaging of the protons on both rings is, without doubt, due to the varying rate of the TiS_5 ring inversion.

In the virtual absence of any information on inorganic ring inversion barriers we thought it of considerable interest to obtain accurate values of the activation parameters for the TiS_5 ring inversion process. Although analogies with other ring systems have been made, close comparisons with $(\eta^5\text{-}C_5H_5)_2TiSe_5$ [7] and $(\eta^5\text{-}C_5H_5)_2VS_5$ [9] have not been possible due to the instability of the former, and the paramagnetism of the latter.

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* Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.

Experimental

$(\eta^5\text{-}C_5H_5)_2TiS_5$ was prepared from ammonium pentasulphide [10] and dicyclopentadienyldichlorotitanium as described by Köpf et al. [7]. An attempt to prepare the analogous $(\eta^5\text{-}C_5H_5)_2ZrS_5$ by a similar route did not succeed in our hands, and we note a photochemical approach by Samuel and Gianotti has similarly failed [11].

All ^{1}H NMR spectra were recorded at 100 MHz on a JEOL MH-100 spectrometer operating under conditions of internal field-frequency lock. A standard JES-VT-3 unit was used to control the probe temperature. Measurements of temperature were made immediately before and after recording spectra, and were considered accurate to ±0.5°C. ^{13}C NMR spectra were recorded at 25 MHz on a JEOL PS/PFT-100 spectrometer equipped with variable temperature control as described above.

Results and discussion

Using toluene-d_8 (%D = 99.6) as solvent, the ^{1}H NMR spectra of $(\eta^5\text{-}C_5H_5)_2TiS_5$ were obtained over the temperature range 30 to 120°C. A typical range of spectra is shown in Fig. 1, where it will be observed that the temperature of coalescence is around 90°C. Very rapid rotation of the cyclopentadienyl group about the ring to metal bond ensures that individual rings have only one proton environment at all temperatures. Coalescence to equate all ten proton environments is due to the chair-to-chair inversion of the TiS_5 as illustrated in Fig. 2.

In structures a and b of Fig. 2 the two sets of ring protons are differentiated since they are axially and equatorially related to the TiS_5 ring. By analogy with cyclohexane systems [12] it is suggested that the upfield $(\eta^5\text{-}C_5H_5)$ signal be assigned to the protons of the axially substituted $\eta^5\text{-}C_5H_5$ group on the tetrahedral titanium atom.

It is noteworthy that the axial-equatorial shift difference in $(\eta^5\text{-}C_5H_5)_2TiS_5$ is only ca. δ 0.1 ppm, which is appreciably less than the corresponding value for cyclohexane. This could be due to the greater average distance of the $(\eta^5\text{-}C_5H_5)$ hydrogens from the TiS_5 ring compared with cyclohexane hydrogens.

An accurate analysis of the lower temperature spectra (25 to 45°C) yielded the chemical shift and line width data, shown in Table 1, which were subsequently used in the band fitting computer program AXSHAP.

The computer program is a modified version of the program SHAPE FUNCTION which is based upon the equations of Nakagawa [13]. For nuclei undergoing site exchanges, it computes theoretical line shapes for different values of rate constant k, or mean life-time τ ($= k^{-1}$). Experimental spectra measured in the range 50 to 110°C were accurately fitted using the above program. Eight of the spectra were fitted, and band shapes were found to match theoretical band shapes based upon rate constants varying between 3 s^{-1} and 91 s^{-1}.

Activation parameters for the TiS_5 ring inversion process were obtained in the usual way from plots of ln k versus T^{-1} (for E_A and $\log_{10} A$) and ln (k/T) versus T^{-1} (for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$). Good linear plots were obtained in both instances

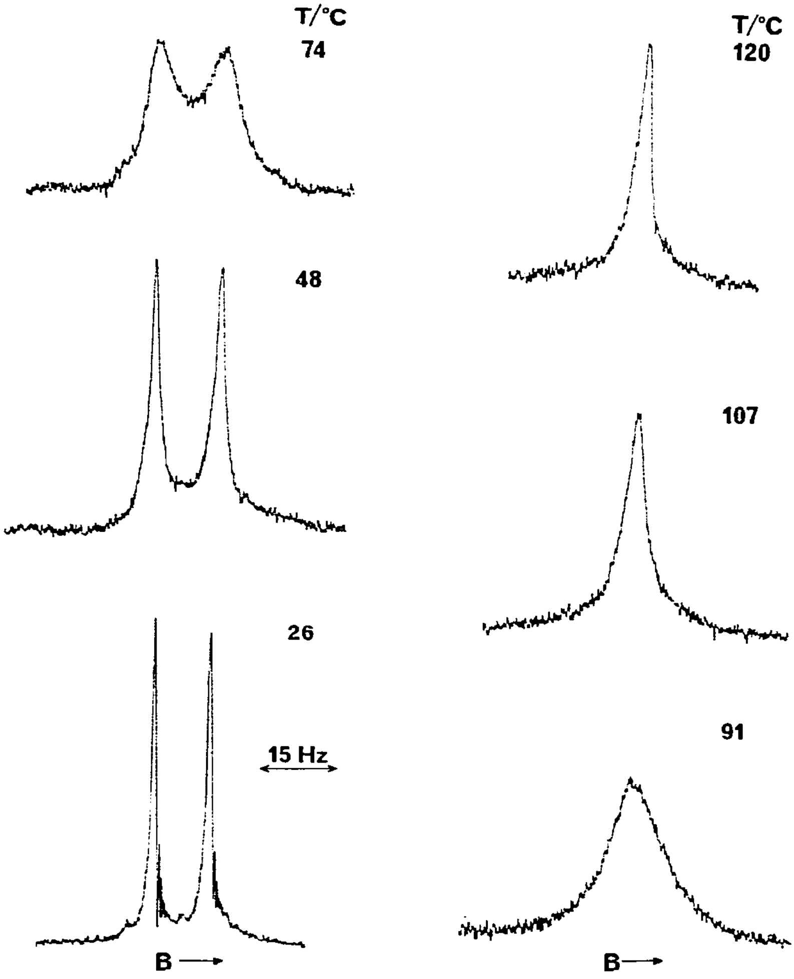

Fig. 1. ^{1}H NMR spectra of $(\eta^5\text{-}C_5H_5)_2TiS_5$ over a range of temperatures.

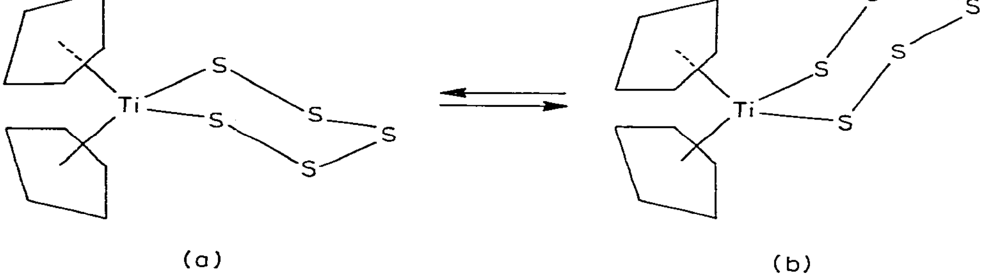

Fig. 2. Chair-to-chair inversion of the TiS_5 ring in $(\eta^5\text{-}C_5H_5)_2TiS_5$.

TABLE 1

CHEMICAL SHIFT AND LINE WIDTH DATA [a]

Solvent	T_c (°C)	Chemical shifts		Temperature variation of shifts	T_2* (sec)
		δ_{ax}	δ_{eq}	$\Delta\nu + b(T\ (°C))$ (Hz)	
Toluene-d_8	88.0	5.57	5.67	7.3 + 0.075 (T(°C))	0.398

[a] T_c = coalescence temperature; T_2* = transverse relaxation time = $(\pi\Delta\nu_{1/2})^{-1}$; $\Delta\nu_{1/2}$ = band width at half maximum height. Chemical shift values refer to 30°C.

and the errors reported are based on least squares fittings of the data.

E_a (kJ mol^{-1})	$\log_{10} A$	$\Delta G^\ddagger$ (kJ mol^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J K^{-1} mol^{-1})
69.1 ± 2.3	11.5 ± 0.3	76.3 ± 4.2	66.2 ± 2.3	—33.9 ± 6.4

The value for $\Delta G^\ddagger$ above was deduced from $\Delta H^\ddagger$ and $\Delta S^\ddagger$ at temperature 298.15 K.

As far as we are aware this is in the first reported example of an accurate ring inversion barrier for a purely inorganic ring system. It is therefore difficult to make meaningful comparisons with related ring systems. The corresponding complexes $(\eta^5\text{-}C_5H_5)_2MS_4$ (M = Mo, W) do not exhibit any observable temperature dependence in their ^{1}H NMR spectra [14,15]. This is not unexpected since the five-membered MS_4 rings in these compounds can only undergo a pseudorotational distortion, and such a mode is invariably of low energy and fast on the NMR experiment time scale.

A variety of six-membered organosulphur rings containing from one to five sulphur atoms have been reported, and results for these are noted in Table 2. It will be seen the introduction of one sulphur atom hardly changes the energy from that of the homocyclic cyclohexane system, but then the successive replacement of ring carbon atoms by sulphur does cause a progressive increase in the ring inversion barrier height as measured by $\Delta G^\ddagger$ values.

Interestingly the S_4C_2 example in Table 2 refers to tetramethyl-*s*-tetrathiane, where the parameters quoted refer to a twist-boat to chair interconversion, the former conformation being unexpectedly the predominant form in solution.

The observed spectral changes in $(\eta^5\text{-}C_5H_5)_2TiS_5$, however, show no evidence of any twist-boat conformation, and our results (for which $\Delta G^\ddagger$ fits neatly

TABLE 2

RING INVERSION BARRIERS IN SIX-MEMBERED SATURATED ORGANOSULPHUR RINGS S_nC_{6-n}

Number of sulphur atoms in ring	T (°C)	$\Delta G^\ddagger_{T_c}$ (kJ mol^{-1})	Ref.
0	—65	42.8	16
1	—81	39.5	17
2	—43	48.7	18
3	—8	55.4	19
4	~25	66.9	20
5	>23	?	21

into the general trend shown in Table 2), are fully explicable on the basis of the usual chair-to-chair interconversion process.

Detailed ^{13}C NMR studies of $(\eta^5\text{-}C_5H_5)_2TiS_5$ were not pursued, as it was clear that no additional information to that obtained from the ^1H spectra was available. However, spectra were measured up to ca. 100°C in $BrCH_2CH_2Br/CDCl_3$ solvent mixture, and the coalescence of the two cyclopentadienyl ^{13}C signals ($\Delta\delta(298\ K) = 1.069$ ppm) was observed to be 90 ± 5°C. This yielded an approximate value for $\Delta G^{\ddagger}$ of 77 ± 1 kJ mol^{-1} (at 363 K) which compared very favourably with the value of 78.5 kJ mol^{-1} obtained from the ^1H spectra.

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