TITANIUM-47 AND TITANIUM-49 NUCLEAR MAGNETIC RESONANCE IN HALF-SANDWICH η^5-CYCLOPENTADIENYL, η^5-METHYLCYCYLOPENTADIENYL, η^5-TETRAMETHYLCYCYLOPENTADIENYL OR η^5-PENTAMETHYLCYCLOPENTADIENYL-TITANIUM(IV) TRIHALIDES

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Dedicated to Professor Jaroslav Holeček on the occasion of his 70th birthday in recognition of his outstanding contribution to the organotin chemistry

The ^{47}Ti and ^{49}Ti NMR spectra of a series of $CpTiX_3$ (Cp $= \eta^5 -C_5H_5$; X = Cl, Br), $Cp'TiX_3$ ($Cp' = \eta^5 -C_5H_4Me$; X = Cl, Br, I), Cp^*TiX_3 ($Cp^* = \eta^5 -C_5HMe_4$; X = Cl, Br, I) and Cp^*TiX_3 ($Cp^* = \eta^5 -C_5Me_5$; X = Cl, Br) half-sandwich complexes are reported. Electron-donating methyl substituents on the cyclopentadienyl ring as well as a halide substitution on the central titanium atom cause contra-intuitive downfield shifts, which are discussed in terms

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of variation in paramagnetic contribution to the observed shielding. A direct correlation between $\delta(^{47, 49}Ti)$ and λ_{max}^{CT}, the longest wavelength charge-transfer transition in the electronic spectrum, has been found.

Introduction

In recent years, the study and development of half-sandwich monocyclopentadienyltitanium(IV) trihalides, $CpTiX_3$ ($Cp = C_5H_5$; X = halide) as alkene polymerisation catalyst precursors has been of considerable interest [1]. The title trihalides are used not only as precursors for catalysts, but they can also be further modified by substituting the halide ligands to obtain a variety of different catalytically active species. The most commonly used precursors are trichloride complexes $CpTiCl_3$ and Cp^*TiCl_3 ($Cp^* = \eta^5-C_5Me_5$). For example, the $CpTiCl_3$ complex and its analogs are effective catalyst precursors for the Ziegler–Natta syndiospecific polymerisation of styrene when activated by an excess of methylaluminoxane [2].

Half-sandwich titanium(IV) complexes contain a formally 12-electron d^0 titanium center and are therefore electronically less saturated as well as sterically less hindered than their 16-electron bent titanocene dihalides, Cp_2TiX_2, counterparts. In accord with these more favourable electronic and steric factors, catalysts based on half-sandwich compounds do indeed exhibit very high catalytic activities for alkene polymerisation [1].

Many investigations using numerous physical and spectroscopic techniques have been carried out on the half-sandwich titanium(IV) trihalides, especially on the (η^5-cyclopentadienyl)titanium(IV) trichloride, which serves as an archetypal half-sandwich complex containing one η^5-bonded cyclopentadienyl ligand. Indeed, $CpTiCl_3$ is the earliest known complex of this type [3].

The single-crystal X-ray diffraction of $CpTiCl_3$ [4] and the gas-phase electron diffraction of $CpTiBr_3$ [5] suggest that their molecular structures are based on those of the corresponding tetrahedral titanium tetrahalides, comprising monomeric species in which a halogen atom has been replaced by an η^5-cyclopentadienyl ligand situated parallel to the plane defined by three halogen atoms. The central Ti atom is equidistant from the five carbon atoms and all C-C as well as Ti-halogen distances are equal so that the $CpTiX_3$ molecule adopts so-called "piano-stool" structure (Fig. 1). As $CpTiX_3$ molecule possesses "cylindrical" symmetry, the intramolecular contribution to the barrier to rotation of the Cp ring around the Ti-Cp(centroid) axis is expected to be small. Proton spin-lattice relaxation time measurement of the $CpTiCl_3$ complex [6] gave a value of 9.6 kJ mol^{-1} for the rotation barrier, whereas in Raman spectroscopic study of gaseous and crystalline $CpTiCl_3$ much lower barriers to rotation of 1.59 kJ mol^{-1} and 2.01 kJ mol^{-1}, respectively, have been observed [7,8]. Expectedly, the gas-

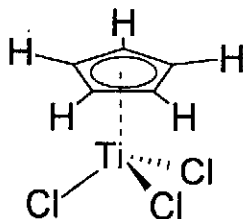phase value is slightly lower than that for the solid.

Fig. 1 Piano-stool structure of $CpTiCl_3$ molecule

The vibrational spectroscopic studies of half-sandwich titanium trihalides date back to late 1960s and early 1970s, when the first reports on the infrared and Raman spectra of $CpTiX_3$ (X = Cl, Br) [9,10], $Cp'TiCl_3$ (Cp' = η^5-C_5H_4Me) [10] and Cp^*TiX_3 (Cp* = C_5Me_5; X = Cl, Br) [9,10] appeared. In order to assign the skeletal modes in the low frequency region, Maslowsky and Nakamoto [11] carried out an approximate normal coordinate analysis (using the Urey–Bradley force field) for the $CpTiCl_3$ molecule making use of its infrared and Raman spectral data. A comparative study by Samuel $et\ al.$ [12] of the infrared and Raman spectra in the low frequency region allowed assignments to be made for the Ti-Cp and Ti-halide stretching modes in $CpTiCl_3$ and $CpTiBr_3$. A group of Italian molecular spectroscopists [7,8] have reported the infrared and Raman spectra of gaseous $CpTiCl_3$ species, the infrared spectra of matrix-isolated (10K) as well as solid $CpTiCl_3$. Particular attention was paid to the assignments of intraring, skeletal and internal rotational modes. The fundamental frequencies derived from the vibrational spectrum of the $CpTiCl_3$ molecule were employed in a calculation of the thermodynamic functions for this molecule in the ideal gas state. Very recently, vibrational overtone spectroscopy of $CpTiCl_3$ has been reported [13].

The He(I) and He(II) photoelectron spectra have been measured [14a] for a series of $CpTiX_3$, $Cp'TiX_3$ and Cp^*TiX_3 (X = Cl, Br) half-sandwich complexes (one member of this series, namely $CpTiCl_3$, had been studied before [15]). On the basis of observed trends in ionization energies and a qualitative theoretical MO model, unambiguous assignments were made of the Cp and halide orbitals. It was concluded that the HOMO in all the half-sandwich complexes of the series above is predominantly Cp in character. The X-ray photoelectron spectroscopy (ESCA) gave the $Ti(2p_{3/2})$ binding energies of two half-sandwich titanium trichlorides, $CpTiCl_3$ and Cp^*TiCl_3 [16]. Mach $et\ al.$ [14b] investigated effects of methyl substituents at the cyclopentadienyl ligand in monocyclopentadienyl titanium(IV) trichlorides on the absorption maxima of the lowest energy transitions in their electronic spectra.

The pioneering work of Kidd et al. [17,18] and subsequent investigations [19–24] demonstrated that the readily accessible [47]Ti and [49]Ti NMR spectra, owing to their simplicity and to relatively narrow signals, have the potential of providing extensive information about titanium(IV)-containing species and represent an effective and useful method for probing the electronic environment at the titanium center. In view of the afore-mentioned potential role of half-sandwich titanium trihalides in Ziegler–Natta catalysis and the potential of titanium NMR spectroscopy it is surprising that relatively little is known about [47]Ti and [49]Ti NMR spectra of such titanium systems. In addition, a few Ti-NMR studies of half-sandwich titanium complexes concern solely the trichloride species. As far as we know, no half-sandwich titanium trihalide bearing halide ligands other than the chloride ones has been examined by means of titanium NMR spectroscopy. The first direct observation of [47]Ti and [49]Ti chemical shifts in two half-sandwich complexes, i.e. $CpTiCl_3$ and $(C_5Me_4Et)TiCl_3$, was reported by Dormond et al. [20] (note: the assignment to [47]Ti and [49]Ti given in this report should be reversed). Later, the spectra of the methyl substituted complexes $Cp'TiCl_3$ and Cp^*TiCl_3 were published [22–24]. Moreover, [47]Ti and [49]Ti NMR spectroscopic data for a series of half-sandwich titanium trichlorides bearing cyclopentadienyl ligands substituted with bulky electron-donating groups have been collected [24].

We present here [47]Ti and [49]Ti NMR and UV-VIS spectroscopic data for a series of titanium(IV) half-sandwich complexes, comprising four trichlorides, $CpTiCl_3$ (1) $Cp'TiCl_3$ (2), Cp^*TiCl_3 (3), Cp^*TiCl_3 (4), four tribromides $CpTiBr_3$ (5), $Cp'TiBr_3$ (6), Cp^*TiBr_3 (7), Cp^*TiBr_3 (8) and two triiodide species, $Cp'TiI_3$ (9), Cp^*TiI_3 (10).

Experimental

Materials and Methods

The half-sandwich titanium(IV) trihalides *1 – 10* were prepared by previously published procedures [25–30]. All were purified by vacuum sublimation. Infrared, Raman [7,8,11,12] and ^{1}H, ^{13}C NMR [25–30] spectroscopies confirmed the identity and the purity of these compounds. All preparative reactions and manipulations were routinely carried out under atmosphere of argon on a Schlenk line or in glove bag. All solvents were reagent grade or spectroscopic grade and dried over appropriate drying agents, distilled under argon and degassed before use.

Spectroscopic Measurements

^{47,49}Ti NMR spectra at 20.308 MHz were obtained on a Bruker AMX360 spectrometer equipped with 5-mm broadband probe at 300K (saturated solutions in $CDCl_3$) and the chemical shifts were referenced to external neat ^{49}TiCl$_4$ isotopomer. Electronic absorption spectra were run on a Jasco V570 spectrometer and a Hewlet-Packard 8453 spectrometer (solvent CH_2Cl_2; $10^{-3} - 10^{-2}$ M solutions in 2-cm cuvette).

Results and Discussion

Table I lists the NMR chemical shifts relative to the two isotopes ^{49}Ti (5.51 %; $I = 7/2$; $Q = 0.24 \times 10^{-28}$ m^2) and ^{47}Ti (7.28 %; $I = 5/2$; $Q = 0.29 \times 10^{-28}$) for the ten half-sandwich titanium(IV) trihalides studied in this work. As the neat TiCl$_4$ was used as an external reference, the negative chemical shift implies that the Ti signal was upfield from TiCl$_4$. Very close magnetogyric ratios for ^{49}Ti and ^{47}Ti nuclei result in very similar resonance frequencies and, therefore, the Ti NMR spectra should be twinned. Indeed, both the ^{49}Ti and ^{47}Ti resonances appear in our spectra (except the ^{47}Ti resonance for Cp$^+$TiI$_3$, see Table I), with the ^{49}Ti nucleus resonating 266.4 ($\pm$0.2) ppm downfield of the ^{47}Ti resonance. Certainly, both the ^{49}Ti and ^{47}Ti NMR chemical shifts are identical when referenced to appropriate isotopomer of the used reference TiCl$_4$. Due to its higher quadrupole moment, the ^{47}Ti resonance line is always broader than the ^{49}Ti line as it can be seen from the line half-width values, $\Delta v_{1/2}$, listed in Table I. Consequently, the ^{49}Ti resonance is the easier to observe, since the usually broader ^{47}Ti signal (theoretically by a factor of 3.43 [19]) may cause the failure either to assess $\Delta v_{1/2}(^{47}$Ti) values (for instance, the Cp$^+$TiBr$_3$ complex in our case) or even to detect a ^{47}Ti resonance (e.g., the C$_5$HMe$_4$TiI$_3$ and C$_5$Me$_5$TiBr$_3$ complexes in our case, see Table I). The line widths are important NMR spectral parameters since they provide direct qualitative, yet useful information about the symmetry of electronic distribution around the titanium center. It is now known that substituents on the cyclopentadienyl ligand in half-sandwich titanium(IV) trichloride complexes have a rather significant effect on the $\Delta v_{1/2}(^{47,49}$Ti) values [22].

The Ti NMR chemical shift data in Table I reveal two contraintuitive trends. Inspection of these chemical shifts shows an unexpected downfield shift in going from trichlorides to tribromides to triiodides in the series of half-sandwich complexes bearing the same cyclopentadienyl or methyl-substituted cyclopentadienyl ligand (i.e., Cp, Cp', Cp$^+$ or Cp*) and an unexpected downfield shift in going from the unsubstituted cyclopentadienyl (Cp) to the methylcyclopentadienyl (Cp') to the tetramethylcyclopentadienyl (Cp$^+$) to the pentamethylcyclopenta-

Table I ^{49}Ti and ^{47}Ti NMR chemical shifts, resonance line half-widths and absorption maxima of the lowest energy charge-transfer transitions in the electronic spectra of half-sandwich titanium(IV) trihalides.

No	Compound[a]	$\delta(^{49}\text{Ti})$, ppm	$\Delta v_{1/2}(^{49}\text{Ti})$, Hz	$\delta(^{47}\text{Ti})$, ppm	$\Delta v_{1/2}(^{47}\text{Ti})$, Hz	1st CT transition	
						$\lambda_{max}^{1,CT}$, nm	$E^{1,CT}$, eV
1	CpTiCl$_3$	−396.5	49	−662.7	74	381	3.25
2	Cp'TiCl$_3$	−332.0	43	−598.6	113	399	3.11
3	Cp*TiCl$_3$	−161.1	37	−427.5	79	426	2.91
4	Cp*TiCl$_3$	−94.7	23	−361.0	39	438	2.83
5	CpTiBr$_3$	−123.8	23	−390.3 .	40	419	2.96
6	Cp'TiBr$_3$	−68.8	27	−335.3	47	423	2.93
7	Cp*TiBr$_3$	123.5	60	−142.7	b	462	2.68
8	Cp*TiBr$_3$	186.7	b	c	c	466	2.66
9	Cp'TiI$_3$	399.5	31	133.3	70	493	2.52
10	Cp*TiI$_3$	589.4	138	c	c	506	2.45

[a] Cp = η^5-C$_5$H$_5$; Cp' = η^5-C$_5$H$_4$Me; Cp* = η^5-C$_5$HMe$_4$; Cp* = η^5-C$_5$Me$_5$
[b] Not determined
[c] Too broad to be observed

dienyl (Cp*) titanium(IV) trihalide systems with the same halide ligands fixed at the titanium central atom.

In the first of the two curious trends above, the Ti nucleus deshielding increases in the order Cl < Br < I against the electronegativity of the halogen. This contraintuitive phenomenon, in which the direction of Ti chemical shifts is the reverse of what might have been intuitively expected on the basis of the electronegativity of halide ligands, is the so-called *inverse halogen dependence* (IHD), first observed in the series TiX$_4$ (X = Cl, Br, I) and Cp$_2$TiX$_2$ (X = F, Cl, Br, I) [17–19] with deshielding of the Ti nuclei increasing as the electronegativity of the X group decreases. The normal halogen dependence (NHD) reflects the halogen deshielding order I < Br < Cl and is observed for main group halides (e.g., ^{27}Al, ^{13}C, ^{29}Si and ^{119}Sn nuclei) and a majority of transition metal nuclei [18]. The ^{49}Ti NMR chemical shift changes observed in going from the more electronegative ligand (Cl) to the less electronegative ones (> I) in the series of half-sandwich complexes possessing the same five-membered ring ligand are shown in Table II.

It may be concluded that the downfield ^{49}Ti chemical shift changes asso-

Table II Downfield $\delta(^{49}\text{Ti})$ chemical shift changes when halide is changed

Series	Cl/Br $\Delta\delta$, ppm	Br/I $\Delta\delta$, ppm
CpTiX$_3$	272.7	-
Cp'TiX$_3$	262.2	468.3
Cp*TiX$_3$	284.6	465.9
Cp*TiX$_3$	281.2	-

ciated with the more electronegative halide/the less electronegative halide substitution vary in rather narrow ranges (Cl/Br 262 – 285 ppm, Br/I 465 – 468 ppm).

The other contraintuitive trend observed on the ten half-sandwich titanium(IV) trihalide complexes in Table I reveals that replacement of cyclopentadienyl hydrogens by electron-donating methyl substituents induces an unexpected deshielding effect of the $^{47,49}\text{Ti}$ NMR resonances. Specifically, a dramatic downfield ^{49}Ti NMR chemical shift is observed in going from the CpTiCl$_3$ [$\delta(^{49}\text{Ti})$ = –396.5 ppm] or CpTiBr$_3$ [$\delta(^{49}\text{Ti})$ = –123.8 ppm] complexes to the Cp*TiCl$_3$ [$\delta(^{49}\text{Ti})$ = –94.5 ppm] or Cp*TiBr$_3$ [$\delta(^{49}\text{Ti})$ = 186.7 ppm] permethylated compounds. Through a comparison of ^{49}Ti NMR chemical shifts and X-ray photoelectron Ti($2p_{3/2}$) binding energies on a series of bent titanocene dihalides, Gassman and co-workers [21] have shown that the IHD is not restricted to halide ligands and that changing from cyclopentadienyl (Cp) ligand to pentamethylcyclopentadienyl (Cp*) ligand can have a greater influence on both inner-shell electron Ti($2p_{3/2}$) binding energies and certain Ti nuclear properties than does changing halide ligands. This inverse relationship of Ti NMR chemical shifts with methyl substitution on Cp ligand is not restricted to the bent titanocene dihalides. Replacement of the cyclopentadienyl (Cp) group of CpTiCl$_3$ [$\delta(^{49}\text{Ti})$ = –396.5 ppm] by the pentamethylcyclopentadienyl (Cp*) ligand giving Cp*TiCl$_3$ [$\delta(^{49}\text{Ti})$ = –94.5 ppm] resulted in 302 ppm downfield shift while the corresponding Ti($2p_{3/2}$) binding energies are 457.2 and 456.4 eV, respectively, indicating that electron-donating methyl substituents on the five-membered ring increase the electron density at the titanium center. Hence, the Ti NMR chemical shift values may not always be an indication of electron density at the Ti atom. A following striking example demonstrating this fact can be given. Replacing one chloride in TiCl$_4$ with more electron-donating cyclopentadienyl ring does shift the ^{49}Ti resonance upfield (–396.5 ppm) as expected, but the half-sandwich trichloride complex with the strongest electron-donating Cp* ligand, i.e., Cp*TiCl$_3$ that should consequently be the most electron-rich at the Ti center, exhibits the lowest field ^{49}Ti resonance [$\delta(^{49}\text{Ti})$ = –94.5]. The $\delta(^{49}\text{Ti})$ = –94.5 NMR chemical shift changes

Table III Downfield $\delta(^{49}Ti)$ chemical shift changes dependent on ring substitution

Series	Cp/Cp$'$	Cp/Cp$^+$	Cp/Cp*	Cp$'$/Cp$^+$	Cp$^+$/Cp*
	$\Delta\delta$, ppm				
(ring)TiCl$_3$	64.5	235.4	301.8	170.9	66.4
(ring)TiBr$_3$	55	247.3	310.5	192.3	63.2
(ring)TiI$_3$	-	-	-	189.9	-

observed in going from the unsubstituted cyclopentadienyl (Cp) to the methylcyclopentadienyl (Cp$'$) to the tetramethylcyclopentadienyl (Cp$^+$) to the pentamethylcyclopentadienyl (Cp*) titanium (IV) trihalides are summarized in Table III.

From these data, the mean downfield $\delta(^{49}Ti)$ chemical shift can be estimated to be 62 ± 4 ppm per methyl group. The total $\delta(^{49}Ti)$ chemical shifts calculated for Cp$^+$ and Cp* complexes using the average chemical shift for one methyl group are only approximately but not exactly additive.

The contraintuitive trends (IHD and inverse methyl substitution dependence) found in ^{49}Ti and ^{47}Ti NMR chemical shift values of half-sandwich titanium(IV) trihalide complexes can be understood as a consequence of a deviation from the usual magnitudes of the diamagnetic, σ_d, and, especially, the paramagnetic, σ_p, terms contributing to nucleus shielding variation due to changing the halide ligands bound to the Ti central atom and/or replacing cyclopentadienyl hydrogen atom(s) by methyl group(s). Similar anomalous Ti NMR chemical shifts observed for the other titanium(IV) halide compounds, such as TiX_4 (X = Cl, Br, I) and Cp_2TiX_2 (X = F, Cl, Br, I), have been attributed to large paramagnetic terms, assuming the diamagnetic contribution remains relatively constant [19]. The σ_p contribution is inversely proportional to the average excitation energy, ΔE, for the molecule [17]. In compounds, such as TiX_4, Cp_2TiX_2 as well as those we studied, with low-lying excited electronic states, the σ_p term acting to deshield the Ti nucleus becomes dominant in determining the resultant Ti NMR chemical shifts. The largest contribution affecting σ_p for titanium(IV) compound should arise from the first excited state affording the smallest ΔE value. Thus, for those titanium complexes, in which σ_p is playing the dominant role in determining the observed Ti NMR chemical shifts, there should be a direct correlation between the observed chemical shift and the lowest energy transition observed in the electronic spectrum, i.e. $\delta(^{49,47}Ti)$ should be related to ΔE^{-1} or λ_{max}^{CT}.

In order to find the desired lowest energy bands, the UV-VIS spectra of all the ten half-sandwich titanium(IV) trihalide complexes (*1 – 10*) were measured. They all exhibit a weak longest wavelength (lowest energy) absorption band between 380 and 506 nm (3.26 – 2.45 eV). These absorption features, listed in
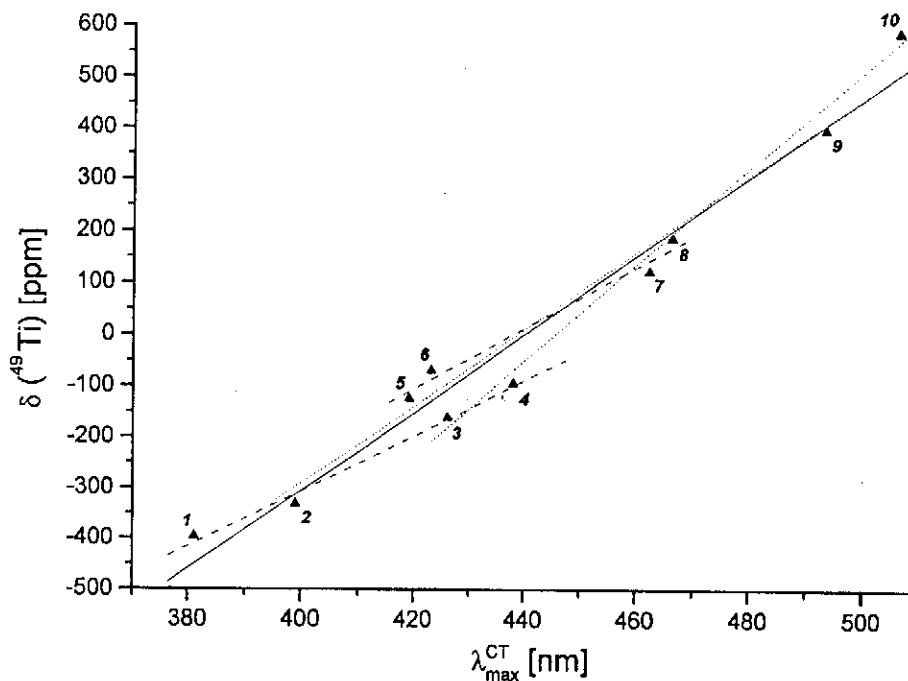
Fig. 2 Plot of $\delta(^{49}Ti)$ versus $\lambda_{max}^{1.CT}$ on half-sandwich titanium(IV) trihalides (1–10)

Table I, can be assigned, on the basis of a theoretical MO for d^0 $CpTiX_3$ type complex [14a], to a first charge-transfer $L \rightarrow M$ transition from the HOMO (localised mainly on Cp ligand) to the LUMO (Ti 3d orbital). The corresponding $\lambda_{max}^{1.CT}$ or $E^{1.CT}$ values are shown in Table I. A closer inspection of the CT bands characteristic of these half-sandwiches reveals that the first CT band maximum moves to lower energy as (*i*) the more electronegative halide ligands are replaced by the less electronegative ones ($E^{1.CT}$ order: Cl > Br > I, or $\lambda_{max}^{1.CT}$ order: I > Br > Cl), and (*ii*) the electron-donating methyl substituents are successively added to the five-membered ring in a isohalide series ($E^{1.CT}$ order: Cp > Cp' > Cp$^+$ > Cp*, or $\lambda_{max}^{1.CT}$ order: Cp* > Cp$^+$ > Cp' > Cp). A plot of the observed $\delta(^{49}Ti)$ values versus the found $\lambda_{max}^{1.CT}$ for our series of ten half-sandwich titanium(IV) trihalides is presented in Fig. 2. It shows the overall $\delta(^{49}Ti)/\lambda_{max}^{1.CT}$ relationship represented by the least-squares solid line (correlation coefficient = 0.9845). The corresponding relationships for the subsets $Cp'TiX_3$ and Cp^*TiX_3 (X = Cl, Br, I) demonstrating the IHD are represented in Fig. 2 by the dotted lines and for subsets of methylated isohalides (X = Br, Cl) by the dashed lines. Clearly, within each subset an excellent correlation exists. It should be emphasised, however, that strictly linear $\delta(^{49}Ti)/\lambda_{max}^{1.CT}$ correlations are not expected since the diamagnetic, σ_d, and the paramagnetic, σ_p, terms will change

with the halide substitution at the Ti center as well as with the methyl substitution(s) on the five-membered ring. Generally, the solid line in Fig. 2 does demonstrate that the longer $\lambda_{max}^{1.CT}$, the farther downfield the corresponding $\delta(^{49}Ti)$ value.

Finally, it is worthwhile to briefly comment on the $\delta(^{49}Ti)$ and $\delta(^{47}Ti)$ resonance line half-widths, $\Delta v_{1/2}$, listed in Table I. These spectral features are known to reflect the electronic symmetry or asymmetry around the Ti central atom. On inspection of the line half-width, $\Delta v_{1/2}$, values for $\delta(^{49}Ti)$ and $\delta(^{47}Ti)$ resonances, a correlation with the symmetry of the methyl substitution pattern becomes evident. Thus, Cp*TiCl$_3$ with a permethylated five-membered ring exhibits the lowest $\Delta v_{1/2}(^{49}Ti)$ value in the trichloride series, whereas half-sandwich titanium trichlorides possessing a more unsymmetrical methyl substitution pattern of the ring exhibit higher $\Delta v_{1/2}(^{49}Ti)$ values. The remarkably high $\Delta v_{1/2}(^{49}Ti)$ value for the parent complex CpTiCl$_3$ was attributed to the ligand-field effect that affects the line half-width [24].

Conclusion

For the first time, the IHD of the Ti NMR chemical shifts has been demonstrated to occur in a set of half-sandwich titanium(IV) trihalide complexes, too. Furthermore, the inverse methyl substitution dependence of the Ti NMR resonances for methylated species is confirmed. If both inverse dependencies are taken into consideration, it may be concluded that Ti NMR chemical shifts are not always an indication of electron density at the titanium central atom. The IHD and inverse methyl substitution dependence are attributed to large paramagnetic term deshielding Ti nucleus, as a consequence of being inversely proportional to the lowest energy charge-transfer transition. For the half-sandwich complexes studied, the direct correlation (^{49}Ti) versus $\lambda_{max}^{1.CT}$ (or $1/E^{1.CT}$) has been found. Concerning the $^{49,47}Ti$ resonance line half-widths that provide qualitative information about the symmetry of electronic distribution at the titanium atom, a correlation with the symmetry of methyl substitution pattern is, as expected, evident.

Acknowledgements

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