presumably steric hindrance toward the addition of THF molecules. Weakening of the ion interactions with increasing salt concentration results in a reversal of these trends and increased solvation.

Stereochemically Nonrigid Organometallic Molecules. XXVII. The Fluxional Behavior of Tetra(cyclopentadienyl)titanium[1,2]

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Abstract: The temperature dependence of the nmr spectrum of tetra(cyclopentadienyl)titanium from $+80°$ to $-140°$ has been studied. The observations can be explained by assuming that the molecule is $(h^1\text{-}C_5H_5)_2(h^5\text{-}C_5H_5)_2$-Ti and that it executes two types of intramolecular rearrangement. At the lowest temperatures of observation the $h^1\text{-}C_5H_5$ rings rotate relatively slowly but by about $-25°$ averaging is rapid enough to give a single line as narrow as that for the protons of the $h^5\text{-}C_5H_5$ rings. Between about $-20°$ and $+35°$ the separate $h^1\text{-}C_5H_5$ and $h^5\text{-}C_5H_5$ lines broaden and coalesce to a single line which continues to become narrower as the temperature is raised further. These changes are attributable to interchange of the $h^1\text{-}C_5H_5$ and $h^5\text{-}C_5H_5$ types of rings and this is the first known observation of such an interchange. The activation parameters are: $E_a = 16.1 \pm 0.3$ kcal/mol and log $A = 13.5 \pm 0.5$. The relatively ready occurrence of this heretofore unknown process is attributable to the presence of an empty valence-shell orbital on the titanium atom of $(h^1\text{-}C_5H_5)_2(h^5\text{-}C_5H_5)_2$Ti which makes a reasonably low-lying transition state accessible. The $(C_5H_5)_3$TiCl molecule has been observed by pmr in solution. It shows a single sharp line down to at least $-100°$.

Many molecules containing *monohapto*-cyclopentadienylmetal groups, $(h^1\text{-}C_5H_5)M$, which are fluxional are known, and several have been studied in detail.[1,4,5] The homologous group $(h^5\text{-}C_5H_5)Fe(CO)_2$-$(h^1\text{-}C_5H_5)$, $(h^5\text{-}C_5H_5)Ru(CO)_2(h^1\text{-}C_5H_5)$, $(h^5\text{-}C_5H_5)Cr$-$(NO)_2(h^1\text{-}C_5H_5)$, has been especially well characterized;[1,4-7] the rearrangements have been shown to occur through 1,2 shifts[1,4-6] involving relatively nonpolar transition states,[7] with activation energies of ~10 kcal/mol.[1] No indication whatever of the ring interchange reaction

$$(h^5\text{-}C_5H_5)^*M(CO)_2(h^1\text{-}C_5H_5) = (h^5\text{-}C_5H_5)M(CO)_2(h^1\text{-}C_5H_5)^*$$
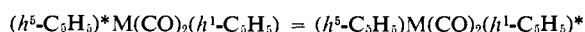
has been seen. It may, of course, take place slowly, but the fact that the isomers $(h^5\text{-}C_5H_5)Fe(CO)_2(h^1$-$C_5H_4R)$ and $(h^5\text{-}C_5H_4R)Fe(CO)_2(h^1\text{-}C_5H_5)$, $R = C_6$-H_5CH_2, have been isolated and can be dissolved and recovered unchanged[8] suggests that the interchange in this case must be exceedingly slow.

The observations reported[9] for $C_5H_5CuP(C_2H_5)_3$ in liquid SO_2 clearly show the presence of a fluxional $(h^1\text{-}C_5H_5)Cu$ group under the experimental conditions; the most recent work[5] shows that, contrary to the original suggestion, this also proceeds by a sequence of 1,2 shifts. However, the fact that $C_5H_5CuPR_3$ molecules in the solid state[10,11] and in more normal solvents[12] contain pentahapto rings beclouds the issue here. Perhaps an SO_2 adduct[13] in which the ring is pealed back, *e.g.*, $(h^1\text{-}C_5H_5)CuP(C_2H_5)_3(SO_2)_x$, $x = 1$ or 2, is the species actually observed in liquid SO_2.

For $(h^1\text{-}C_5H_5)_2Hg$ the structure and fluxional character have been established,[14] but not the rearrangement pathway. For $(h^1\text{-}C_5H_5)M(CH_3)_3$ (M = Si, Ge, Sn) the pathway has been shown to be 1,2 shifts.[15,16]

The compound $(C_5H_5)_3MoNO$ is the first one in which interconversion of differently bonded C_5H_5 rings is observed.[17] The possibility that the compound might contain $h^1\text{-}C_5H_5$, $h^3\text{-}C_5H_5$, and $h^5\text{-}C_5H_5$ rings, which was considered plausible at first, has been invalidated for the crystalline material,[18] and is thus considered unlikely in solution as well. As seen in the crystal, the molecule contains an $h^1\text{-}C_5H_5$ ring, but each of the other two rings is bound in essentially the same severely tilted poly-

(1) Previous paper in this series, part XXVI: F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 91, 7523 (1969).

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hapto fashion (Mo–C distances $\sim$2.34, $\sim$2.34, $\sim$2.43, $\sim$2.60, $\sim$2.60 Å). It has, in fact, been argued that a true $(h^3\text{-}C_5H_5)M$ arrangement cannot actually be realized owing to the geometric and bonding constraints inherent in the situation.[19]

Thus, on the basis of the literature summarized above, our knowledge of the structural and dynamical behavior of C_5H_5M groups at the time the work reported here was undertaken could be summarized as follows. (1) The commonest structural situations are $(h^5\text{-}C_5H_5)$-M (*i.e.*, essentially C_{5v} symmetry) and $(h^1\text{-}C_5H_5)M$. (2) The $(h^1\text{-}C_5H_5)M$ groups are usually fluxional, the more so when M is a transition metal or a heavier nontransition metal. (3) In all cases where firm evidence is available, the rearrangement pathway for $(h^1\text{-}C_5H_5)M$ systems is, predominently if not exclusively, by 1,2 shifts. (4) In no case had the direct interchange of $h^1\text{-}C_5H_5$ and $h^5\text{-}C_5H_5$ rings been observed, or even indirect exchange of these two extreme types.

In view of all of the above facts and conclusions, we were led to consider what behavior might be found in the $(C_5H_5)_4M$ compounds, where M = Ti, Zr, or Hf. Various combinations of ring binding motifs are possible. For instance, if a total of 18 electrons is to be engaged in metal-to-ring binding, the most obvious *formal* possibility is $(h^1\text{-}C_5H_5)(h^3\text{-}C_5H_5)(h^5\text{-}C_5H_5)_2M$, and ring interchange might be expected to be rapid. However, in view of the unrealistic nature of the formal designation $h^3\text{-}C_5H_5$ it might be more reasonable to postulate that in addition to one $h^1\text{-}C_5H_5$ and one $h^5\text{-}C_5H_5$ ring there could be two of the severely tilted C_5H_5M groupings found in $(C_5H_5)_3MoNO$. This structure, too, would probably lead to rapid ring interchange.

There is also the further *formal* possibility $(h^3\text{-}C_5H_5)_3$-$(h^5\text{-}C_5H_5)M$; this too, on relaxing the formalism of the $h^3\text{-}C_5H_5$ designation to some less regular but more realistic specification, would lead to the expectation of rapid interchange of ring types.

$(C_5H_5)_4Zr$ and $(C_5H_5)_4Hf$ have, in fact, been reported in the literature,[20,21] and their pmr spectra have been described as sharp singlets at 25°. Several years ago, experiments in this laboratory[22] showed that these signals remain sharp down to temperatures as low as $-150°$ for both compounds. It can thus be said that the experimental observations on $(C_5H_5)_4Zr$ and $(C_5H_5)_4Hf$ are consistent with some 18-electron structure, or mixture of such structures, though by no means is any such structure proved by the nmr data. Further discussion of this proposal will be found in the following paper.[23]

It is also possible, in these group IV compounds, to consider the possibility of some 16-electron structure or structures, since these earliest of transition elements often—indeed, characteristically—fail to achieve an 18-electron configuration. The two most obvious formal possibilities are $(h^1\text{-}C_5H_5)(h^3\text{-}C_5H_5)_2(h^5\text{-}C_5H_5)M$ and $(h^1\text{-}C_5H_5)_2(h^5\text{-}C_5H_5)_2M$. The former cannot be taken literally, but perhaps with some relaxation of the h^3-C_5H_5 formalism (say, to a set of four, approximately

equivalent, skew-bonded rings) would be tenable; it would readily explain the pmr observations on the Zr and Hf compounds. The other 16-electron structure has strong appeal because there are many known $(h^5\text{-}C_5H_5)_2MX_2$ compounds, *e.g.*, where X = Cl, Br, C_6H_5, C_6F_5, etc. However, it contains only the two most disparate types of ring, $h^5\text{-}C_5H_5$ and $h^1\text{-}C_5H_5$, and direct, rapid interchange of these has not previously been observed. This is not to say, however, that such an exchange could not occur in these compounds. In fact, there is one circumstance here which favors it.

The presence of an empty, low-lying metal orbital would allow one or more of the rings to slip temporarily into some form of bonding intermediate between $(h^1\text{-}C_5H_5)M$ and $(h^5\text{-}C_5H_5)M$. From there, interchange could occur with facility.

Unfortunately, the persistence of the single sharp signal for the Zr and Hf compounds at all temperatures precludes getting any experimental data for choosing among the various possibilities just discussed for the molecules in solution. We have also tried to obtain crystallographic structural data for each of these compounds, but have been frustrated by the difficulty of growing crystals. Hence, the structural and dynamical nature of the Zr and Hf compounds remains speculative.[23]

With $(C_5H_5)_4Ti$, which was only recently reported in the literature,[24] there appeared to be excellent opportunities for productive study, both by pmr spectroscopy on solutions and by X-ray crystallography. In this paper the spectroscopic study is reported in detail. The X-ray work, which is in excellent accord with the conclusions drawn from these solution studies, is reported in detail in the following paper.[23]

Experimental Section

General. All experiments were carried out in an atmosphere of either purified nitrogen or argon. All solvents were purified by standard methods and freed from oxygen prior to use. Bis-(cyclopentadienyl)titanium dichloride was obtained from Alfa Inorganics, Inc., and was used without further purification. Microanalyses for C and H were performed in our department by Mrs. N. Alvord under the supervision of Dr. J. S. Fleming. The proton magnetic resonance spectra were recorded with a Varian HA-100 spectrometer equipped with a variable-temperature probe. Chemical shifts were obtained by internal referencing with TMS.

Tetra(cyclopentadienyl)titanium. To 12.5 g (50 mmol) of bis-(cyclopentadienyl)titanium dichloride, as a slurry in 300 ml of tetrahydrofuran under nitrogen or argon at $-10°$, was slowly added a colorless solution of sodium cyclopentadienide (8.8 g, 100 mmol, in 200 ml of tetrahydrofuran) over a period of 4 hr. The color of the reaction mixture changed gradually from orange to dark blue. The reaction mixture was maintained at $-10°$ and stirred for an additional 2 hr. The solvent was then removed *in vacuo* ($-10°$, 10^{-2} mm) and the dry residue was extracted with 250 ml of toluene. The solution was filtered and the filtrate cooled to $-10°$ for 12 hr. Greenish black crystals separated from the solution. Two additional extractions and crystallizations using toluene resulted in an approximately 80% yield of the very air- and moisture-sensitive compound.

Anal. Calcd for $C_{20}H_{20}Ti$: C, 77.91; H, 6.54. Found: C, 77.6; H, 6.45.

Tris(cyclopentadienyl)titanium Chloride. To 11.25 g (45 mmol) of bis(cyclopentadienyl)titanium dichloride, as a slurry in 200 ml of methylene chloride under nitrogen or argon at $-78°$, was added 5.23 g (42 mmol) of solid cyclopentadienylmagnesium chloride. An excess of the Grignard reagent should be avoided. The reactants were stirred at $-78°$ for 3 hr, and then for an additional 2 hr

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(23) J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *J. Amer. Chem. Soc.*, **93**, 3592 (1971).

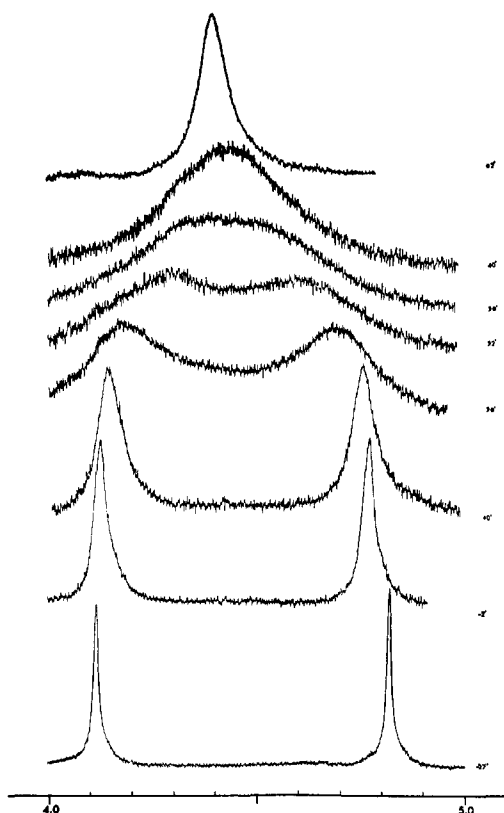(24) F. W. Siegert and H. J. De Liefde Meijer, *J. Organometal. Chem.*, **20**, 141 (1969).

Figure 1. The pmr spectra of $(C_5H_5)_4Ti$ in toluene.

as the temperature was allowed to rise to about 0°. The reaction mixture was filtered at this temperature and the solvent removed from the dark orange filtrate *in vacuo* (0°, 10⁻² mm), leaving a sticky residue. The nmr spectra of this crude material showed the presence of unreacted bis(cyclopentadienyl)titanium dichloride in about the same proportion as the desired compound, which appeared as a single, sharp peak. Extraction of the crude material with hexane and subsequent crystallization at −10° resulted in the elimination of the bis-cyclopentadienyl compound, but considerable decomposition also occurred. Best results were obtained by extracting the crude compound with toluene and cooling the filtrate at −10°. Orange crystals, which proved to be bis(cyclopentadienyl)titanium dichloride, separated. The solution was filtered and the solvent was removed *in vacuo*, leaving a very small amount (~80 mg) of a dark orange solid. The tris(cyclopentadienyl)titanium chloride obtained in this way was still contaminated with about 5% $(C_5H_5)_2TiCl_2$. The compound is air, moisture, and light sensitive. Because of the very minute amounts obtained and the extreme difficulties in handling this compound, no effort was made to characterize it analytically. Solutions of it in solvents other than toluene appeared to decompose very rapidly. The appearance of only one sharp peak in its pmr spectrum at τ 4.25 in toluene at 25° together with its mode of preparation and the known positions for the $(C_5H_5)_2TiCl_2$ and (averaged) $(C_5H_5)_4Ti$ resonances was taken as adequate evidence for its identification as the desired $(C_5H_5)_3TiCl$.

Results

The pmr spectra of $(C_5H_5)_4Ti$ at various temperatures from +62 to −142° and in different solvents are shown in Figures 1–3. Many spectra at other temperatures in this range and also in the range +62 to +80° were also recorded. In all solvents from +36 to +62°, the single line becomes steadily narrower, reaching a limiting width at half-height of 4.1 Hz above 61.7° in toluene. As may be seen, the line broadens and splits into two and each of these sharpens to a width at half-height of 0.6 Hz in the temperature range +80 to −30°. The two components have equal intensity.
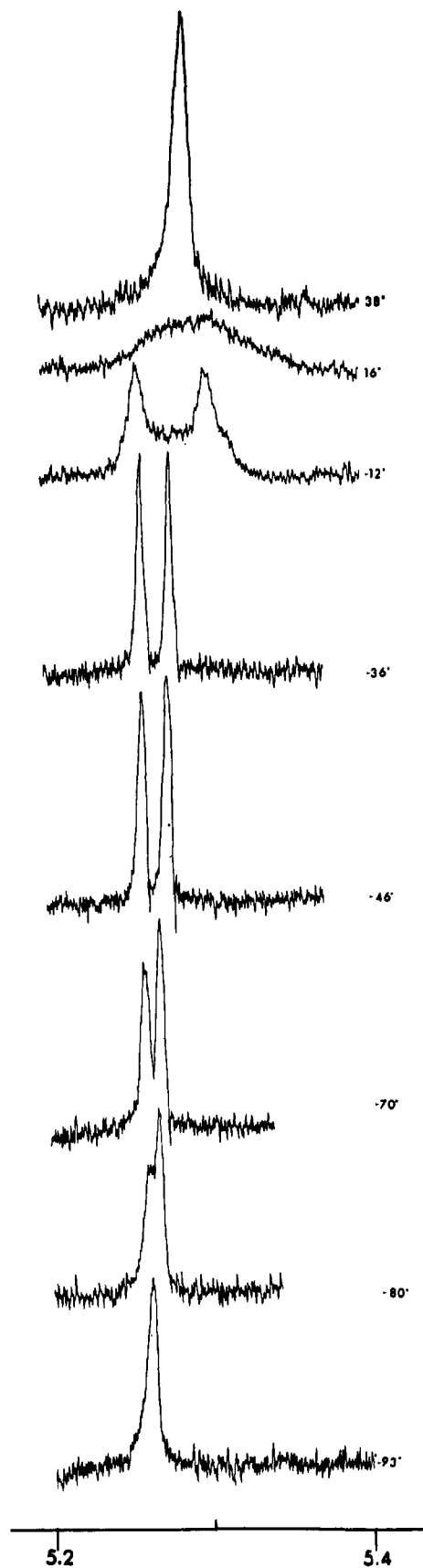

Figure 2. The pmr spectra of $(C_5H_5)_4Ti$ in a mixture of toluene and diethyl ether (*ca.* 2:1).

Because of viscosity effects it was not feasible to study changes at still lower temperatures using pure toluene as a solvent. With a toluene–diethyl ether mixture, the
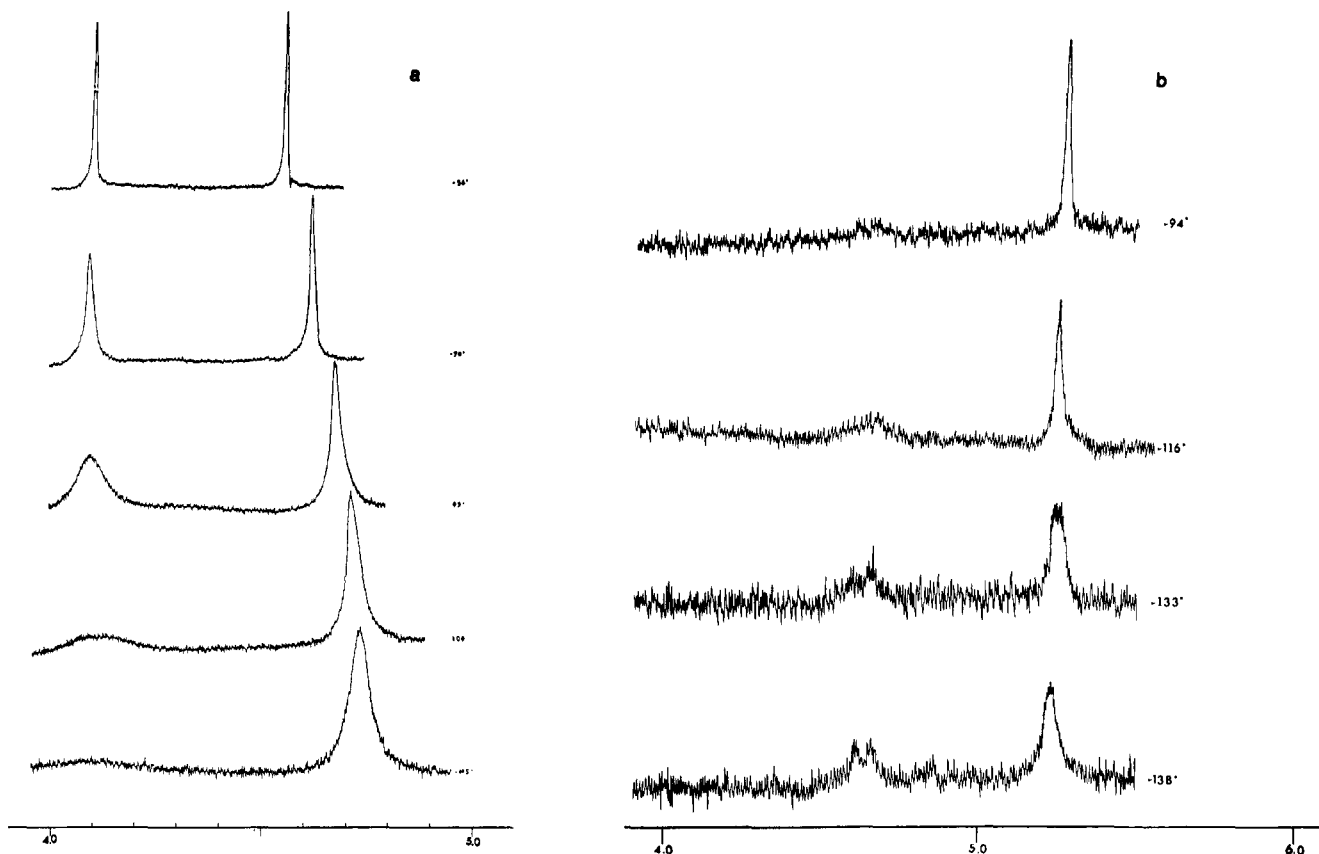
Figure 3. The pmr spectra of $(C_5H_5)_4Ti$ in diethyl ether.

results shown in Figure 2 were obtained. It is seen that at temperatures below $-40°$ the low-field line broadens markedly and eventually becomes undetectable at about $-115°$. However, even the mixed solvent system suffers from increasing viscosity below this temperature and further studies were carried out in diethyl ether; representative spectra are shown in Figure 3.

In ether, the chemical shifts of the h^1-C_5H_5 and h^5-C_5H_5 protons were distinctly temperature sensitive, in such a way that the positions of the two signals became virtually identical after the h^1-C_5H_5 signal began to broaden. However, it was possible to observe not only the complete collapse of the h^1-C_5H_5 resonance but the appearance of signals of the proper chemical shift and shape to be attributable to the olefinic protons of a slow-moving h^1-C_5H_5 ring at about $-139°$.

The line-shape data in the range $+62$ to $-30°$ conform to the behavior expected for a process in which equal numbers of equivalent spins occupy each of two types of sites and site exchange proceeds with an Arrhenius activation energy of 16.1 ± 0.3 kcal/mol and a frequency factor, A, such that $\log A = 13.5 \pm 0.5$.

Because of the poor quality of the spectra at lower temperatures, no attempt was made to evaluate the kinetic parameters quantitatively for what we presume to be the site exchanges accompanying fluxional rearrangement of the h^1-C_5H_5 rings. However, by comparing the spectra obtained here at various temperatures with the similar spectra for $(h^5$-$C_5H_5)M(CO)_2$-$(h^1$-$C_5H_5)$ (M = Fe, Ru), where E_a is ~ 10 kcal/mol, it would appear that a similar but perhaps slightly lower Arrhenius activation energy pertains here.

The $(C_5H_5)_3TiCl$ molecule in toluene solution exhibits a single, narrow proton resonance line from room

temperature to about $-100°$. Only at the lowest temperatures is there any indication of broadening, and this may well be due to increasing viscosity and/or crystallization of the substance from solution. Evidently all 15 protons maintain time-average equivalence throughout this temperature range.

Discussion

The earliest report[25] of $(C_5H_5)_4Ti$ described an apparently impure material and afforded no clues as to structure. The recent paper of Siegert and De Liefde Meijer,[24] in which the preparation was accomplished by the action of C_5H_5Na on $(C_5H_5)_2TiCl_2$, describes a crystalline compound with satisfactory analyses. The infrared spectrum was reported and constitutes the sole basis for their postulate of the $(h^1$-$C_5H_5)_2(h^5$-$C_5H_5)_2Ti$ structure.[26] The results reported here substantiate Siegert and De Liefde Meijer's empirical interpretation of their infrared spectra, but we believe that their deductions were not intrinsically secure for two reasons. First, the logic was circular in that no reference compound whose spectrum was shown had been independently *proved* to contain the assumed numbers of h^1-C_5H_5 and h^5-C_5H_5 groups; thus, at best, no more than a satisfactory degree of internal consistency among the several spectra could actually be claimed. Second, the

(25) H. Breederveld and H. I. Waterman, U. S. Patent 3,089,886 (1963); *Chem. Abstr.*, **59**, 11557g (1963).

(26) Siegert and De Liefde Meijer reported seeing a sharp peak and a broad peak in the nmr spectrum, presumably at about 25°, and took this as evidence that "not all the cyclopentadienyl protons are equivalent." As shown here, however, the correct interpretation of this observation is quite different and more complex than they suggest, and the raw observation does not actually afford any evidence favoring the $(h^1$-$C_5H_5)_2(h^5$-$C_5H_5)_2Ti$ structure.

general correlations of Fritz,[27] to which the ultimate appeal was made, are now known to be, in part, unreliable.[12] Thus we believe that the work reported here and in the following paper constitutes the first satisfactory delineation of the structural and dynamical character of tetra(cyclopentadienyl)titanium.

We believe that the pmr spectra at various temperatures, as illustrated by the representative traces shown in Figures 1–3, can be given only one plausible interpretation. In this we first assume that the instantaneous structure of the molecule in solution is $(h^1\text{-}C_5H_5)_2(h^5\text{-}C_5H_5)_2Ti$. As shown in the following paper this is the structure which the molecule has in the crystal.

We must next postulate that the $h^1\text{-}C_5H_5$ rings undergo rearrangement of the type already extensively studied in other $(h^1\text{-}C_5H_5)M$ moieties.[1,4–7,9] This must be sufficiently rapid to cause collapse of the complex spectrum, characteristic of such a ring in a static condition, to begin at temperatures as low as $\sim -130°$, and leads to the ultimate degree of line narrowing at about $-30°$. This sort of behavior is in no way novel or surprising.

At still higher temperatures we postulate a form of fluxional behavior which is, on the contrary, entirely novel, though, as shown below, not really surprising. The collapse of the two-line spectrum, a process with an activation energy of about 16 kcal mol, is attributed to a rearrangement in which $h^1\text{-}C_5H_5$ and $h^5\text{-}C_5H_5$ rings increasingly rapidly exchange their structural roles in the molecule.

The occurrence of rapid $(h^1\text{-}C_5H_5)(h^5\text{-}C_5H_5)$ ring interchange in this molecule but in no other one so far examined may be attributed to the configuration of 16 valence-shell electrons on the metal atom in this case as compared to the 18-electron configurations found in the cases where such exchange is very much slower (by perhaps 10^{-8}) if, indeed, it occurs at all. In the 16-elec-

(27) H. P. Fritz in F. G. A. Stone and R. West, Eds., *Advan. Organometal. Chem.*, 1, 239 (1964).

tron configuration, the metal atom has an additional empty, low-lying valence-shell orbital which can be used to stabilize a transition-state geometry in which one or more C_5H_5 rings adopt a geometric relationship to the metal which is intermediate between the $h^1\text{-}C_5H_5$ and $h^5\text{-}C_5H_5$ extremes. At the risk of being unjustifiably explicit, we suggest, in order to be specific about this proposal, that such a transition state might be attained by having one $h^1\text{-}C_5H_5$ and one $h^5\text{-}C_5H_5$ ring simultaneously shift into the severely tilted configuration already found[18] for the two equivalent rings in $(C_5H_5)_3MoNO$. From this structure, a return to the ground-state $(h^1\text{-}C_5H_5)_2(h^5\text{-}C_5H_5)_2Ti$ structure could occur with exchange of two of the rings. This postulated transition state requires the metal atom to use one more valence-shell orbital than it employs in the ground-state structure. In cases where the metal atom cannot bring an additional empty valence orbital into play, there is no energetically economical way to reach this or any similar transition state, and rapid ring interchange is thus not possible.

Our examination of $(C_5H_5)_3TiCl$ has been somewhat cursory, but the results achieve our principal objective, which is to show that the sharp peak seen in spectra of $(C_5H_5)_4Ti$ previously reported by Siegert and De Liefde Meyer and in Figure 1 is due to $(C_5H_5)_3TiCl$. We have shown that $(C_5H_5)_3TiCl$ has a single sharp peak at the appropriate τ value at each temperature.

The fact that $(C_5H_5)_3TiCl$ exhibits only a single sharp line down to about $-100°$ is, itself, very interesting. It is *possible* that this molecule has as its instantaneous structure one comparable to $(C_5H_5)_4Ti$, namely $(h^1\text{-}C_5H_5)(h^5\text{-}C_5H_5)_2TiCl$, and that for some reason contingent upon the substitution of one $h^1\text{-}C_5H_5$ ring by Cl the ring interchange process becomes enormously faster. We are more inclined to believe, however, that the instantaneous structure may be different, perhaps involving an 18-electron configuration with two severely tilted rings, in close analogy to the structure we are suggesting in the following paper for the $(C_5H_5)_4Zr$ and $(C_5H_5)_4Hf$ molecules.