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NMR Data of Methyltitanium Trichloride and Related Organometallic Compounds. A Combined Experimental and Theoretical Study of Me$_n$XCl$_{4-n}$ (n = 0−4; X = C, Si, Sn, Pb, Ti)

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Abstract: The complete series of Me$_n$TiCl$_{4-n}$ compounds has been prepared and the NMR spectra were recorded. The measured values are compared with the data of the main group equivalents Me$_n$XCl$_{4-n}$ with X = C, Si, Sn, and Pb. The ^{1}H, ^{13}C, ^{29}Si, and ^{47,49}Ti chemical shifts of the compounds Me$_n$XCl$_{4-n}$ (X = C, Si, Ti) were calculated using the IGLO approach, based on optimized geometries at the HF and MP2 levels of theory. Theory and experiment agree that the central carbon atom of Me$_n$CCl$_{4-n}$ shows a deshielding trend from n = 4 to 0. The central titanium atom in Me$_4$TiCl$_{4-n}$ exhibits the opposite behavior, it becomes more shielded from n = 4 to 0. The calculated and experimental results show that the ^{13}C and ^{47,49}Ti chemical shifts of MeTiCl$_3$ are not anomalous, the data fit into the pattern observed and calculated for the whole series of Me$_n$TiCl$_{4-n}$ compounds. The silicon series Me$_n$SiCl$_{4-n}$ exhibits a U-shaped curve. The analysis of the bond orbital contributions to the calculated shifts shows that the X−C and X−Cl localized bonds clearly dominate the theoretically predicted chemical shift of the atom X. The partitioning of the bond contributions into the diamagnetic and paramagnetic parts clearly demonstrates, that the paramagnetic contributions determine the trend of the chemical shifts of the three series of compounds. The diamagnetic parts are nearly constant. The paramagnetic contributions are particularly large for the Ti compounds, because Ti has low-lying empty d orbitals, which can interact with the bond orbitals by the action of the off-center angular momentum operator of Ti. The paramagnetic contributions are much lower for the Si and C compounds, because there are no low-lying empty orbitals available. The analysis of the chemical bonds using the NBO partitioning scheme shows that the polarization and sp^n hybridization of the C−CH$_3$, C−Cl, Si−CH$_3$, and Si−Cl bonds show the expected trends. The Ti−CH$_3$ and Ti−Cl bonds are essentially sd^3 hybridized with negligible p contribution at Ti.

Introduction

The structural data of methyltitaniumtrichloride MeTiCl$_3$ (**1d**), an important organometallic reagent,[1,2] have been controversially debated over the last two decades. An early report[3] on IR and ^{1}H NMR data commented on the rather high frequency proton signal, with δ = 2.78 compared to δ = 2.70 of the carbon equivalent MeCCl$_3$ (**2d**), although titanium is less electronegative than carbon. In addition, these authors observed a $^1J_{(C,H)}$ spin coupling constant of 134 Hz, which again required a "strong electronegative substituent". By comparing the proton data of **1d** and a series of MeTiY$_3$ (Y = halogen) compounds, subsequent work suggested a p$_\pi$−d$_\pi$ interaction between titanium and chlorine in MeTiCl$_3$.[4] In preliminary work we have shown that the ^{47,49}Ti NMR signal of **1d** is also strongly deshielded compared with other titanium compounds.[5] We could confirm the ^{13}C result of other authors who found an astonishing ^{13}C chemical shift value of δ = 118.2 for the methyl group of MeTiCl$_3$.[6] These authors also reported, on the basis of electron diffraction data, a considerable flattening of the methyl group, supported by a very low frequency rocking mode in the IR spectrum. They concluded that an agostic hydrogen atom would be present, which they related to a *positive* geminal H,H spin coupling constant of the methyl group. This sign was measured on a deuterated isotopomer and was the only example of a positive $^2J_{(H,H)}$ in a methyl group. However, besides the very unusual ^{13}C chemical shift, all other data from this paper[6] seem to be wrong.

Although theoretical work using extended Hückel calculations reproduced the positive sign of the spin coupling constant, and related this effect to a small Ti−C−H angle,[7] a more recent experimental redetermination of this sign showed that it is indeed *negative,* like all other similar geminal spin coupling constants.[8] By measuring the temperature dependence of the ^{1}H NMR spectra of deuterated species of methyl- and ethyltitanium trichloride, the agostic nature of the hydrogen atoms was not confirmed[9] and no isotopic perturbation of a conformational equilibrium was found.[10] New gas electron diffraction data also could not be interpreted in terms of an unusual methyl group geometry but showed a normal Ti−C−H angle of ca. 109°.[11] This is in accordance with high level quantum chemical calculations, which also obtain a normal methyl group geometry.[12] The large difference in the low frequency rocking mode

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[1] Reetz, M. T.; Hüllmann, M.; Seitz, T. *Angew. Chem.* **1987**, *99*, 478; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 477.

[2] Reetz, M. T.; Kesseler, K.; Schmidtberger, S.; Wenderoth, B.; Steinbach, R. *Angew. Chem.* **1983**, *95*, 1007; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 989.

[3] Hanlan, J. F.; McCowan, J. D. *Can. J. Chem.* **1972**, *50*, 747.

[4] Blandy, C.; Guerreiro, R.; Gervais, D. *C. R. Acad. Sci. Ser. C* **1974**, *278*, 1323.

[5] Berger, S.; Bock, W.; Marth, C. F.; Raguse, B.; Reetz, M. T. *Magn. Reson. Chem.* **1990**, *28*, 559.

[6] Berry, A.; Dawoodi, Z.; Derome, A. E.; Dickinson, J. M.; Downs, A. J.; Green, J. C.; Green, M. L. H.; Hare, P. M.; Payne, M. P.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Chem. Commun.* **1986**, 520.

[7] Green, J. C.; Payne, M. P. *Magn. Reson. Chem.* **1987**, *25*, 544.

[8] Green, M. L. H.; Hughes, A. K. *J. Chem. Soc., Chem. Commun.* **1991**, 1231.

[9] Bresler, L. S.; Kachurin, A. M.; Polyanskii, V. I. *Zh. Obschch. Khim.* **1989**, *59*, 1567.

[10] Green, M. L. H.; Hughes, A. K.; Popham, N. A.; Stephens, A. H. H.; Wong, L.-L. *J. Chem. Soc., Dalton Trans.* **1992**, 3077.

[11] Briant, P.; Green, J.; Haaland, A.; Maellendal, H.; Rypdal, K.; Tremmel, J. *J. Am. Chem. Soc.* **1989**, *111*, 3434.

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of **1d** compared with $MeGeCl_3$ was ascribed by these authors to the fact that the d orbitals of Ge have very high energy, whereas for the titanium compound a rehybridization of the carbon metal bond should be feasible due to the low lying d orbitals of titanium.[12a] A close geometrical resemblance to the new gas electron diffraction data was also obtained using pseudopotential calculations not only for **1d** but also for the series of Me_nTiCl_{4-n}[13] and Me_nXCl_{4-n} compounds with X = C, Si, Ge, Sn, and Pb.[14] In summary, the current theoretical and structural data maintain that the methyl group in **1d** has a normal geometry, while the carbon chemical shift is completely out of range. A survey of ^{13}C data banks such as SPECINFO[15] reveals that there is a huge gap between the measured value of $\delta = 118$ and the highest frequency value reported for non-titanium-bonded methyl groups at $\delta = 75$.

In order to understand the very unusual NMR data of this compound, we have initiated a project to experimentally determine the carbon chemical shifts in the complete series of Me_nTiCl_{4-n} (**1**) compounds. We wanted to find out whether the outstanding ^{13}C chemical shift is restricted to the trichloride. Furthermore, we decided to compare the results with the series of main group element compounds Me_nXCl_{4-n} with X = C, Si, Sn, and Pb (**2**–**5**), looking not only at carbon chemical shifts but also at the chemical shift of the central atoms.

In the course of this study, we found that the ^{13}C and $^{47,49}Ti$ chemical shifts of **1d** are not anomalous, the data fit into the pattern observed and calculated for the whole series of Me_nTiCl_{4-n} compounds. The order of the $^{47,49}Ti$ chemical shift in the series Me_nTiCl_{4-n} is unusual, however, compared with the carbon and silicon analogues.

The Ti atom shows a trend toward more shielding from n = 4 to 0. The central carbon atom in Me_4CCl_{4-n} exhibits the opposite behavior, it becomes more deshielded from n = 4 to 0. The silicon series Me_nSiCl_{4-n} shows a U-shaped curve. This study attempts to give an explanation for the different trends of the three series of related compounds.

The experimental study was complemented by quantum mechanical *ab initio* calculations of the geometries and the chemical shifts of the Me_nXCl_{4-n} compounds for X = C, Si, Ti. The chemical shifts are predicted using the IGLO method.[16] The performance of the IGLO method for calculating the chemical shifts of elements of the first, second, and third rows of the periodic system has been documented previously.[16b] However, the accuracy of theoretically predicted $^{47,49}Ti$ chemical shifts using IGLO has not been studied before. Thus, the present work gives important information about the performance of IGLO for calculating $^{47,49}Ti$ chemical shifts. We want to point out that the calculated data refer to isolated molecules, while the experimentally observed chemical shifts are measured in solution. This may lead to errors, which are not due to the theoretical model. Previous studies have shown, however, that a meaningful comparison between calculated relative shifts of isolated molecules with solution experiments can be made.[16b] It seems that the solvent effect upon the *difference* in chemical shifts cancels to a good extent. The results presented here show that this seems to hold also for Ti compounds. In this paper we report the results of the experimental and theoretical investigations.

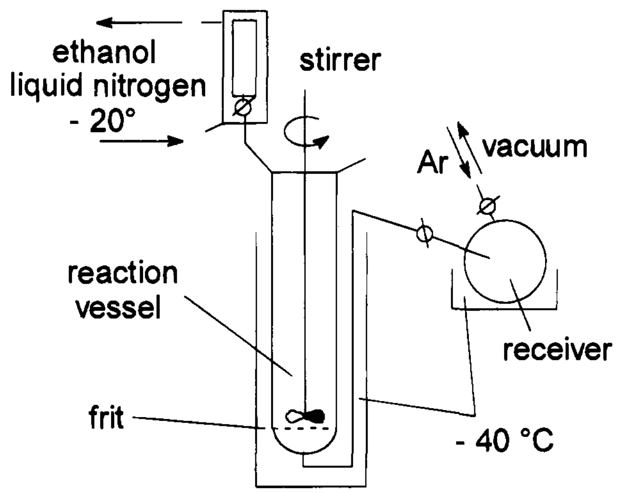

Figure 1. Apparatus used for the preparation of the methyltitanium chlorides.

Experimental and Theoretical Methods

Methyltitanium chlorides are unstable to air and moisture and decompose below 0 °C, except for methyltitanium trichloride. All preparations, manipulations, and reactions were carried out under an inert atmosphere of argon. We had to find a way to filter the solutions without allowing them to warm above −40 °C. The apparatus used is shown in Figure 1. It allows the filtration of the reaction mixture by connecting the receiver to the vacuum line, while cooling the reaction mixture and the receiver.

The methyltitanium compounds were prepared by methods similiar to those used by Claus and Beermann[17] as well as Schlegel and Thiele.[18] Thus, they can be prepared by mixing methylmagnesium iodide and titanium tetrachloride in the right stoichiometric ratio, or by mixing the corresponding amounts of titanium tetrachloride and tetramethyltitanium. Special care has to be taken in the preparation of tetramethyltitanium and particularly trimethyltitanium chloride, because they decompose at −30 °C and −40 °C, respectively. A solution of trimethyltitanium chloride concentrated enough to detect an $^{47,49}Ti$-NMR signal could only be made by direct reaction of titanium tetrachloride with methylmagnesium iodide, without any steps of purification or yield optimization. The preparation of dimethyltitanium dichloride is much less difficult; it is stable up to −10 °C. Trimethyltitanium chloride melts at 29 °C and does not decompose until 40 °C.

General Procedure for the Reaction of Methylmagnesium Iodide with Titanium Tetrachloride. The reaction vessel was charged with 100 cm^3 of diethyl ether at −40 °C. Titanium tetrachloride was added slowly, dropwise from a syringe. To this yellow suspension, an etheral solution of methylmagnesium iodide, which has been precooled to −20 °C in the addition funnel, was added over several hours. After complete addition, the mixture was stirred for 2 h. A brown solid is formed from which the solution of tetramethyltitanium is separated by connecting the receiver to the vacuum line. The yield can be improved by washing the solid with further precooled diethyl ether until the filtrate is no longer orange. We usually avoided this step because we were interested in obtaining concentrated solutions. The solution of the methyltitanium compound is concentrated under vacuum. This takes several days, and one has to ensure that the temperature never rises above the temperature of decomposition. The solutions can be stored at −78 °C for several weeks. For NMR measurements, they are transferred into NMR tubes, which are sealed *in vacuo*.

General Procedure for the Preparation of Methyltitanium Chlorides from Tetramethyltitanium and Titanium Tetrachloride. For this reaction, the concentration of the solution of tetramethyltitanium in diethyl ether has to be known. Therefore, 5 cm^3 of the solution were transferred into a 50 cm^3 round-bottom Schlenk flask and 1.00 g (7.88 mmol) of iodine was added. After the reaction $Me_4Ti + 4I_2 \rightarrow TiI_4 + 4MeI$ is quenched with 20 cm^3 of water, an aqueous solution of starch is added. The excess iodine is then titrated with a solution of sodium thiosulfate, until the mixture remains colorless. A direct titration

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(12) (a) Williamson, R. L.; Hall, M. B. *J. Am. Chem. Soc.* **1988**, *110*, 4428. (b) Krömer, R.; Thiel, W. *Chem. Phys. Lett.* **1992**, *189*, 105.

(13) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Comp. Chem.* **1992**, *13*, 919.

(14) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Comp. Chem.* **1992**, *13*, 935.

(15) *Specinfo, NMR Data Bank*; Chemical Concepts: Weinheim.

(16) (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR: Basic Princ. Prog.* **1990**, *23*, 165.

(17) Claus, K.; Beermann, C. *Angew. Chem.* **1959**, *19*, 627.

(18) Schlegel, M.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1985**, *526*, 43.

of the solution of tetramethyltitanium with a solution of iodine is impossible because of the orange color of tetramethyltitanium.

A round-bottom Schlenk flask is charged with a solution of tetramethyltitanium of known concentration and titanium tetrachloride diluted with pentane is added at −78 °C in the right stoichiometric ratio. The solution is then concentrated under vacuum. This takes several days and one has to ensure that the temperature never rises above the temperature of decomposition. For NMR measurements, the solutions are concentrated as much as possible and are transferred into 5 mm NMR tubes, which are sealed *in vacuo*.

The measurement was performed on a Bruker AMX-500 spectrometer with internal reference versus the residual solvent peak for ^{1}H and ^{13}C and external reference for X = ^{47,49}Ti versus $TiCl_4$ and for ^{207}Pb versus Me_4Pb.

The quantum chemical calculations of the chemical shifts δ for Me_nXCl_{4-n} (X = C, Si, Ti) have been carried out with the IGLO method.[16] Two types of basis sets were used. Basis set I is a standard 6-31G(d) basis set[19] at H, C, Si, and Cl in combination with an effective core potential (ECP) for Ti.[20] The valence basis set at Ti has (441/2111/41) quality. Basis set II is a [11s7p2d]/(7s6p2d) basis set for Si and Cl, [9s5p1d]/(5s4p1d) for C, and [5s1p]/(3s1p) for H.[16,21] For Ti, an all electron [14s9p5d]/(8s5p3d) basis set from Wachters[22a] was chosen, augmented by additional 4p functions, as recommended by Wachters, and a set of diffuse d functions.[22b] This gives a [14s11p6d]/(8s7p4d) basis set for Ti. The geometries have been optimized at the Hartree−Fock (HF) and MP2 (Møller−Plesset second-order perturbation theory[23]) levels of theory using the Gaussian92[24] and Turbomole[25] program systems. The electronic structure of the molecules has been investigated with the natural bond orbital (NBO) partitioning scheme developed by Weinhold and co-workers.[26] The chemical shifts are predicted at the HF/II level of theory using geometries optimized at HF/II and MP2/II with the direct IGLO program.[27a] The localized orbitals necessary for the IGLO calculations were calculated using the method suggested by Foster and Boys.[27b]

Experimental Results

All members of the Me_nTiCl_{4-n} **1a−e** series were prepared from methylmagnesium iodide and $TiCl_4$ by comproportionation reaction between **1a** and **1e**. The compounds were transferred into NMR tubes under carefully controlled conditions, and the corresponding ^{1}H, ^{13}C, and ^{47,49}Ti NMR spectra were recorded. The results for **1a−e** are given in Table 1, the ^{47,49}Ti NMR spectra are shown in Figure 2, and the dependence of both the ^{47,49}Ti and ^{13}C NMR data on the number of methyl groups *n* is illustrated in Figure 3.

Table 1. Experimental Chemical Shifts of Methyltitanium Chlorides Me_nTiCl_{4-n} ($n = 0-4$)

	$TiCl_4$	$MeTiCl_3$[a]	Me_2TiCl_2[b]	Me_3TiCl[c]	Me_4Ti[d]
$\delta_{^1H}$		2.88	2.11	1.86	1.41
$\delta_{^{13}C}$		113.7	87.8	79.8	69.3
$\delta_{^{47,49}Ti}$	0	613	907	1188	1325
$^{1}J_{C,H}$ (Hz)		134	128	122	119
$\Delta\nu_{1/2}$ (Hz)	3	40	1200	2700	770

[a] In $CDCl_3$, 253 K. [b] In Et_2O/CH_2Cl_2, 233 K. [c] In Et_2O/CH_2Cl_2, 223 K. [d] In Et_2O, 233 K.

As can be immediately seen from Figures 2 and 3, **1d** is not a special exception, but its NMR data fit in homogeneously in the whole series. We observe a strong deshielding of the Ti chemical shift, as one replaces the chlorine atoms in $TiCl_4$ (**1e**) by methyl groups one by one. The first increment is, with about 600 ppm, rather large, the next two replacements cause a further deshielding by 300 ppm each, and the final step is only 150 ppm. As can be seen from Figure 2, for symmetry reasons, the quadrupolar ^{47,49}Ti signals at both ends of the series have the lowest half width. The ^{47,49}Ti NMR spectra of **1d** can only be obtained if the compound is prepared in the absence of ether and THF, although the ^{1}H and ^{13}C NMR spectra do not differ significantly in ether or CH_2Cl_2 solutions. The ^{1}H and ^{13}C chemical shifts move in the opposite direction; these signals are shielded on replacement of a chlorine by a methyl group. The first increment going from **1d** to **1c** for ^{13}C and ^{1}H is rather large, with −25 and −0.8 ppm, respectively, then the effects become smaller with roughly 10 ppm for carbon and 0.4 ppm for proton. The $^{1}J_{(C,H)}$ spin coupling constants similarily decrease on replacement of chlorine by methyl groups, thus nicely indicating the change in electronegativity.

For comparison, the data of the main group equivalents Me_nXCl_{4-n} with X = C (**2a−e**), Si (**3a−e**), Sn (**4a−e**), and Pb (**5a−e**) were collected. The data of **2a−e**,[28] **3a−e**,[29] and **4a−e**[30] could be taken from the literature, but they were redetermined by us in order to obtain a homogeneous data set in the same solvent. The lead organic compounds **5a−e** have been prepared by literature procedures. The data are given in Table 2 and are graphically shown for the the central atoms X in Figure 4 and for the methyl groups in Figure 5.

Chemical Shifts of the Central Atoms. The data in Figure 4 are normalized to the chemical shift difference $\delta_{X(max)} - \delta_{X(min)}$ of the different nuclei X, in order to show a common illustration of the chemical shift data, which cover a large range of absolute numbers. As can be seen from Figure 4, the signals of the central carbon atoms behave oppositely to those of the titanium compounds. Replacing chlorine by methyl groups yields a shielding effect. For the silicon, tin, and lead compounds the behavior is more complicated. Here one observes a typical U-shaped curve[31] with the minimum shielding seen for the Me_2XCl_2 compound. This point was discussed controversially in the literature. One model interprets the U curves as the maximum p-electron imbalance giving a maximum of paramagnetic contribution.[30] The U curves can be calculated by assuming different bond polarity parameters for the X−Cl and X−Me bonds. A different argument maintains that the relative contribution of electronegativity and $p_\pi - d_\pi$ back donation is best balanced for the Me_2XCl_2 compounds.[32] Experimentally, however, carbon and titanium form the two ends of this characteristic behavior, and neither display a U-shaped chemical

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(19) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (d) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(20) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(21) Huzinaga, S. *Approximate Atomic Wave Functions*; University of Alberta, Edmonton, Alberta.

(22) (a) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033. (b) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377.

(23) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

(24) GAUSSIAN 92, Revision C: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1992.

(25) TURBOMOLE: (a) Häser, M.; Ahlrichs, R. *J. Comput. Chem.* **1989**, *10*, 104. (b) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. M. *Chem. Phys. Lett.* **1989**, *162*, 165. (c) Horn, H.; Weiss, H.; Häser, M.; Ehrig, M.; Ahlrichs, R. *J. Comput. Chem.* **1991**, *12*, 1058. (d) Häser, M.; Almlöf, J.; Feyereisen, M. W. *Theor. Chim. Acta* **1991**, *79*, 115. (e) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571. (f) Häser, M.; Ahlrichs, R.; Baron, H. P.; Weis, P.; Horn, H. *Theor. Chim. Acta* **1992**, *83*, 455. (g) Haase, F.; Ahlrichs, R. *J. Comput. Chem.* **1993**, *14*, 907.

(26) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(27) (a) Meier, U.; van Wüllen, C.; Schindler, M. *J. Comput. Chem.* **1992**, *13*, 551. (b) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296, 303, 305.

(28) Kalinowski, H. O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; Wiley: Chichester 1988.

(29) Nguyen, D. C.; Chvalovsky, V.; Schraml, J.; Mägi, M.; Lippmaa, E. *Collect. Czech. Chem. Commun.* **1975**, *40*, 875.

(30) Radeglia, R.; Engelhardt, G. *Z. Chem.* **1974**, *14*, 319.

(31) Harris, R. K.; Kennedy, J. D.; McFarlane W. In *NMR and the Periodic Table*; Academic Press: London, 1978; p 309.

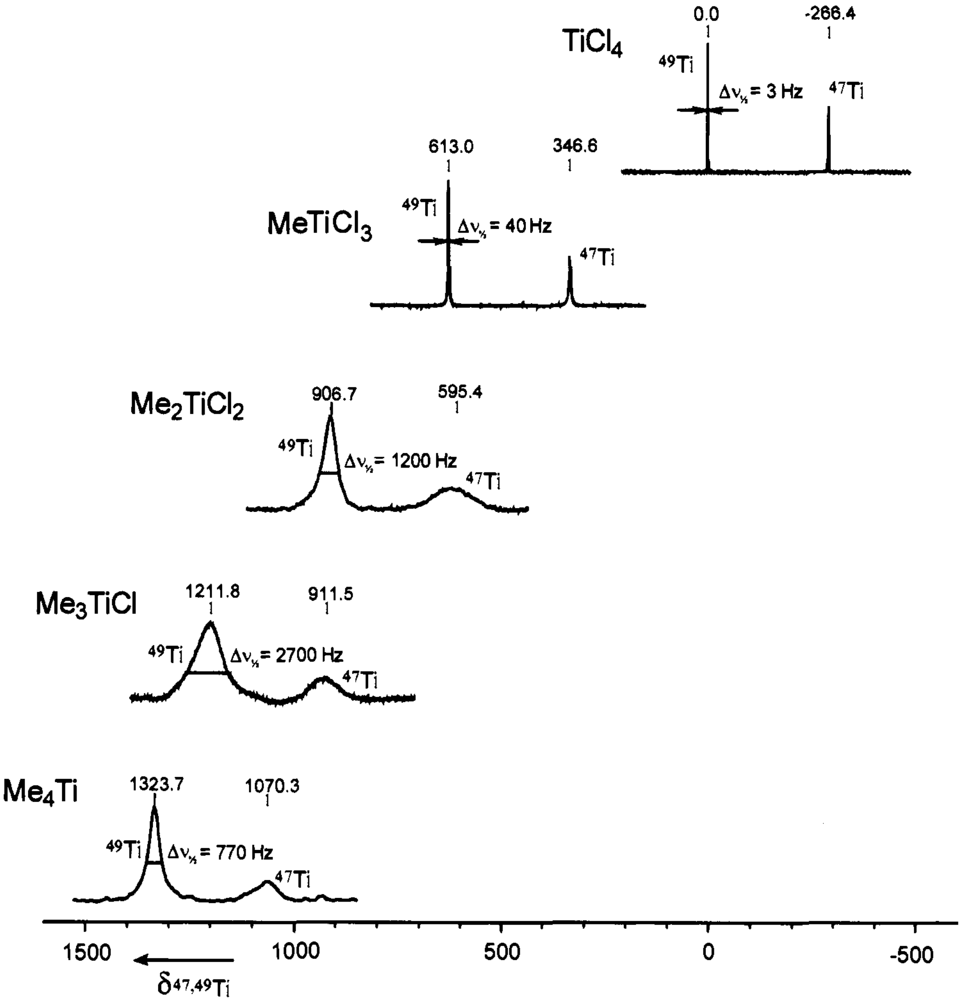

Figure 2. ^{47,49}Ti-NMR spectra of methyltitanium chlorides Me_4TiCl_{4-n}.

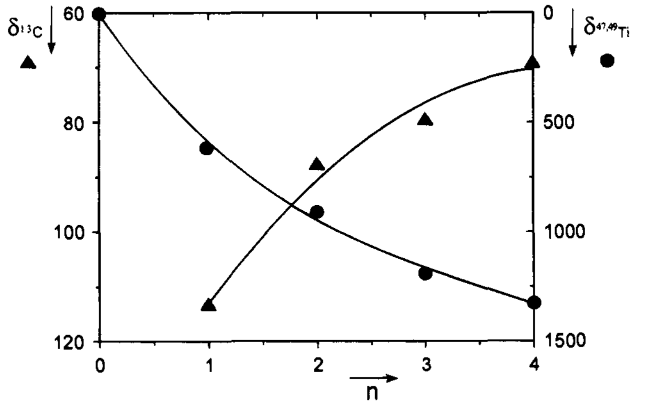

Figure 3. ^{13}C and ^{47,49}Ti chemical shifts of methyltitanium chlorides Me_4TiCl_{4-n} ($n = 0-4$).

shift curve. Within the second model, this might be explained by assuming that for carbon solely electronegativity and for titanium only $p_\pi-d_\pi$ back donation dominates through the whole series leading to the opposite sign of their chemical shift correlation.[32]

Chemical Shifts of the Methyl Groups. The ^{13}C NMR data for the methyl groups in compounds **1**–**5** are shown in Figure 5. Qualitatively, they all show a nearly parallel behavior—there are no sign differences between the main group elements and titanium. This is not unexpected, since the point of substituent change is two bonds away from the methyl groups. The chemical shift changes follow the decrease in electronegativity—changes in $p_\pi-d_\pi$ back donation would not reach the methyl groups.

Table 2. Experimental Chemical Shifts of Methyl Chlorides Me_nXCl_{4-n} ($n = 0-4$; X = C, Si, Sn, Pb)

X		n =				
		0	1	2	3	4
C	$\delta_{^1H}$		2.74	2.17	1.60	0.98
	$\delta_{^{13}C,Methyl}$		46.3	39.2	34.3	31.4
	$\delta_{^{13}C,Central}$	96.7	96.2	85.9	66.9	27.4
Si	$\delta_{^1H}$		1.08	0.74	0.36	0
	$\delta_{^{13}C}$		7.32	4.19	0.76	0
	$\delta_{^{29}Si}$	−21.4	9.8	29.7	28.6	0
Sn	$\delta_{^1H}$		1.66	1.19	0.59	0.05
	$\delta_{^{13}C}$		10.8	7.5	−0.8	−9.3
	$\delta_{^{119}Sn}$	−150.7	17.8	133.2	167.8	0
Pb	$\delta_{^1H}$			1.56	1.58	0.88
	$\delta_{^{13}C}$			20.8	19.0	−4.1
	$\delta_{^{207}Pb}$	−790.0		385.5	413.2	0

Interesting, however, is the large vertical gap in Figure 5 between the main group element compounds and the titanium series. Thus, in order to explain the very unusual ^{13}C chemical shift of $MeTiCl_3$ (**1d**), which was the original intent of this work, it is sufficient to explain the chemical shift value of $\delta = 69$ for Me_4Ti, compared with −9.3 to 31.4 ppm for all other Me_4X compounds, without taking the additional chemical shift effects of chlorine into account. Although titanium is less electronegative than carbon, the methyl groups in Me_4Ti are deshielded by some 40 ppm compared with Me_4C. A most important experimental fact, which should elucidate the problem further,

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[32] McFarlkane, W.; Maire, J. C.; Delmas, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1862. van den Berghe, E. V.; van der Kelen, G. P. *J. Organomet. Chem.* **1973**, *59*, 175.

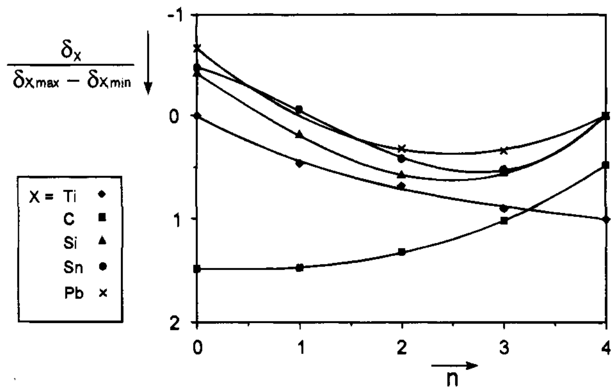

Figure 4. Relative chemical shifts $\delta_X/(\delta_{X,\max} - \delta_{X,\min})$ of central atoms X in methyl chlorides Me_4XCl_{4-n} (n = 0–4; X = C, Si, Sn, Pb, Ti).

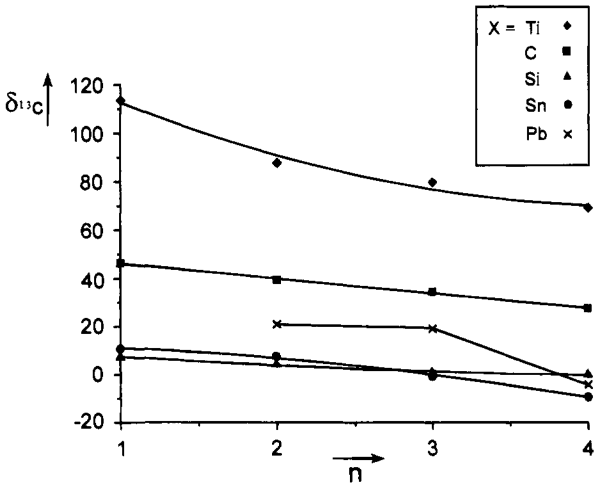

Figure 5. ^{13}C chemical shifts of methyl groups in methyl chlorides Me_4XCl_{4-n} (n = 0–4; X = C, Si, Sn, Pb, Ti).

is the ^{13}C chemical shift of Me_4Zr. Here we measure a quite normal chemical shift of δ = 33.2 and a C,H spin coupling constant of 111.7 Hz. Thus, the titanium values remain outstanding, compared with both the main group equivalents and the closest second row transition metal analogue. Since experimentally the problem could not be further clarified, we turned to extensive theoretical calculations.

Theoretical Results

Table 3 shows the optimized geometries at the MP2/II level of theory for Me_nXCl_{4-n} (X = C, Si, Ti) together with the experimental data. The optimized geometries at HF/I, HF/II, and (for the Ti compounds) MP2/I are given as supplementary material. The theoretical geometries predicted at the different levels of theory are very similar. The theoretical geometries are in good agreement with the experimental data (Table 3).

Table 3. Calculated and Experimental Geometries of Me_nXCl_{4-n} (n = 0–4; X = Ti, C, Si) [Bond Lengths in Å, Angles in deg]

structure	X	no.	method	X–Cl	X–C	C–X–Cl	C–X–C	Cl–X–Cl
Me_4Ti	Ti	**1a**	MP2/II		2.075		109.5	
Me_3TiCl	Ti	**1b**	MP2/II	2.223	2.062	113.0	105.7	
Me_2TiCl_2	Ti	**1c**	MP2/II	2.203	2.054	108.1	102.2	120.8
$MeTiCl_3$	Ti	**1d**	MP2/II	2.186	2.058	104.4		114.1
			exp.[a]	2.182	2.048	105.8		112.9
$TiCl_4$	Ti	**1e**	MP2/II	2.182				109.5
			exp.[b]	2.170				109.5
Me_4C	C	**2a**	MP2/II		1.520		109.5	
			exp.[c]		1.537		109.5	
Me_3CCl	C	**2b**	MP2/II	1.824	1.512	107.4	111.4	
			exp.[d]	1.828	1.528	107.1	111.7	
Me_2CCl_2	C	**2c**	MP2/II	1.801	1.504	108.7	113.5	108.4
			exp.[e]	1.799	1.523	108.9	113.0	108.3
$MeCCl_3$	C	**2d**	MP2/II	1.784	1.503	110.0		108.9
			exp.[f]	1.771	1.535	110.5		108.4
CCl_4	C	**2e**	MP2/II	1.773				109.5
			exp.[g]	1.765				109.5
Me_4Si	Si	**3a**	MP2/II		1.875		109.5	
			exp.[h]		1.875		109.5	
Me_3SiCl	Si	**3b**	MP2/II	2.085	1.861	107.3	111.6	
			exp.[i]	2.022	1.857	110.5		
Me_2SiCl_2	Si	**3c**	MP2/II	2.064	1.849	108.4	114.5	108.5
			exp.[j]	2.054	1.850	108.7	114.2	107.5
$MeSiCl_3$	Si	**3d**	MP2/II	2.045	1.838	110.3		108.7
			exp.[k]	2.026	1.848	110.3		108.6
$SiCl_4$	Si	**3e**	MP2/II	2.028				109.5
			exp.[l]	2.019				109.5

[a] Reference 33. [b] Reference 34. [c] Reference 35. [d] Reference 36. [e] Reference 37. [f] Reference 38. [g] Reference 39. [h] Reference 40. [i] Reference 41. [j] Reference 42. [k] Reference 43. [l] Reference 44.

Table 4 shows the calculated and experimental chemical shifts of the three series of compounds. The theoretical data shown in Table 4 are obtained at the HF/II level using the MP2/II optimized geometries. In order to study the influence of the geometry upon the predicted chemical shifts we also calculated the shifts at the HF/II level using the HF/II optimized geometries. The two different sets of calculated chemical shifts are very similar. The shifts calculated at HF/II//HF/II are given as supplementary material. In the following, the chemical shifts at HF/II calculated with the MP2/II optimized geometries are used for the discussion.

The theoretically predicted deshielding trend for the central carbon atom from Me_4C (**2a**) $\delta(C_c)$ = 24.2 to CCl_4 (**2e**) $\delta(C_c)$ = 118.2 is in qualitative agreement with the experimental observation (Table 4).

However, the experimental values do not increase as much as the theoretical data. In particular, the very small increase of the experimental values from $MeCCl_3$ (**2d**) $\delta(C_c)$ = 96.2 to CCl_4 (**2e**) $\delta(C_c)$ = 96.7 is in disagreement with the calculated values, which predict a much larger increase from $\delta(C_c)$ = 106.8 (**2d**) to $\delta(C_c)$ = 118.2 (**2e**). At present, we do not have an explanation for the difference between theory and experiment concerning the $\delta(C_c)$ values of **2d** and **2e**.[45] We want to point out, however, that the general trend of increasing $\delta(C_c)$ values for **2a** to **2e** is correctly predicted by the theoretical calculations.

The comparison of the experimental and theoretical chemical shifts for the Si series, Me_nSiCl_{4-n} (**3a–3e**), shows similar results as for the carbon analogues **2a–e**. The theoretically predicted relative chemical shifts δ for the ligand atoms

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(33) McKean, D. C.; McQillan, G. P.; Torto, I.; Bednell, N. C.; Downs, A. J.; Dickinson, J. M. *J. Mol. Struct.* **1991**, *247*, 73. See also ref 11.

(34) Callomon, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. *Structure Data on Free Polyatomic Molecules*; Springer Verlag: Berlin, 1976; Landolt Börnstein, New Series, Group II, Vol. 7.

(35) Bartell, L. S.; Bradford, W. F. *J. Mol. Struct.* **1977**, *37*, 113.

(36) Braun, W.; Günther, H.; Umbrecht, H.; Zeil, W. *Z. Phys. Chem. Frankfurt* **1974**, *93*, 247.

(37) Hirota, M.; Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1589.

(38) Iijima, T.; Wada, R. I. *J. Mol. Struct.* **1990**, *221*, 7.

(39) Bazhanov, V. I.; Ul'yanova, E. L. *J. Struct. Chem.* **1979**, *20*, 138. Bazhanov, V. I.; Ul'yanova, E. L. *Zh. Strukt. Khim.* **1979**, *20*, 165.

(40) Beagley, B.; Monaghan, J. J.; Hewitt, T. G. *J. Mol. Struct.* **1971**, 8, 401.

(41) Durig, J. R.; Carter, R. O.; Li, Y. S. *J. Mol. Spectrosc.* **1972**, *44*, 18.

(42) Belyakov, A. V.; Zavgorodnii, V. S.; Mastryukov, V. S. *J. Struct. Chem.* **1989**, *30*, 27. Belyakov, A. V.; Zavgorodnii, V. S.; Mastryukov, V. S. *Zh. Strukt. Khim.* **1989**, *30*, 34.

(43) Takeo, H.; Matsumura, C. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1633.

(44) Ryan, R. R.; Hedberg, K. *J. Chem. Phys.* **1969**, *50*, 4986.

(45) Calculation of the carbon chemical shift of CCl_4 with the GIAO-MP2 method[46] and a TZP basis set results in a δ value of 129.3 ppm relative to CH_4 for C, which agrees even less well with the experimental value.

Table 4. Calculated and Experimental Chemical Shifts (ppm) for X, ^{13}C, and ^1H in Me_nXCl_{4-n} (n = 0–4; X = Ti, C, Si)[b]

structure	X	no.	method	σ(X)	δ(X)	σ(C)	δ(C)	σ(H)	δ(H)
Me_4Ti	Ti	**1a**	HF/II//MP2/II	−1672.74	1251	130.14	68.3	30.48	1.38
			exp.		1325		69.3		1.41
Me_3TiCl	Ti	**1b**	HF/II//MP2/II	−1473.26	1052	120.41	78.0	30.11[a]	1.75[a]
			exp.		1188		79.8		1.86
Me_2TiCl_2	Ti	**1c**	HF/II//MP2/II	−1252.49	831	104.63	93.8	29.71[a]	2.15[a]
			exp.		907		87.8		2.11
$MeTiCl_3$	Ti	**1d**	HF/II//MP2/II	−964.63	543	81.81	116.6	29.14	2.72
			exp.		613		113.7		2.88
$TiCl_4$	Ti	**1e**	HF/II//MP2/II	−421.37	0				
			exp.		0				
Me_4C	C	**2a**	HF/II//MP2/II	174.22	24.2	166.09	32.3	30.90	0.96
			exp.		27.4		31.4		0.98
Me_3CCl	C	**2b**	HF/II//MP2/II	134.49	63.9	163.26	35.2	30.33[a]	1.53[a]
			exp		66.9		34.3		1.60
Me_2CCl_2	C	**2c**	HF/II//MP2/II	109.01	89.4	159.08	39.3	29.89[a]	1.97[a]
			exp.		85.9		39.2		2.17
$MeCCl_3$	C	**2d**	HF/II//MP2/II	91.65	106.8	153.61	44.8	29.55	2.31
			exp		96.2		46.3		2.74
CCl_4	C	**2e**	HF/II//MP2/II	80.21	118.2				
			exp		96.7				
Me_4Si	Si	**3a**	HF/II//MP2/II	379.43	0	198.42	0	31.86	0
			exp.		0		0		0
Me_3SiCl	Si	**3b**	HF/II//MP2/II	348.68	30.8	195.39	3.0	31.53[a]	0.33[a]
			exp.		28.6		0.8		0.36
Me_2SiCl_2	Si	**3c**	HF/II//MP2/II	341.74	37.7	192.38	6.0	31.24[a]	0.62[a]
			exp.		29.7		4.2		0.74
$MeSiCl_3$	Si	**3d**	HF/II//MP2/II	352.83	26.6	189.61	8.8	31.00	0.86
			exp.		9.8		7.3		1.08
$SiCl_4$	Si	**3e**	HF/II//MP2/II	372.96	6.5				
			exp.		−21.4				

[a] Average values for all hydrogens. [b] In the case of X = C, X = central carbon and C = ligand carbon.

Table 5. Calculated and Experimental Chemical Shifts (ppm) for X (X = ^{13}C, ^{29}Si, $^{47,49}Ti$) Relative to δ(Me_4X) = 0

structure	method	δ(X=C)	δ(X=Si)	δ(X=Ti)
Me_4X	HF/II//HF/II	0	0	0
	HF/II//MP2/II	0	0	0
exp.		0	0	0
Me_3XCl	HF/II//HF/II	40.8	31.6	−203
	HF/II//MP2/II	39.7	30.8	−199
exp.		39.5	28.6	−137
Me_2XCl_2	HF/II//HF/II	63.0	38.4	−412
	HF/II//MP2/II	65.2	37.7	−420
exp.		58.5	29.7	−418
$MeXCl_3$	HF/II//HF/II	78.4	26.9	−678
	HF/II//MP2/II	82.6	26.6	−708
exp.		68.8	9.8	−712
XCl_4	HF/II//HF/II	88.6	6.6	−1265
	HF/II//MP2/II	94.0	6.5	−1251
exp.		69.3	−21.4	−1325

hydrogen and carbon are in good agreement with experiment. The calculated δ(Si) values show the same U-shaped trend (Table 4) as the experimental values. The absolute numbers are somewhat different, however. In order to demonstrate that the difference between theoretical and experimental values for the chemical shift of the central atom in the series Me_nCCl_{4-n} and Me_nSiCl_{4-n} is very similar, we show in Table 5 the δ values of the central atoms using Me_4X (X = C, Si, Ti) as a standard (δ(X) = 0). It is obvious that the difference between theory and experiment is nearly the same for the corresponding carbon and silicon compounds.

The trends of the theoretical and experimental chemical shifts of the central atom X in the series Me_nXCl_{4-n} for X = C and Si are shown in Figures 6 and 7. Note that the theoretical and experimental δ(X) values for Me_4X have been arbitrarily set equal to zero. It is obvious that the calculated σ(X) values indicate stronger deshielding for CCl_4 and $SiCl_4$ than experimentally observed.

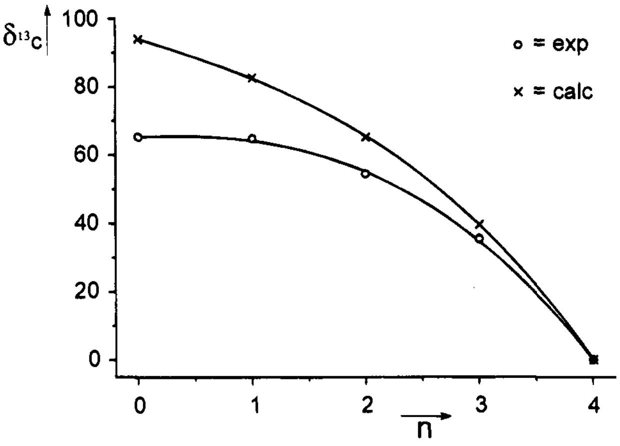

Figure 6. Trend of the theoretical and experimental chemical shift of the central atom C in the series Me_nCCl_{4-n}.

The theoretical and experimental values for the chemical shifts of the Ti compounds Me_nTiCl_{4-n} (**1a**–**e**; Table 4) show a good agreement between theory and experiment for the δ values of the hydrogen and carbon atoms. Theory and experiment agree that there is a strong *shielding* trend for the central Ti atom from Me_4Ti (**1a**) to $TiCl_4$ (**1e**). The differences between the calculated and experimental δ(Ti) absolute values are larger than in the case of the C and Si compounds. This becomes obvious when the theoretical and observed δ(Ti) values are compared using Me_4Ti as a standard (Table 5). However, the overall trend toward higher shielding from Me_4Ti to $TiCl_4$ is very well reproduced at the HF/II level of theory. Figure 8 shows good agreement between the theoretical and experimental data. The calculated σ(Ti) value of $TiCl_4$ indicates less shielding than experimentally observed, but the difference between theory and experiment is not very large.

Table 6. Contributions of the Localized Valence Orbitals to σ_C(Central) in Me_nCCl_{4-n} (n = 0−4)

structure	Me_4C	Me_3CCl	Me_2CCl_2	$MeCCl_3$	CCl_4
C−Cl dia		6.53 × 1	7.39 × 2	8.22 × 3	8.99 × 4
para		−9.28 × 1	−20.87 × 2	−30.13 × 3	−37.25 × 4
Σ		−2.74 × 1	−13.48 × 2	−21.91 × 3	−28.26 × 4
C−C dia	11.95 × 10^4	12.67 × 3	13.37 × 2	14.01 × 1	
para	−18.76 × 10^4	−33.97 × 3	−44.77 × 2	−52.25 × 1	
Σ	−6.81 × 10^4	−21.30 × 3	−31.40 × 2	−38.25 × 1	
C−H Σ	<0.1	<0.3	<0.7	<0.7	
LP Cl Σ		<1.0	<1.0	<1.4	<0.7
$\Delta(\sigma)_{C-C,C-Cl}$[a]		−39.40	−23.12	−14.22	−9.06
ΣC−Cl/C−C	−27.24	−66.64	−89.76	−103.98	−113.04
Σval	−26.66	−66.45	−91.99	−109.33	−120.81
core C	200.88	200.92	200.95	200.99	201.02
dia Σ	253.71	251.71	250.00	248.44	246.91
para Σ	−79.49	−117.24	−141.04	−156.78	−166.70
σ_{tot}	174.22	134.47	108.96	91.66	80.21

[a] $\Delta(\sigma)_{C-C,C-Cl}$ gives the sum of the differences, which arise only from the σ_{C-C} and σ_{C-Cl} contributions between consecutive compounds Me_nCCl_{4-n} from n = 4 to 0 to $\sigma(C)_C$. Average values for chemically equivalent nuclei are given.

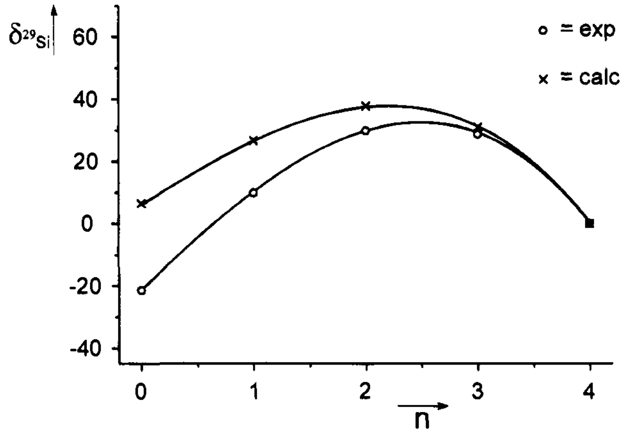

Figure 7. Trend of the theoretical and experimental chemical shift of the central atom Si in the series Me_nSiCl_{4-n}.

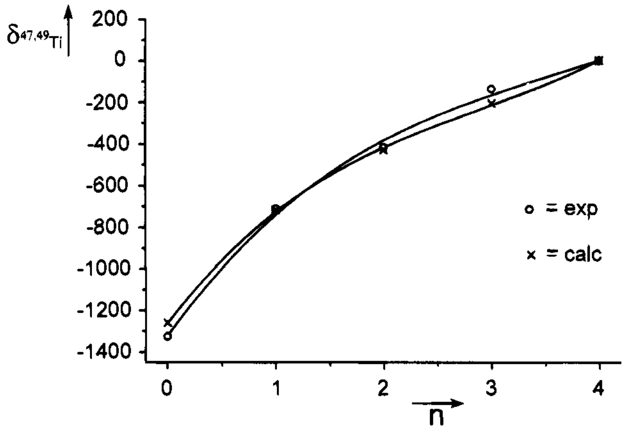

Figure 8. Trend of the theoretical and experimental chemical shift of the central atom Ti in the series Me_nTiCl_{4-n}.

Although there are some differences between the theoretical and experimental values for the chemical shifts of the central atoms, theory and experiment agree that the three series of Me_nXCl_{4-n} compounds exhibit different trends of the chemical shift from n = 0 to 4. We analyzed the calculated chemical shifts of the central atom in the series Me_nXCl_{4-n} in order to explain the different trends for X = C, Si, Ti. The calculated absolute values of the chemical shieldings in the IGLO method are the sum of the orbital contributions to σ(X). The contributions of the localized valence orbitals to the chemical shifts of the central atoms are shown in Tables 6−8. The contributions of the core orbitals are nearly constant, and may be neglected for a discussion of the trend of the σ(X) values.

Table 6 shows that the dominant contributions to the chemical shieldings $\sigma(C_c)$ of the compounds Me_nCCl_{4-n} come from the C−C and C−Cl localized bond orbitals. The magnitude of the deshielding contribution by the C−Cl and C−C bonds increases from Me_4C (**2a**) to CCl_4 (**2e**). The C−C bonds contribute more strongly to the $\sigma(C_c)$ values than do the C−Cl bonds in a given molecule, but the decreasing contribution when C−Me is substituted by C−Cl from n = 4 to 0 is compensated for by the increase in the single contributions. This yields a steady deshielding trend from Me_4C to CCl_4. The dominant influence of the C−C and C−Cl contributions upon the trend of the ^{13}C chemical shift of the central carbon atom becomes obvious by looking at the calculated $\Delta(\sigma)_{C-C,C-Cl}$ values shown in Table 6. $\Delta(\sigma)_{C-C,C-Cl}$ gives the sum of the differences, which arise *only* from the σ_{C-C} and σ_{C-Cl} contributions between consecutive compounds Me_nCCl_{4-n} from n = 4 to 0 to $\sigma(C)_C$. The $\Delta(\sigma)_{C-C,C-Cl}$ values are always negative, which indicates a continuous deshielding (Table 6). Note that the absolute values of $\Delta(\sigma)_{C-C,C-Cl}$ decrease from **2a** to **2e**.

Table 7 shows the orbital contributions to σ(Si) in Me_nSiCl_{4-n}. As for the carbon analogues, the only significant contributions to the change in σ(Si) come from the localized orbitals of the Si−C and Si−Cl bonds. It should be noted, however, that the contributions by the core orbitals to the ^{29}Si chemical shift are not transferable as they are in the case of the carbon compounds (Table 6), where they are practically constant. The sum of the two contributions $\sigma(Si)_{Si-C}$ and $\sigma(Si)_{Si-Cl}$ shows the same U trend as the total values for σ(Si) (Table 7). The $\sigma(Si)_{Si-C}$ and $\sigma(Si)_{Si-Cl}$ contributions are deshielding; the absolute values become stronger in the series Me_nSiCl_{4-n} from n = 4 to 0. The Si−C bonds deshield more than the Si−Cl bonds in a given molecule. What then is the reason that the Si compounds have a U trend while the carbon atoms exhibit a continuously deshielding trend from n = 4 to 0? A first hint is given by the *relative magnitudes* of the X−C and X−Cl bonds to σ(X). In the case of Si, the decrease in the deshielding effect when one Si−C bond is substituted by Si−Cl is compensated for by the increase of $\sigma(Si)_{Si-C}$ of the remaining Si−C bonds only for Me_4Si (**3a**) and Me_3SiCl (**3b**) but not for Me_2SiCl_2 (**3c**). This is shown by the calculated $\Delta(\sigma)_{Si-C,Si-Cl}$ values given in Table 7. The consecutive values for the sum of the differences, which arise only from the σ_{Si-C} and σ_{Si-Cl} contributions to σ(Si), show the same U-shaped trend as the experimental and theoretical σ(Si) values. It is the relative magnitude of the contributions by the X−C and X−Cl bonds to the chemical shift σ(X) of the compounds Me_nCCl_{4-n} and Me_nSiCl_{4-n} which determines the

Table 7. Contributions of the Localized Valence Orbitals to σ_{Si} in Me_nSiCl_{4-n} ($n = 0-4$)

structure	Me_4Si	Me_3SiCl	Me_2SiCl_2	$MeSiCl_3$	$SiCl_4$
Si−Cl dia		1.69 × 1	1.88 × 2	2.10 × 3	2.34 × 4
para		−58.82 × 1	−74.83 × 2	−86.65 × 3	−94.68 × 4
Σ		−57.13 × 1	−72.95 × 2	−84.55 × 3	−92.34 × 4
Si−C dia	3.71 × 4	3.99 × 3	4.30 × 2	4.65 × 1	
para	−88.67 × 4	−109.12 × 3	−123.80 × 2	−129.18 × 1	
Σ	−84.96 × 4	−105.13 × 3	−119.50 × 2	−124.53 × 1	
C−H Σ	<0.3	<0.3	<0.6	<0.5	
LP Cl Σ		<0.7	< 0.8	<0.8	<0.6
$\Delta(\sigma)_{Si-C,Si-Cl}$[a]		−32.68	−12.38	+6.72	+8.82
Σ Si−Cl/Si−C	−339.84	−372.52	−384.90	−378.18	−369.36
Σval	−343.17	−374.31	−385.19	−376.75	−363.73
core Si	722.56	722.99	726.99	729.45	736.60
dia Σ	767.08	766.92	766.76	766.53	766.14
para Σ	−387.69	−418.24	−424.96	−413.83	−393.28
σ_{tot}	379.39	348.68	341.80	352.70	372.87

[a] $\Delta(\sigma)_{Si-C,Si-Cl}$ gives the sum of the differences, which arise only from the σ_{Si-C} and σ_{Si-Cl} contributions between consecutive compounds Me_nSiCl_{4-n} from $n = 4$ to 0 to σ(Si). Average values for chemically equivalent nuclei are given.

Table 8. Contributions of the Localized Valence Orbitals to σ_{Ti} in Me_nTiCl_{4-n} ($n = 0-4$)

structure	Me_4Ti	Me_3TiCl	Me_2TiCl_2	$MeTiCl_3$	$TiCl_4$
Ti−Cl dia		4.23 × 1	4.70 × 2	5.32 × 3	6.14 × 4
para		−386.20 × 1	−399.59 × 2	−426.64 × 3	−487.09 × 4
Σ		−381.97 × 1	−394.89 × 2	−421.32 × 3	−480.95 × 4
Ti−C dia	9.04 × 4	10.15 × 3	11.65 × 2	13.61 × 1	
para	−882.90 × 4	−980.58 × 3	−1135.34 × 2	−1392.00 × 1	
Σ	−873.86 × 4	−970.42 × 3	−1123.69 × 2	−1378.39 × 1	
C−H Σ	−7.87 × 12	−10.42 × 9	−14.00 × 6	−19.24 × 3	
LP Cl Σ 1012		−12.82 × 3	−17.45 × 6	−24.58 × 9	−35.77 × 12
$\Delta(\sigma)_{Ti-C,Ti-Cl}$[a]		+202.21	+256.07	+394.81	+718.55
ΣTi−Cl/Ti−C	−3495.44	−3293.23	−3037.16	−2642.35	−1923.80
Σval	−3589.81	−3425.49	−3225.81	−2921.26	−2352.95
core Ti	1917.07	1953.11	1973.29	1956.35	1931.85
dia Σ	1422.79	1424.10	1424.77	1425.18	1424.33
para Σ	−3095.53	−2896.49	−2677.29	−2390.09	−1845.43
σ_{tot}	−1672.74	−1472.38	−1252.52	−964.91	−421.10

[a] $\Delta(\sigma)_{Ti-C,Ti-Cl}$ gives the sum of the differences, which arise only from the σ_{Ti-C} and σ_{Ti-Cl} contributions between consecutive compounds Me_nTiCl_{4-n} from $n = 4$ to 0 to σ(Ti). Average values for chemically equivalent nuclei are given.

trend from $n = 4$ to 0. The contributions by the C−H bonds and Cl lone pairs (π-bond contributions) are negligible.

Now we turn to the Ti compounds **1a**−**e**. Table 8 shows the calculated contributions of the valence localized orbitals to the chemical shift $\sigma(^{47,49}Ti)$. The dominant contributions come from the Ti−C and Ti−Cl bonds, while the contributions of the C−H bonds and the Cl lone-pair electrons (π-bond contributions) are much smaller, and may be neglected for a discussion of the trend of the σ(Ti) values. The Ti−C and Ti−Cl bonds have large negative σ values, which indicate deshielding contributions. Note that the absolute values of the deshielding contributions by the Ti−C and Ti−Cl bonds are much higher than the carbon and silicon analogues (Tables 6 and 7). The magnitude of the deshielding contributions increases steadily from Me_4Ti to $TiCl_4$ (Table 8). However, the overall trend of σ(Ti) is toward more shielding, which is dictated by the relative magnitude of the $\sigma(Ti)_{Ti-C}$ and $\sigma(Ti)_{Ti-Cl}$ contributions. The latter are significantly lower than the former, which means that the substitution of a methyl group by chlorine in the series Me_nTiCl_{4-n} has a shielding effect. This becomes obvious when the $\Delta(\sigma)_{Ti-C,Ti-Cl}$ values are calculated, which are also shown in Table 8. The consecutive values for the sum of the differences, which arise only from the σ_{Ti-C} and σ_{Ti-Cl} contributions to σ(Ti), show a clear trend toward higher shielding from Me_4Ti to $TiCl_4$.

The contributions by the core orbitals are not constant, but the differences are negligible relative to the changes calculated for the Ti−C and Ti−Cl bonds. The large differences between the contributions by the Ti−C and Ti−Cl bonds to the chemical shifts explain the somewhat paradoxical result that Ti becomes more shielded from Me_4Ti to $TiCl_4$, although the Ti−C and Ti−Cl bonds become more deshielding.

The ^{13}C chemical shifts of the compounds Me_nTiCl_{4-n} are also determined by the contributions of the LMOs of the respective bond orbitals, i.e. the Ti−C and C−H bonds. Table 9 shows that the most important contributions arise from the Ti−C bond orbitals, which are strongly negative.

So far we have shown that the trend in the chemical shifts is dominated by the contributions of the respective σ-type bond orbitals. There is clearly a correlation between the bond orbital contributions and the total chemical shifts. However, the question why the contributions from the individual LMO's yield qualitatively different chemical shifts in particular for the Ti compounds has not been answered yet. In order to give a better understanding of the magnetic properties of the compounds, we analyzed the diamagnetic and paramagnetic contributions to the chemical shifts calculated by the IGLO method. Our interpretation of the chemical shifts in terms of the contributions given by the IGLO results is similar to the analysis presented by Kutzelnigg et al.[16b] The calculated diamagnetic and paramagnetic parts of the chemical shifts are shown in Tables 6−8.

For the three series of compounds Me_nXCl_{4-n} (X = C, Si, Ti) it holds that the diamagnetic contributions are rather constant.

Table 9. Contributions of the Localized Valence Orbitals to σ_C in Me_nTiCl_{4-n} ($n = 1-4$)[a]

structure	Me_4Ti	Me_3TiCl	Me_2TiCl_2	$MeTiCl_3$
Ti−C dia	14.96	14.12	12.93	11.28
para	−62.53	−66.05	−70.82	−75.37
Σ	−47.57	−51.93	−57.90	−64.09
C−H dia	12.82	12.94	13.08	13.23
para	−19.91	−22.34	−26.30	−32.40
Σ	− 7.09	−9.40	−13.22	−19.17
Ti−C′ Σ	−1.08 × 3	−0.76 × 2	−0.17 × 1	
Ti−Cl Σ		−0.65 × 1	−0.54 × 2	−0.30 × 3
ΣTi−C/C−H	−68.84	−80.13	−97.56	−121.60
Σval	−70.72	−80.46	−96.24	−119.03
core C	200.86	200.86	200.86	200.87
dia Σ	254.75	254.45	253.87	252.81
para Σ	−124.61	−134.05	−149.25	−170.97
σ_{tot}	130.14	120.40	104.62	81.84

[a] Average values for chemically equivalent nuclei are given.

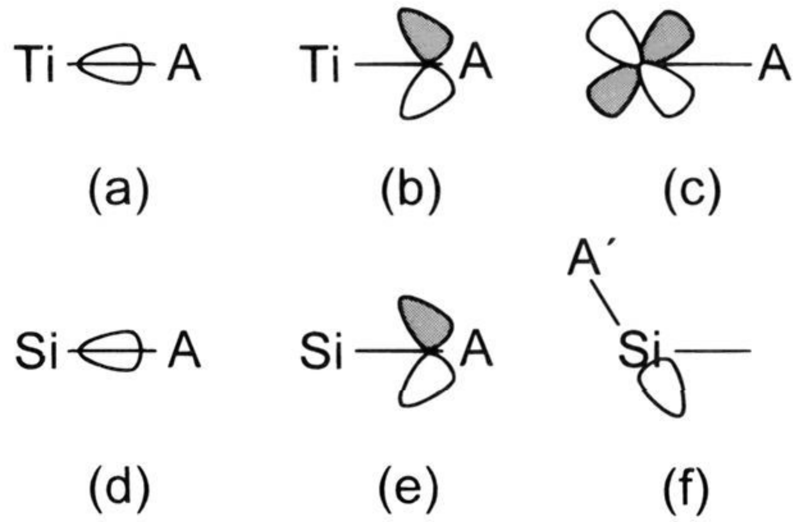

Figure 9. Explanation of the occurrence of a paramagnetic current in Me_nTiCl_{4-n} and Me_nSiCl_{4-n}: (a) Ti−A bond orbital (mainly sp^3 at A = C, Cl); (b) action of the off-center angular momentum operator through Ti upon the Ti−A bond orbital; (c) empty d-orbital at Ti; (d) Si−A bond orbital (mainly sp^3 at A = C, Cl); (e) action of the off-center angular momentum operator through Si upon the Si−A bond orbital; (f) empty Si−A′ antibonding orbital (mainly sp^3 at Si).

It is the paramagnetic part of the chemical shift which determines the trend. This holds for the total chemical shifts as well as for the dominant contributions by the bond orbitals (Tables 6−8). That is, the paramagnetic contribution to the chemical shift of the central atom increases for the carbon compounds from Me_4C to CCl_4, it shows a U turn from Me_4Si to $SiCl_4$, while it strongly decreases from Me_4Ti to $TiCl_4$. The paramagnetic contributions also determine the trend of the ^{13}C chemical shift in the series Me_nTiCl_{4-n} (Table 9).

The calculations support the suggestion by Radeglia and Engelhardt[30] that the paramagnetic contribution to the ^{29}Si chemical shifts of Me_nSiCl_{4-n} has a maximum for $n = 2$. The paramagnetic part of the $^{47,49}Ti$ chemical shift is particularly large, and it is larger than the diamagnetic contribution (Table 8). Paramagnetic contributions can only arise if there is a significant deviation of the LMO's from spherical symmetry. This may be caused by the shape of the LMO and/or by action of an off-center angular momentum operator upon the LMO. The localized orbitals of the Me_nTiCl_{4-n} compounds have local σ symmetry. However, action of an off-center angular momentum operator in field direction may change a σ to a π-type MO.[16b] This is illustrated for the Ti−A (A = C, Cl) σ-type bond orbitals in Figures 9a and 9b. As shown below, the Ti−C and Ti−Cl bonds are polarized toward carbon and chlorine, respectively. The effect of the off-center angular momentum operator of Ti through the Ti nucleus upon the Ti−A bond leads to a π-orbital which has a large overlap with a low-lying unoccupied d-orbital at Ti (Figure 9c). This interaction leads to a strong paramagnetic current as demonstrated by the dominantly paramagnetic contributions of the Ti−C and Ti−Cl bonds to the chemical shifts (Table 8).

The presence of a low-lying empty orbital with the proper symmetry, which can interact with the occupied Ti−C and Ti−Cl bond orbitals through the off-center angular momentum operator, explains the strong paramagnetic contributions to the $^{47,49}Ti$ chemical shifts.

The Ti−C bond is shorter than the Ti−Cl bond, which leads to a larger overlap of the interacting orbitals (Figure 9). The contributions are also larger for Me_4Ti than for $TiCl_4$, because the orbital describing the Ti−C bond is higher in energy than the Ti−Cl bond orbital. It has been shown that the matrix elements of the paramagnetic part of the orbital contribution can be approximated by an expression which has the energy difference between the occupied orbital a and the unoccupied orbital b $\epsilon_a - \epsilon_b$ as denominator.[16b] Although localized orbitals do not have an energy eigenvalue, it is possible to define an energy value associated with an LMO which can be used in the expression for the paramagnetic contribution.[16b] The trend of the ^{13}C chemical shifts toward more shielding in the series Me_nTi_{4-n} is also caused by the paramagnetic contributions (Table 9). It follows that the unusual ^{13}C and $^{47,49}Ti$ chemical shifts are dominated by paramagnetic contributions. These contributions arise from the action of an off-center angular momentum operator upon the σ-type LMO's yielding a π-type MO, which has a large overlap with a low-lying empty d(Ti) orbital. The paramagnetic contributions to the chemical shifts of the carbon and silicon compounds are much lower than those for the Ti compounds, because the main-group elements do not have low-lying empty d orbitals. The smallest paramagnetic contributions to the ^{29}Si shifts are calculated for Me_4Si and $SiCl_4$, which have nearly the same size (Table 7). The largest paramagnetic contributions are calculated for Me_2SiCl_2. Figures 9d−f show that action of the angular momentum operator of Si upon the Si−A bond results in an orbital that can interact with an unoccupied antibonding orbital of the Si−A′ bond. The Si−C bonding orbital is higher in energy than the Si−Cl bonding MO, but the Si−Cl antibonding orbital is lower in energy than the Si−C antibonding orbital. These two trends apparently cancel for Me_4Si and $SiCl_4$. In case of Me_2SiCl_2 there are two relatively high lying Si−C bond orbitals and two relatively low lying Si−Cl empty orbitals. This yields a maximum for the paramagnetic contributions to the ^{29}Si chemical shifts of the Me_nSiCl_{4-n} compounds. In the case of carbon, the nearly unpolar C−C bonds have very high lying unoccupied orbitals. Therefore, the shift of the paramagnetic contributions is dominated by the number of unoccupied C−Cl antibonding orbitals, which has a maximum for CCl_4.

We want to point out that the interpretation of the trend in the chemical shifts in terms of orbital contributions presented here is based upon the IGLO method. One should be careful when comparisons of results are made using different methods. It is interesting to note, however, that in a recent work by Tossell[47] about the NMR spectra of SiH_nCl_{4-n} using conventional coupled Hartree−Fock calculations as well as the RPA LORG[48] method, the interpretation of the paramagnetic contributions to the ^{29}Si chemical shifts is very similar as presented here.[47] This author found for SiH_3Cl large contributions from the predominant Cl 3p π-type HOMO with significant Si−H σ^* contributions, which interacts with the Si−Cl σ^* LUMO.[47] A difference is that the LORG calculations of SiH_nCl_{4-n} gave

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(46) (a) Gauss, J. *Chem. Phys. Lett.* **1992**, *191*, 614. (b) Gauss, J. *J. Chem. Phys.* **1993**, *99*, 3629.

(47) Tossell, J. A. *Chem. Phys. Lett.* **1994**, *219*, 65.

(48) Hansen, A. E.; Bouman, T. D. *J. Chem. Phys.* **1985**, *82*, 5033.

Table 10. NBO Analysis of Me_nXCl_{4-n} (X = C, Si, Ti; n = 0–4) at HF/I//HF/I[b]

	X–Cl[a]				X–Me[a]			
	% X	% s(X)	% p(X)	% d(X)	% X	% s(X)	% p(X)	% d(M)
Me_4C					50.6	25.0	74.9	0.1
Me_3CCl	41.9	15.5	84.2	0.4	51.8	28.2	71.6	0.1
Me_2CCl_2	45.5	18.7	80.9	0.4	53.0	31.4	68.5	0.1
$MeCCl_3$	48.3	21.9	77.7	0.4	54.0	34.4	65.5	0.1
CCl_4	50.6	25.0	74.6	0.4				
Me_4Si					24.7	25.0	73.2	1.8
Me_3SiCl	21.3	18.9	78.0	3.1	25.4	27.0	71.1	1.9
Me_2SiCl_2	22.4	20.7	76.0	3.3	26.2	29.3	68.8	2.0
$MeSiCl_3$	23.7	22.8	73.8	3.4	27.3	31.7	66.3	2.0
$SiCl_4$	25.0	25.0	71.5	3.5				
Me_4Ti					24.4	25.0	0.3	74.7
Me_3TiCl	15.5	28.7	0.3	71.0	24.8	23.6	0.4	76.0
Me_2TiCl_2	16.6	27.1	0.3	72.6	29.5	22.7	0.1	77.2
$MeTiCl_3$	18.1	26.0	0.3	73.7	31.2	21.9	0.1	78.0
$TiCl_4$	19.1	25.0	0.3	74.7				

[a] % X gives the polarization of the X–Cl and X–Me bond, respectively. % s(X), % p(X), and % d(X) give the hybridization at X for the respective bonds. [b] For technical reasons, the NBO analysis of the Ti compounds was carried out at MP2/I//MP2/I.

large variations of the diamagnetic contributions for the different compounds.[47]

The *magnetic* interactions of the empty orbitals (d(Ti)-orbital in the case of the Ti compounds) with the orbitals resulting from the action of the off-center angular momentum operator upon the bond LMO's should not be confused with the chemical model of a partial p(π)–d(π) double bond. The large paramagnetic contributions to the ^{47,49}Ti chemical shifts of the molecules Me_nTiCl_{4-n} do *not* necessarily indicate partial Ti–C or Ti–Cl double bond character.

In order to investigate the nature of the chemical bonds, we analyzed the X–C and X–Cl bonds of the three series Me_4XCl_{4-n} using the NBO[26] partitioning scheme. The results are shown in Table 10. The polarization and hybridization of the C–Cl and C–Me bonds show the expected trends. The C–Cl bonds are more polarized toward chlorine, while the C–Me bonds are more polarized toward the central carbon atoms. The C–Me bonds always have a higher percent s character at the central carbon atom than the C–Cl bonds, which is in agreement with Bent's rule.[49] The trend of the silicon compounds Me_4SiCl_{4-n} is similar to that of the carbon analogues. The Si–C and Si–Cl bonds are more polarized toward the ligand atoms than the C–Me and C–Cl bonds, because silicon is less electronegative than carbon.

Significant differences are calculated for the Ti compounds. The most important difference is that the Ti–C and Ti–Cl bonds at Ti are sd hybridized rather than sp hybridized. The contribution by the d orbitals is rather high and comparable in magnitude to the p-orbital contributions at C and Si in the C–Me, C–Cl, Si–C, and Si–Cl bonds (Table 10). This result is not trivial. It has recently been suggested[50] that the major bonding contribution in high-valent (first row) transition metal compounds arises from interactions between the ligands and the metal 4s orbitals. The 3d orbitals should play only a minor role because of their poor overlap possibilities, and the 4p orbitals should have only a small role because of their poor energy match with the ligand functions.[50] The results in Table 10 do not support this view. The Ti–C and Ti–Cl bonds at Ti show essentially sd^3 hybridization. We want to point out that the percent s character at Ti in the Ti–C bonds is always *higher* than that in the Ti–Cl bonds, and that the percent s(Ti) character in both bonds *decreases* in Me_4TiCl_{4-n} from n = 4 to 0, which appears to be in conflict with Bent's rule. Bent's rule states that the percent s character at atom A in a bond A–X decreases with higher electronegativity of X.[49] This rule, however, was formulated for sp-hybridized molecules. It has been shown that Bent's rule is valid also for sd hybridization if the relative energies of the s and d orbitals are considered.[51]

Conclusion

The analysis of the theoretically predicted chemical shifts for the compounds Me_nXCl_{4-n} can be summarized as follows. The trend of the chemical shifts of the carbon, silicon, and titanium analogues is dominated by the contributions of the X–C and X–Cl bonds to σ(X). The $\sigma(X)_{X-C}$ and $\sigma(X)_{X-Cl}$ contributions are deshielding for all compounds, and the magnitude of the deshielding increases for Me_nXCl_{4-n} from n = 4 to 0. The contributions by $\sigma(X)_{X-C}$ are always larger than those by $\sigma(X)_{X-Cl}$. However, the relative magnitude of $\sigma(X)_{X-C}$ and $\sigma(X)_{X-Cl}$ is different for X = C, Si, Ti. This yields a continuously deshielding trend for the carbon molecules, a U trend for the Si compounds, and a trend toward more shielding for the Ti molecules from n = 4 to 0.

The partitioning of the chemical shift into the diamagnetic and paramagnetic parts shows that the trends are always dominated by the latter contributions. The paramagnetic contributions are particularly large for the Ti compounds, because Ti has low-lying empty d orbitals. Action of the off-center angular momentum operator of Ti through the Ti nucleus upon the σ-type Ti bond orbitals leads to π-type orbitals, which can strongly overlap with a low-lying unoccupied d orbital of proper symmetry at Ti. The paramagnetic contributions are much lower for the Si and C compounds, because there are no low-lying empty orbitals available. The unusual ^{13}C chemical shifts of the methyl carbon atoms in Me_nTiCl_{4-n} can be explained in the same fashion. The low-lying empty d orbital of Ti overlaps strongly with the π component of the Ti–C bond, which gives a large paramagnetic contribution to the ^{13}C chemical shift.

The analysis of the chemical bonds using the NBO partitioning scheme shows that the polarization and sp^n hybridization of the C–CH_3, C–Cl, Si–CH_3, and Si–Cl bonds show the expected trends. The Ti–CH_3 and Ti–Cl bonds are essentially sd^3 hybridized with negligible p contribution at Ti.

The much higher absolute values for the deshielding contributions of the Ti–C and Ti–Cl bonds are explained by the nature of these bonds, which are sd hybridized at Ti, while the Si–C, Si–Cl, C–C(Me), and C–Cl bonds are sp hybridized at C and Si, respectively.

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Supplementary Material Available: Tables of experimental and calculated geometries and calculated chemical shifts for Me_nCCl_{4-n}, Me_nSiCl_{4-n}, and Me_nTiCl_{4-n} (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(49) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(50) Gerloch, M. *Coord. Chem. Rev.* **1990**, *99*, 117.

(51) Jonas, V.; Frenking, G. *Angew. Chem.*, submitted for publication.