

Rainer Koch · Torsten Bruhn

## Theoretical $^{49}\text{Ti}$ NMR chemical shifts

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**Abstract**  $^{49}\text{Ti}$  chemical shifts for a total of 20 titanium complexes are reported, and several levels of theory are evaluated in order to identify a reliable approach for the calculation of titanium NMR data. The popular B3LYP/6–31G(d)//B3LYP/6–31G(d) proves to give very good agreement with experimental data over a range from 1,400 to –1,300 ppm. The MP2/6–31G(d)//MP2/6–31G(d) level computes even smaller average deviations but fails for  $\text{TiI}_4$ . This behavior together with its huge demand for computational resources requires careful handling of this theoretical level. In addition, NMR data for five titanium fulvene (or related) complexes are given.

**Keywords** NMR chemical shifts · Density functional calculations ·  $^{49}\text{Ti}$  NMR

### Introduction

Nuclear magnetic resonance spectroscopy has always been an invaluable tool for obtaining information on geometries and electronic structures of mainly “organic” molecules [1]. In recent years, NMR spectroscopy of transition metal complexes has developed to a fully validated method that also allows examination of transition metal nuclei [2, 3]. Paralleling this development, many theoretical calculations have been carried out to assist the spectroscopist in analyzing and understanding the spectra obtained, and as the ultimate goal, to predict them [4–6]. Considerable methodological effort has been made in order to improve the treatment of transition metal elements, in particular the heavier third-row

nuclei, where relativistic effects are a requirement for correct description of NMR chemical shifts and spin-spin coupling constants [7–9]. First-row and most of the second-row elements can be treated at a non-relativistic level, and there are numerous computational studies demonstrating the applicability of density functional theory, [10–15] mainly by Michael Bühl. This is also true for  $^{49}\text{Ti}$ , where two theoretical studies have been published: the first shows good agreement between theory (IGLO, individual gauge for localized orbitals) and experiment for  $\delta$  ( $^{49}\text{Ti}$ ) for the  $\text{TiCl}_n\text{Me}_{4-n}$  set of molecules [16]. However, deficiencies in the derivation of chemical shifts for later transition metals with the Hartree–Fock level of theory, [15, 17] which was used in this work, require a more robust testing of additional levels of theory. The second thorough study deals mainly with DFT-based approaches and gives reasonably good agreement for a somewhat larger but still limited test set [18]. It also suggests that line widths, which can become an issue for the NMR-active  $^{47}\text{Ti}$  and  $^{49}\text{Ti}$ , cannot be reproduced using B3LYP-based electric field gradients.

Due to the still small number of molecules included in the evaluation of theoretical approaches and the neglect of perturbation theory in the calculation of chemical shifts, we set out to extend the existing theoretical knowledge to a broader foundation, using both a larger test set and more levels of theory.

### Materials and methods

All geometries were fully optimized at different levels of theory with the Gaussian 03 program package [19]. The first employs the hybrid functional by Becke and Lee, Yang and Parr (denoted B3LYP) [20, 21] together with the standard 6–31G(d) basis set [22, 23] for all atoms with the exception of iodine and additional calculations for bromine, where the Stuttgart–Dresden effective-core potentials (SDD) were used. The second level differs only in the use of second order perturbation theory (MP2) [24, 25] instead of B3LYP, while the third again uses B3LYP in connection with a larger 6–311G(3df,2p) basis set. The nature of all local minimum

Dedicated to Professor Dr. Paul von Ragué Schleyer on the occasion of his 75th birthday

R. Koch (✉) · T. Bruhn  
Institut für Reine und Angewandte Chemie,  
Carl von Ossietzky Universität Oldenburg,  
P.O. Box 2503, 26111 Oldenburg, Germany  
e-mail: rainer.koch@uni-oldenburg.de  
Tel.: +49-441-7983653  
Fax: +49-441-7983329

structures found was confirmed by the lack of an imaginary harmonic vibrational frequency. Absolute magnetic shieldings were determined with the GIAO (gauge—including atomic orbital) method [26–28] at the HF, [29] B3LYP and MP2 levels of theory as implemented in Gaussian 03. The shielding tensors obtained were referenced against titanium tetrachloride to yield relative chemical shifts. Basis sets used herein range from the relatively small 6–31G(d) to the more demanding 6–311G(3df,2pd). It also includes the IGLO II [30] basis set, which was used for all atoms except Ti where 6–31G(d) and 6–311G(2df) were employed. For details on method/basis set combinations, see Table 1. Calculations including solvent effects used the polarized continuum

model (PCM) [31–33] and dichloromethane as solvent ( $\epsilon=8.93$ ).

## Results and discussion

In order to obtain reliable relative chemical shifts, it is important to verify that the geometry of a molecule under investigation is in agreement with experimental results. Table 2 therefore lists important geometrical parameters of the optimized molecules studied herein, together with experimental data if available.

All three levels of theory present reliable results for the molecules studied. The structures derived from the DFT

**Table 1** Selected structural data for titanium complexes (bond lengths in Å, angles in °)

Compound	Variable	Experiment	B3LYP/ 6–31G(d)	B3LYP/ 6–311G(3df,2p)	MP2/ 6–31G(d)
TiCl <sub>4</sub> <sup>b</sup>	Ti–Cl	2.170	2.178	2.177	2.172
MeTiCl <sub>3</sub> <sup>c</sup>	Ti–Cl	2.185	2.193	2.193	2.178
–	Ti–C	2.047	2.029	2.039	2.054
–	Cl–Ti–C	105.6	104.8	105.1	104.4
Me <sub>2</sub> TiCl <sub>2</sub> <sup>d</sup>	Ti–Cl	2.196	2.212	2.211	2.197
–	Ti–C	2.058	2.043	2.051	2.054
–	Cl–Ti–Cl	117.3	118.7	118.1	120.5
–	C–Ti–C	102.8	103.8	104.4	101.9
Me <sub>3</sub> TiCl	Ti–Cl	–	2.231	2.229	2.220
–	Ti–C	–	2.058	2.066	2.065
Me <sub>4</sub> Ti	Ti–C	–	2.076	2.082	2.080
CpTiCl <sub>3</sub> <sup>e</sup>	Ti–Cl	2.224	2.233	2.232	2.219
–	Ti–x <sup>a</sup>	2.010	2.051	2.052	2.043
Cp <sub>2</sub> TiCl <sub>2</sub> <sup>f</sup>	Ti–Cl	2.364	2.349	2.344	2.334
–	Ti–x <sup>a</sup>	2.058	2.099	2.103	2.069
–	x–Ti–x <sup>a</sup>	130.9	131.6	131.5	130.6
–	Cl–Ti–Cl	94.4	96.3	96.6	98.8
TiBr <sub>4</sub> <sup>g</sup>	Ti–Br	2.339	2.319	–	2.326
TiBr <sub>4</sub> (Br=SDD)	Ti–Br	2.339	2.346	–	–
TiI <sub>4</sub> (I=SDD) <sup>g</sup>	Ti–I	2.546	2.560	–	2.571
MeTiBr <sub>3</sub>	Ti–Br	–	2.332	–	2.327
–	Ti–C	–	2.032	–	2.058
Cp <sub>2</sub> TiBr <sub>2</sub> <sup>h</sup>	Ti–Br	2.490	2.495	–	2.499
–	Ti–x <sup>a</sup>	2.050	2.101	–	2.071
–	x–Ti–x <sup>a</sup>	131.2	131.7	–	131.0
–	Br–Ti–Br	94.7	96.4	–	98.3
Cp <sub>2</sub> TiBr <sub>2</sub> (Br=SDD)	Ti–Br	2.490	2.565	–	–
–	Ti–x <sup>a</sup>	2.050	2.085	–	–
–	x–Ti–x <sup>a</sup>	131.2	132.1	–	–
–	Br–Ti–Br	94.7	95.4	–	–
Cp <sub>2</sub> TiF <sub>2</sub>	Ti–F	–	1.802	–	1.825
–	Ti–x <sup>a</sup>	–	2.125	–	2.081
–	x–Ti–x <sup>a</sup>	–	132.1	–	131.5
–	F–Ti–F	–	98.5	–	99.8
Cp*TiCl <sub>3</sub> <sup>i</sup>	Ti–Cl	2.245	2.247	–	2.231
–	Ti–x <sup>a</sup>	2.021	2.053	–	2.046
Ti(CO) <sub>6</sub> <sup>2j</sup>	Ti–C	2.038	2.051	–	2.038
Ti(NMe <sub>2</sub> ) <sub>4</sub>	Ti–N	–	1.918	–	1.916

<sup>a</sup>x is the centre of the cyclopentadienyl ring

<sup>b</sup>[40]

<sup>c</sup>[41]

<sup>d</sup>[42]

<sup>e</sup>[43]

<sup>f</sup>[44] and [45]

<sup>g</sup>[46]

<sup>h</sup>[47] and [48]

<sup>i</sup>[49]

<sup>j</sup>[50]

optimization are largely unaffected by the basis set: the much larger triple- $\zeta$  basis does not give better results compared to the standard 6-31G(d) basis set. The calculations using an SDD ECP for bromine also do not lead to significant

improvement. The only minor difficulties in reproducing the experimental data are encountered for titanium cyclopentadienyl complexes: some of the DFT-calculated Ti-centroid distances tend to be too long by about 3–5 ppm. MP2 ge-

**Table 2** Experimental and calculated relative chemical shifts  $\delta$  (in ppm), errors and unsigned averaged deviations for a test set of titanium compounds

	Experimental	B3LYP/6-31G(d)// B3LYP/6-31G(d)	Deviation	B3LYP/6-311G(3df,2pd)// B3LYP/6-31G(d)	Deviation	HF/6-31+G(d,p)// B3LYP/6-31G(d)	Deviation
TiCl <sub>4</sub> <sup>d</sup>	0	0.0	0.0	0.0	0.0	0.0	0.0
MeTiCl <sub>3</sub> <sup>d</sup>	613	456.0	157.0	452.1	160.9	488.0	125.0
Me <sub>2</sub> TiCl <sub>2</sub> <sup>d</sup>	907	815.6	91.4	815.3	91.7	718.8	188.3
Me <sub>3</sub> TiCl <sup>d</sup>	1,188	1,098.8	89.2	1,105.8	82.2	884.9	303.1
Me <sub>4</sub> Ti <sup>d</sup>	1,325	1,320.5	4.5	1,334.7	-9.7	1,029.5	295.5
CpTiCl <sub>3</sub> <sup>e</sup>	-390	-385.8	-4.2	-457.8	67.8	-536.1	146.1
Cp <sub>2</sub> TiCl <sub>2</sub> <sup>f</sup>	-773	-785.8	12.8	-898.5	125.5	-983.6	210.6
Average deviation	-	-	59.9	-	89.6	-	211.4
		MP2/6-31G(d)// B3LYP/6-31G(d)	Deviation	B3LYP/6-311G(3df,2p)// B3LYP/6-311G(3df,2p)	Deviation	MP2/6-31G(d)// MP2/6-31G(d)	Deviation
TiCl <sub>4</sub>	0	0.0	0.0	0.0	0.0	0.0	0.0
MeTiCl <sub>3</sub>	613	430.2	182.8	465.4	147.6	438.8	174.2
Me <sub>2</sub> TiCl <sub>2</sub>	907	885.8	21.2	836.8	70.2	917.8	-10.8
Me <sub>3</sub> TiCl	1,188	1,192.8	-4.8	1,133.9	54.1	1,237.1	-49.1
Me <sub>4</sub> Ti	1,325	-1,411.2	-86.2	1,371.1	-46.1	1,450.7	-125.7
CpTiCl <sub>3</sub>	-390	-328.7	-61.3	-461.6	71.6	-363.0	-27.0
Cp <sub>2</sub> TiCl <sub>2</sub>	-773	-722.6	-50.4	-904.6	131.6	-766.9	-6.1
Average deviation	-	-	67.8	-	86.9	-	65.5
	Experimental	B3LYP/IGLOII <sup>a</sup> // MP2/6-31G(d)	Deviation	B3LYP/IGLOII <sup>b</sup> // MP2/6-31G(d)	Deviation	B3LYP/6-31+G(d,p)// MP2/6-31G(d)	Deviation
TiCl <sub>4</sub>	0	0.0	0.0	0.0	0.0	0.0	0.0
MeTiCl <sub>3</sub>	613	431.3	181.7	423.9	189.1	435.0	178.0
Me <sub>2</sub> TiCl <sub>2</sub>	907	794.8	112.2	790.2	116.8	799.8	107.2
Me <sub>3</sub> TiCl	1,188	1,076.2	111.8	1,088.6	99.4	1,077.9	110.1
Me <sub>4</sub> Ti	1,325	1,286.6	38.4	1,326.8	-1.8	1,287.6	37.4
CpTiCl <sub>3</sub>	-390	-448.8	58.8	-505.7	115.7	-435.2	45.2
Cp <sub>2</sub> TiCl <sub>2</sub>	-773	-874.8	101.8	-967.6	194.6	-833.8	60.8
Average deviation	-	-	100.8	-	119.6	-	89.8
		HF/II <sup>c</sup> //BP86/AE1	Deviation	BPW91/II <sup>c</sup> //BP86/AE1	Deviation	B3LYP/II <sup>c</sup> //BP86/ AE1	Deviation
TiCl <sub>4</sub>	0	0	0	0	0	0	0
MeTiCl <sub>3</sub>	613	512	101	431	182	443	170
Me <sub>2</sub> TiCl <sub>2</sub>	907	776	131	800	107	796	111
Me <sub>3</sub> TiCl	1,188	978	210	1,103	85	1,077	111
Me <sub>4</sub> Ti	1,325	1,163	162	1,369	-44	1,317	8
CpTiCl <sub>3</sub>	-390	-512	122	-424	34	-454	64
Cp <sub>2</sub> TiCl <sub>2</sub>	-773	-951	178	-864	91	-892	119
Average deviation	-	-	150.7	-	90.5	-	97.2

<sup>a</sup>6-31G(d) basis set for Ti

<sup>b</sup>6-311G(2df) basis set for Ti

<sup>c</sup>II<sup>c</sup> denotes an augmented Wachters basis for Ti, IGLO II for all other atoms except H (double-zeta basis). For details see [18]

<sup>d</sup>[16]

<sup>e</sup>[38]

<sup>f</sup>[39]

ometries are slightly better in this respect but are not generally superior. All in all, the three different levels produce reliable geometrical data that can be used for subsequent determination of chemical shieldings.

With a solid foundation of reliable geometries, chemical shift calculations with several combinations for NMR single point//geometry levels of theory were performed. Table 1 gives an overview of nine different approaches for a set of seven titanium complexes. For comparison, we have included Bühl's data based on BP86/AE1 geometries [18].

It can be clearly seen that, regardless of the geometry employed, large basis sets do not improve the description of chemical shifts, a behavior encountered before [34–36]. Also, the Hartree–Fock-based calculations fail dramatically. Interestingly, calculations with the recommended IGLO II basis set [18] for all atoms except for Ti where either a 6–31G(d) or a 6–311G(2df) is used, give chemical shifts significantly inferior to the best data obtained. The same is true for the data presented by Bühl, where a very similar basis was used. The combination of B3LYP/6–31+G(d,p) GIAO calculation based on a MP2/6–31G(d) geometry, which has previously been successful for organic molecules, does not reproduce the experimental data accurately. According to the results in Table 1, the method of choice appears to be the very popular B3LYP/6–31G(d)//B3LYP/6–31G(d) level of theory with an average deviation of only 60 ppm for the test set, possibly GIAO–MP2/6–31G(d) with the same DFT geometries (68 ppm) and MP2/6–31G(d)//MP2/6–31G(d) (66 ppm).

One note on the experimental result for MeTiCl<sub>3</sub>: all methods have enormous difficulties reproducing this value, averaging at an error of around 150 ppm to a higher field! In particular the GIAO–MP2 calculations, which generally tend to give low-field shifted results, stand out with the largest deviations. Although there are two experimental reports of 613 and 618 ppm (although from the same group) and the signal has been measured as a sharp line, one has at least to question the influence of solvent (possible adduct formation) and reaction conditions on the relative shifts [36]. We therefore ran a series of NMR calculations in a simulated solvent environment (Polarized

Continuum Model; CH<sub>2</sub>Cl<sub>2</sub> as solvent) comparing its influence on the optimization, the GIAO NMR calculations and both optimization and NMR calculations (Table 3).

As expected, the absolute shifts for the T<sub>d</sub>-symmetric and hence dipole moment-free TiCl<sub>4</sub> (serving as reference) and TiMe<sub>4</sub> are almost unaffected. In all other cases, the determination of relative chemical shifts using a gas phase geometry and PCM GIAO NMR calculations leads to a low-field shift of about 25 to 45 ppm. The alternative approach, using simulated solvent geometries and gas phase shifts leads to not so obvious results: while some molecules, the less polar di- and trimethylchlorotitanium are not strongly influenced (9 and 2 ppm, respectively), the others again show a pronounced low-field shift of around 30 to 40 ppm.

These two effects are almost exactly composite as shown for the solvent geometry/solvent NMR calculations. For the above mentioned MeTiCl<sub>3</sub>, which cannot be accurately reproduced by any methods, the error is reduced by more than 70 ppm from 157 to now 83 ppm! In general, the inclusion of a solvation environment for the chemical shift calculations reduces the overall error to only 45 ppm, mainly due to the general high-field shift of the chosen level of theory.

Although the first results are very promising, this test set is not very thorough, so that we decided to evaluate the best of the above levels of theory further, i.e. the B3LYP/and MP2/6–31G(d) NMR calculations based on the B3LYP/6–31G(d) structures and the MP2/6–31G(d)//MP2/6–31G(d) level of theory. These data are summarized in Table 4, again together with experimental and Bühl's values.

Even with this extended test set, the ever-popular B3LYP/6–31G(d) level proves to give the best results over a range from +1,400 to –1,300 ppm: the average unsigned error is slightly increased to 68 ppm, clearly ahead of the best of Bühl's methods (at 104 ppm), and the relative chemical shifts are typically shifted to a higher field. MP2/6–31G(d) NMR investigation also yields good agreement with the experimental data, with the exception of TiI<sub>4</sub>. Both calculations, based on different geometries, fail dramatically, giving relative chemical shifts which are high-field shifted

**Table 3** Influence of solvent effects (PCM; CH<sub>2</sub>Cl<sub>2</sub> as solvent) on calculated relative chemical shifts  $\delta$  (B3LYP/6–31G(d)//B3LYP/6–31G(d)) in ppm, errors and unsigned averaged deviations for the test set from Table 1

	Experimental	Optimization		Optimization		Optimization		Optimization	
		NMR	Deviation	NMR solvent	Deviation	NMR solvent	Deviation	NMR solvent	
TiCl <sub>4</sub>	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MeTiCl <sub>3</sub>	613	456.0	157.0	489.1	123.9	495.5	117.5	529.6	83.4
Me <sub>2</sub> TiCl <sub>2</sub>	907	815.6	91.4	862.3	44.7	824.7	82.3	872.0	35.0
Me <sub>3</sub> TiCl	1,188	1,098.8	89.2	1,133.3	54.7	1,101.0	87.0	1,135.7	52.3
Me <sub>4</sub> Ti	1,325	1,320.5	4.5	1,319.8	5.2	1,313.4	11.6	1,312.6	12.4
CpTiCl <sub>3</sub>	–390	–385.8	–4.2	–358.4	–31.6	–353.6	–36.4	–325.1	–64.9
Cp <sub>2</sub> TiCl <sub>2</sub>	–773	–785.8	12.8	–762.8	–10.2	–751.5	–21.5	–730.0	–43.0
Average deviation	–	–	59.9	–	45.1	–	59.4	–	48.5

**Table 4** Experimental and calculated relative chemical shifts  $\delta$  (in ppm), errors and unsigned averaged deviations for the extended test set

	Experimental	B3LYP/6-31G(d)// B3LYP/6-31G(d)	Deviation	MP2/6-31G(d)// B3LYP/6-31G(d)	Deviation	MP2/6-31G(d)// MP2/6-31G(d)	Deviation
TiBr <sub>4</sub> <sup>b</sup>	483	418.0	65.0	290.8	192.2	322.5	160.5
Cp <sub>2</sub> TiBr <sub>2</sub> <sup>b</sup>	-668	-679.1	11.1	-642.3	-25.7	-665.6	-2.4
Cp <sub>2</sub> TiF <sub>2</sub> <sup>c</sup>	-1051	-1,177.1	126.1	-1,132.4	95.4	-1,115.9	64.9
Ti(CO) <sub>6</sub> <sup>2d</sup>	-1,389	-1,510.4	121.4	-1,405.8	16.8	-1,399.8	10.8
MeTiBr <sub>3</sub> <sup>e</sup>	825	752.0	73.0	697.0	128.0	731.9	93.1
Cp*TiCl <sub>3</sub> <sup>f</sup>	-85	-170.3	85.3	-71.3	-13.7	-115.3	30.3
Ti(NMe <sub>2</sub> ) <sub>4</sub> <sup>e</sup>	-231	-276.0	45.0	-213.4	-17.6	-207.9	-23.1
TiI <sub>4</sub> <sup>b</sup>	1,278	1,231.7 <sup>h</sup>	46.3	-473.2 <sup>h</sup>	1,751.2	-525.1 <sup>h</sup>	1,803.1
CpTi(6-methyl-fulvene) Cl	-	-414.2	-	-	-	-	-
CpTi(6-tert.butyl- fulvene)Cl	-	-405.7	-	-	-	-	-
CpTi(1-neopentyl-Cp) ClOH	-	-943.4	-	-	-	-	-
Cp <sub>2</sub> Ti(H <sub>2</sub> C=C=NH)	-	85.0	-	-	-	-	-
Cp <sub>2</sub> Ti(H <sub>2</sub> C=C=NH) xHCN	-	60.7	-	-	-	-	-
Average deviation first seven molecules <sup>i</sup>	-	-	75.6	-	69.9	-	55.0
Average deviation all eight molecules	-	-	71.6	-	280.1	-	273.5
Total average deviation <sup>i,j</sup>	-	-	68.1	-	68.9	-	59.8
-	-	HF/II <sup>a</sup> //BP86/AE1	Deviation	BPW91/II <sup>a</sup> //	-	-	-
BP86/AE1	Deviation	B3LYP/II <sup>a</sup> //BP86/ AE1	Deviation	-	-	-	-
TiBr <sub>4</sub> <sup>b</sup>	483	499.0	-16.0	394.0	89.0	480.0	3.0
Cp <sub>2</sub> TiBr <sub>2</sub> <sup>b</sup>	-668	-845.0	177.0	-720.0	52.0	-742.0	74.0
Cp <sub>2</sub> TiF <sub>2</sub> <sup>c</sup>	-1,051	-1,223.0	172.0	-1,161.0	110.0	-1,245.0	194.0
Ti(CO) <sub>6</sub> <sup>2d</sup>	-1,389	-1,202.0	-187.0	-1,620.0	231.0	-1,646.0	257.0
MeTiBr <sub>3</sub> <sup>e</sup>	825	-	-	-	-	-	-
Cp*TiCl <sub>3</sub> <sup>f</sup>	-85	-	-	-	-	-	-
Ti(NMe <sub>2</sub> ) <sub>4</sub> <sup>e</sup>	-231	-	-	-	-	-	-
TiI <sub>4</sub> <sup>b</sup>	1,278	1,617.0	-339.0	1,024.0	254.0	1,307.0	-29.0
Average deviation first seven molecules <sup>i</sup>	-	-	-	-	-	-	-
Average deviation all eight molecules	-	-	178.2	-	147.2	-	111.4
Total average deviation <sup>i,j</sup>	-	-	163.2	-	111.3	-	103.6

<sup>a</sup>II' denotes an augmented Wachters basis for Ti, IGLO II for all other atoms except H (double-zeta basis). For details see [18]

<sup>b</sup>[51]

<sup>c</sup>[39]

<sup>d</sup>[52]

<sup>e</sup>[53]

<sup>f</sup>[16]

<sup>g</sup>Not feasible

<sup>h</sup>The SDD basis set/ECP is used for iodine

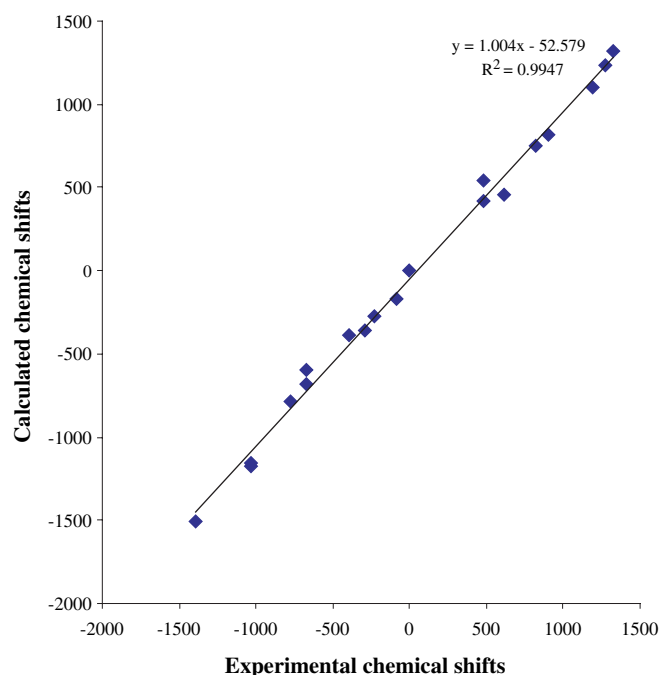
<sup>i</sup>Excluding the TiI<sub>4</sub> deviation

<sup>j</sup>Total unsigned average deviation (from Tables 1 and 4)

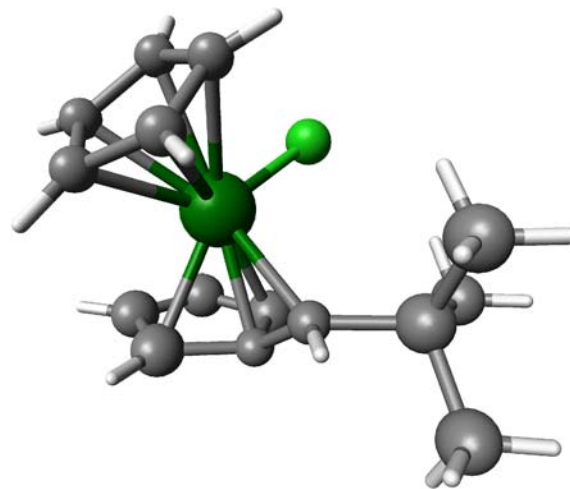
by about 1,800 ppm, although the corresponding DFT data are very reasonable. Interestingly, HF-based calculations predict the Ti signal 1,000 ppm at a lower field compared to the experimental data! From our results one can clearly see that perturbation theory cannot handle the NMR determination of iodine-containing systems, in contrast to DFT approaches. Without inclusion of these deficiencies, both MP2 NMR calculations are at least as good as the DFT results, in the case of underlying MP2 geometries, there is a reduction of the total average error to 60 ppm! Although the deviation is somewhat smaller, due to its very demanding need for computational resources, the general use of MP2/6-31G(d)//MP2/6-31G(d) is only recommended for smaller systems, thus allowing more economic studies with B3LYP/6-31G(d)//B3LYP/6-31G(d). Figure 1 shows a plot of the experimental versus calculated values for the large dataset at B3LYP/6-31G(d)//B3LYP/6-31G(d) with remarkable agreement ( $R^2=0.9967$ ) and an almost ideal slope of the regression line of 1.002.

As can be seen from Table 2, additional optimizations of several compounds with halogen atoms have been performed employing the SDD basis set/ECP for the halogen atoms. Subsequent NMR calculations with SDD on halogen do not, however, lead to better results. As one might expect, the data for  $\text{TiBr}_4$ ,  $\text{Cp}_2\text{TiBr}_2$ , and  $\text{Cp}_2\text{TiF}_2$  are of equal quality compared to the B3LYP/6-31G(d).

Due to the quadrupole moment of the NMR-active titanium nuclei, line widths are considered as important. Although the use of electric field gradients for estimating line widths has proven successful for many other nuclei, it had been shown that this concept does not work in the case of titanium [18].



**Fig. 1** Experimental and calculated  $^{49}\text{Ti}$  chemical shifts  $\delta$  obtained from Tables 1 and 4 at B3LYP/6-31G(d)//B3LYP/6-31G(d)



**Fig. 2** Calculated structure of  $\text{CpTi}(6\text{-tert. butyl-fulvene})\text{Cl}$  at B3LYP/6-31G(d)//B3LYP/6-31G(d)

We extended the investigation to a series of fulvene systems and related complexes (an example is shown in Fig. 2) which have been synthesized [37] in the Beckhaus group in our institute. The DFT results, included in Table 4, indicate a variation of the  $^{49}\text{Ti}$  signal from  $-950$  to  $100$  ppm. Unfortunately, the experimentalists have not been able to obtain a clear  $^{49}\text{Ti}$  signal for those complexes, most likely due to very wide signals, so that a comparison with experimental data is not possible.

## Conclusions

The use of an extended reference set of molecules and the extension of tested levels of theory for the evaluation of  $^{49}\text{Ti}$  chemical shifts results in significant improvements over the present “best” choice [18] (B3LYP/II//BP86/AE1). The average error is reduced from 107 to 68 ppm with the relatively inexpensive B3LYP/6-31G(d)//B3LYP/6-31G(d). Even better results can be obtained using the MP2/6-31G(d)//MP2/6-31G(d) level of theory. However, it fails dramatically when investigating  $\text{TiI}_4$ , so the approach has to be handled with care. Furthermore, its huge demand for computational resources limits its general applicability. The excellent performance of the relatively small basis sets used herein and in other studies has to be treated with caution and cannot be generalized. Apparently due to error cancellation, these theoretical approaches give better results than larger basis sets, which are systematically better. The demonstrated influence of a simulated solvent environment on the chemical shifts leaves the question open for a general solvation inclusion for these calculations.

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