

An Unusual Relationship between ^{49}Ti Chemical Shift and $\text{Ti}(2p_{3/2})$ Binding Energy. The Use of ^{49}Ti NMR in Evaluating the Electronic Effect of Methyl Substitution on the Cyclopentadienyl Ligand

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The ^{49}Ti NMR chemical shifts of a series of titanocene derivatives have been shown to have an inverse relationship to the $\text{Ti}(2p_{3/2})$ binding energies of these same compounds as measured by X-ray photoelectron spectroscopy (ESCA). Replacement of one cyclopentadienyl (Cp) group of the titanocene difluorides, dichlorides, and dibromides by a pentamethylcyclopentadienyl (Cp*) moiety resulted in an average *downfield* shift in the ^{49}Ti NMR absorption of 148 ppm. Substitution of both Cp groups by Cp* groups resulted in an average *downfield* shift of 312 ppm.

In view of the widespread use of titanium derivatives in Ziegler-Natta catalysis and in a variety of other transformations of organic molecules, it was surprising to us that relatively little is known about titanium nuclear magnetic resonance, even though both ^{49}Ti and ^{47}Ti are NMR active.¹⁻⁴ One of the more curious aspects of Ti NMR is inverse halogen dependence (IHD)²⁻⁴ in which the direction of chemical shifts is the reverse of what might have been predicted on the basis of the electronegativity of halogen substituents. We now wish to report that through a comparison of ^{49}Ti NMR shifts and $\text{Ti}(2p_{3/2})$ binding energies on a series of titanocene derivatives, we have shown that the inverse halogen dependence is not restricted to halogens²⁻⁴ and that changing from cyclopentadienyl (Cp) ligands to pentamethylcyclopentadienyl (Cp*) ligands can have a greater influence on both inner-shell electron binding energies and certain nuclear properties than does changing halogens. We have also demonstrated that the readily accessible ^{49}Ti NMR spectra have the potential of providing extensive information about titanium-containing intermediates in a variety of stoichiometric and catalytic reactions.

Table I lists the NMR chemical shifts for ^{49}Ti (5.5%; $I = 7/2$; $Q = 0.24 \times 10^{-28} \text{ m}^2$; $D_{49}^{\text{P}} = 2.07 \times 10^{-4}$) in parts per million upfield from titanium tetrachloride as an external standard as measured at 16.9000 MHz by using a 31 250-Hz sweep width and a pulse time of 32 ms on a Nicolet NT-300 WB spectrometer. Also listed in Table I are the $\text{Ti}(2p_{3/2})$ binding energies for this series of compounds, as measured on a Physical Electronics Industries' ESCA-Auger-SIMS system utilizing Mg $K\alpha$ radiation. ESCA samples were run on a polyethylene backing, and each sample was calibrated against the C(1s) binding energy (284.6 eV) of polyethylene. With this calibration procedure, binding energies of ± 0.1 eV could be routinely reproduced on various samples by different researchers on different machines, since this calibration technique eliminated variations due to sample charging.⁵ Figure 1 shows

Table I. ^{49}Ti NMR Chemical Shifts (vs. TiCl_4 , δ 0.00) and $\text{Ti}(2p_{3/2})$ Binding Energies

compd	^{49}Ti , ^{a,b} δ	$\text{Ti}(2p_{3/2})$, ^c ± 0.1 eV
Cp_2TiF_2	-1051	457.5
$\text{CpCp}^*\text{TiF}_2$	-964	457.0
$\text{Cp}^*_2\text{TiF}_2$	-823	456.7
Cp_2TiCl_2	-773	456.9
Cp_2TiBr_2	-671	456.8
$\text{CpCp}^*\text{TiCl}_2$	-601	456.6
$\text{CpCp}^*\text{TiBr}_2$	-486	456.5
$\text{Cp}^*_2\text{TiCl}_2$	-443	456.1
$\text{Cp}^*_2\text{TiBr}_2$	-293	455.9

^a TiCl_4 was used as an external standard. ^b NMR spectra were measured in CDCl_3 . ^c All binding energies are calibrated vs. C(1s) of polyethylene.

a plot of ^{49}Ti NMR chemical shifts vs. $\text{Ti}(2p_{3/2})$ binding energies. As can be seen from Figure 1, a reasonable *inverse* correlation exists between these two molecular properties.

In the progression from Cp_2TiF_2 , which has the most electronegative substituents on titanium, to $\text{Cp}^*_2\text{TiBr}_2$, which has the least electronegative substituents on titanium, the binding energies of the inner-shell electrons on titanium undergo a systematic decrease. This is as expected on the basis of the electronic effects of the substituents.⁵ Of particular interest was the relatively large effect of methyl substitution on the cyclopentadienyl ligands relative to binding energies. Examination of the ^{49}Ti NMR chemical shifts showed an upfield shift in going from bromides to chlorides to fluorides and in going from the decamethyl to the pentamethyl to the nonsubstituted bis(cyclopentadienyl) systems. We see this inverse relationship of chemical shift to methyl substitution on the cyclopentadienyl ligands to be quite interesting.

The overall relationship of the binding energies and chemical shifts of the titanocenes shown in Figure 1 is represented by the least-squares solid line (correlation coefficient = 0.944). The relationship between the subsets of decamethyltitanocenes, pentamethyltitanocenes, and titanocenes is represented in Figure 1 by the dashed lines. Clearly, within these subsets an excellent correlation exists

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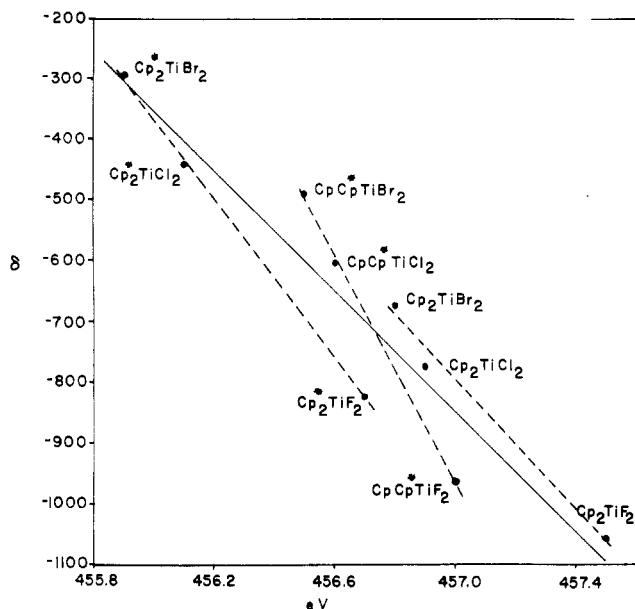


Figure 1. Plot of X-ray photoelectron binding energies (± 0.1 eV) for Ti($2p_{3/2}$) vs. chemical shifts of ^{49}Ti relative to $^{49}\text{TiCl}_4 = 0.00$ ppm (external standard). Solid line represents the least-squares relationship of all data. Dashed lines represent the same relationship for the subsets of decamethyltitanocenes, pentamethyltitanocenes, and titanocenes.

between the inverse halogen dependence and the Ti($2p_{3/2}$) binding energy.

The inverse relationship of chemical shift with methyl substitution was not restricted to the titanocenes. Replacement of the cyclopentadienyl group of cyclopentadienyltitanium trichloride (^{49}Ti NMR, -393 ppm)⁶ by a pentamethylcyclopentadienyl group (^{49}Ti NMR, -96 ppm)⁸ resulted in 297 ppm downfield shift while the corresponding Ti($2p_{3/2}$) binding energies were 457.2 and 456.9 eV, respectively.

These studies corroborate our earlier work,⁵ which indicated the dramatic electronic influence of substituting a pentamethylcyclopentadienyl group for cyclopentadienyl. Since relatively dilute (10^{-3} M) solutions of titanium compounds can be readily measured by NMR spectroscopy,⁷ titanium NMR should prove useful in the study of a wide variety of catalytic and stoichiometric reactions involving titanium derivatives. The inverse relationships discussed above are significant to our ability to interpret chemical shift data for titanium derivatives.

Experimental Section

General Details. ^1H NMR spectra were obtained on a Hitachi Perkin-Elmer R-24B spectrometer at 60 MHz and on a Nicolet WB-300 NMR spectrometer at 300 MHz. The NMR solvent was CDCl_3 , and tetramethylsilane was used as the internal reference. ^{49}Ti and ^{47}Ti NMR spectra were obtained on a Nicolet WB-300 NMR spectrometer at 16.9000 MHz; samples were referenced to $^{49}\text{TiCl}_4$ (at δ 0.00), as a neat liquid run coaxially in a 5-mm NMR tube, and CDCl_3 was used as the NMR solvent. Photoelectron spectra were obtained on a Physical Electronics Industries, Inc., ESCA-Auger-SIMS system equipped with a Model 15-720 specimen introduction/reaction chamber, utilizing Mg K α radiation. The samples were run on a polyethylene-coated aluminum chip, and each sample was calibrated against the C(1s) binding energy

(284.6 eV) of polyethylene. Mass spectrometry was performed on an AET MS 30 or on a Finnigan 4000 mass spectrometer. Microanalyses were obtained from Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Materials. Bis(η^5 -cyclopentadienyl)titanium dichloride was purchased from Strem Chemicals, Inc., and was recrystallized once from methylene chloride/hexane prior to use. (η^5 -Pentamethylcyclopentadienyl)titanium trichloride and bis(pentamethylcyclopentadienyl)titanium dichloride were prepared according to literature procedures.⁸ (η^5 -Pentamethylcyclopentadienyl)(η^5 -cyclopentadienyl)titanium dichloride was prepared according to the method of Nesmeyanov et al.,⁹ and (η^5 -cyclopentadienyl)titanium trichloride was prepared according to the method of Nesmeyanov et al.¹⁰ The difluoro and dibromo analogues of bis(η^5 -cyclopentadienyl)titanium dichloride were prepared according to the procedures described by Lappert.¹¹ The identities of all of the above compounds were confirmed by comparison of ^1H NMR and mass spectral data with literature values. Preparation of the difluoro and dibromo analogues of bis(η^5 -pentamethylcyclopentadienyl)- and (η^5 -pentamethylcyclopentadienyl)(η^5 -cyclopentadienyl)titanium dichloride were carried out by modifications of the procedures of Lappert and co-workers (vide post).¹¹

Bis(η^5 -pentamethylcyclopentadienyl)titanium Difluoride.

In a 50-mL, single-necked, round-bottomed flask was placed bis(η^5 -pentamethylcyclopentadienyl)titanium dichloride (0.25 g, 0.64 mmol), sodium fluoride (0.81 g, 19.2 mmol), and 25 mL of methanol. The resultant mixture was refluxed for 3 h, during which time the color changed from red-brown to yellow-orange. The reaction mixture was allowed to cool to ambient temperature and filtered, and the solvent was removed from the filtrate under reduced pressure. The resulting solid residue was recrystallized from hexane and sublimed to yield 0.093 g (41% yield) of the title compound as an orange crystalline material: mp 208–210 °C; ^1H NMR (CDCl_3) δ 1.93 (s); exact mass m/e 356.1796 (calcd m/e 356.1795). Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{F}_2\text{Ti}$: C, 67.41; H, 8.49. Found: C, 67.47; H, 8.54.

(η^5 -Pentamethylcyclopentadienyl)(η^5 -cyclopentadienyl)titanium Difluoride. The preparation of (η^5 -pentamethylcyclopentadienyl)(η^5 -cyclopentadienyl)titanium difluoride was carried out by a halide-exchange reaction, as described above for bis(η^5 -pentamethylcyclopentadienyl)titanium difluoride, using 0.21 g (0.64 mmol) of (η^5 -pentamethylcyclopentadienyl)(η^5 -cyclopentadienyl)titanium dichloride, 0.80 g (19.1 mmol) of sodium fluoride, and 25 mL of methanol. The product was recrystallized from hexane and sublimed to give 0.046 g (25% yield) of bright orange crystals: mp 153–155 °C; ^1H NMR (CDCl_3) δ 6.16 (5 H, t, $J_{\text{HF}} = 1.34$ Hz), 1.99 (15 H, s); exact mass m/e 286.1010 (calcd m/e 286.1012). Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{F}_2\text{Ti}$: C, 62.94; H, 7.04. Found: C, 62.40; H, 7.14.

Bis(η^5 -pentamethylcyclopentadienyl)titanium Dibromide.

In a small Schlenk tube was placed 0.25 g (0.64 mmol) of bis(η^5 -pentamethylcyclopentadienyl)titanium dichloride and 15 mL of dry methylene chloride. The solution was stirred under a nitrogen atmosphere, and 0.77 mL (0.77 mmol) of a 1.0 M solution of boron tribromide in methylene chloride was added via syringe. The reaction mixture was stirred for 1.5 h, and the solvent was then removed under reduced pressure. The solid residue was dissolved in methylene chloride and filtered, and the filtrate was concentrated. Addition of hexane promoted precipitation of a solid, which was recrystallized from methylene chloride/hexane to give 0.16 g (54% yield) of the desired dibromide as black crystals: mp 260–262 °C; ^1H NMR (CDCl_3) δ 2.09 (s); exact mass m/e 476.0190 (calcd m/e 476.0193). Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{Br}_2\text{Ti}$: C, 50.23; H, 6.32. Found: C, 50.29; H, 6.41.

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(7) Dilution over 2 orders of magnitude resulted in no change in chemical shift. Line widths at half-height varied from 13 to 1058 Hz, with the chlorides and bromides having an average line width of 166 Hz, while the fluorides averaged 776 Hz. In the case of the fluorides, the line width may have been due partially to fluorine coupling.

was carried out as described above for bis(η^5 -pentamethylcyclopentadienyl)titanium dibromide, by using 0.21 g (0.64 mmol) of (η^5 -pentamethylcyclopentadienyl)(η^5 -cyclopentadienyl)titanium dichloride, 0.77 mL (0.77 mmol) of 1.0 M boron tribromide in methylene chloride, and 15 mL of methylene chloride. The product was recrystallized from methylene chloride/hexane to give 0.15 g (58% yield) of the desired dibromide as black crystals: mp 250-252 °C; $^1\text{H NMR}$ (CDCl_3) δ 6.37 (5 H, s), 2.12 (15 H, s); exact mass m/e 405.9417 (calcd m/e 405.9410). Anal. Calcd for

$\text{C}_{15}\text{H}_{20}\text{Br}_2\text{Ti}$: C, 44.15; H, 4.94. Found: C, 44.14; H, 4.99.

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Registry No. Cp_2TiF_2 , 309-89-7; $\text{CpCp}^*\text{TiF}_2$, 38496-78-5; $\text{Cp}^*_2\text{TiF}_2$, 87050-22-4; Cp_2TiCl_2 , 1271-19-8; Cp_2TiBr_2 , 1293-73-8; $\text{CpCp}^*\text{TiCl}_2$, 38496-87-6; $\text{CpCp}^*\text{TiBr}_2$, 87050-23-5; $\text{Cp}^*_2\text{TiCl}_2$, 11136-36-0; $\text{Cp}^*_2\text{TiBr}_2$, 87050-24-6.

Orientation and Structure of (η^5 -Cyclopentadienyl)rhenium and -manganese Tricarbonyl Complexes Dissolved in Liquid Crystal Solvents

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The anomalous ratios of the direct dipole coupling constants obtained from the proton NMR spectra of oriented solutions of (η^5 -cyclopentadienyl)manganese tricarbonyl dissolved in two different nematic liquid crystal solvents are also found for the analogous rhenium compound. For a solvent in which the orientation of the solutes is parallel to the liquid crystal axis, the ratios of the direct dipole coupling constants are temperature dependent. The orientation in a phenylcyclohexyl-type solvent is perpendicular to the liquid crystal axis and independent of temperature. The effects are attributed to an exchange between two sites, parallel and perpendicular to the liquid crystal axis.

The proton NMR spectra of oriented (η^5 -cyclopentadienyl)manganese(I) tricarbonyl, $\text{CpMn}(\text{CO})_3$, dissolved in nematic liquid crystal solvents have been reported by several different groups.¹⁻⁴ The ratio of the two different direct dipole coupling constants (or of the interproton distance) in a regular pentagonal ring structure should be independent of the actual carbon-carbon and carbon-hydrogen bond lengths, but all the investigations have shown that deviations occur from the expected value of 4.236, or 4.216 if vibrationally corrected.⁵ Since there is currently some theoretical interest in the conformations of organometallic complexes^{6,7} and in the implications that distortions of the cyclopentadienyl ring have with regard to the bonding of this ligand,⁷⁻¹⁰ we have investigated the oriented NMR spectrum of the analogous rhenium complex, $\text{CpRe}(\text{CO})_3$. Two different solvents were used: a nematic mixture (EK X-11643) from Eastman Kodak with a nematic range of 12-100 °C and a cyanophenylcyclohexyl (PCH) mixture, Merck 1132, temperature range -6 to +70 °C. As a consequence of the results we have also reexamined the manganese compound.

Results and Discussion

The results of the spectral analyses are given in Table I, where the errors are derived from the probable errors of the D_{ij} values given by the LAOCOON3 fit. Similar results were obtained for both the rhenium and manganese complexes. (The rhenium complex, $\text{CpRe}(\text{CO})_3$, was prepared as previously described;⁸ the manganese compound was a generous gift from Ethyl Corp. Solute concentrations are approximately 5% by weight of $\text{CpMn}(\text{CO})_3$ and 1.5% of $\text{CpRe}(\text{CO})_3$. Proton NMR spectra were obtained for the

manganese complex in M1132 using a Bruker WH90 and the others on a Varian HR200. Spectra were analyzed by using a version of LAOCOON3 modified for oriented spectra. The indirect coupling constants were taken to be $^3J = 2.7$ Hz and $^4J = 1.48$ Hz, the averages of the values obtained when these parameters were allowed to vary in the initial analyses.) In the PCH solvent, the dipole coupling constants were found to be negative, and therefore the orientation of the solvent molecule must be perpendicular to the liquid crystal axis. The ratio, D_{12}/D_{13} , is much lower than that found for the EK solvent and reported in the literature for other solvents.¹⁻⁴ This implies that a greater distortion of the cyclopentadienyl ring occurs for this solvent mixture. However, the ratio appears to be independent of temperature whereas, in the EK solvent, it decreased with increasing temperature.

There is now both theoretical and experimental evidence that the carbon-carbon bonds in the cyclopentadienyl ligand are not of equal length. The results of the crystallographic structure study of the manganese tricarbonyl

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