Solid-State 91Zr NMR Spectroscopy Studies of Zirconocene Olefin Polymerization Catalyst Precursors

Aaron J. Rossini, University of Windsor
Ivan Hung, University of Windsor
Samuel A. Johnson, University of Windsor
Carla Sledonick, Virginia Polytechnic Institute and State University
Mike Mensch, Virginia Polytechnic Institute and State University, et al.

Available at: https://works.bepress.com/aaron-rossini/22/
固态\textsuperscript{47/49} Ti NMR of Titanocene Chlorides

Aaron J. Rossini, Ivan Hung, and Robert W. Schurko*
Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada

ABSTRACT Magic angle spinning (MAS) and static\textsuperscript{47/49} Ti solid-state NMR (SSNMR) spectra of the cyclopentadienyl (Cp) titanium chloride compounds, Cp\textsubscript{2}TiCl\textsubscript{2} (1), \textsubscript{Cp}^*\textsubscript{2}TiCl\textsubscript{2} (2) [\textsubscript{Cp}^* = \textsubscript{C}_5\textsubscript{Me}_5], CpTi\textsubscript{2}Cl\textsubscript{2} (3), and \textsubscript{Cp}^*TiCl\textsubscript{3} (4) have been acquired at magnetic field strengths of 21.1 and 9.4 T. From these spectra, it is possible to measure anisotropic \textsuperscript{47/49} Ti NMR interaction parameters, which are extremely sensitive to differences in molecular structure. At a magnetic field of 21.1 T, the\textsuperscript{47/49} Ti spectra can be acquired efficiently with standard echo pulse sequences. Quantum chemical calculations of \textsuperscript{47/49} Ti electric field gradient (EFG) and chemical shielding (CS) tensor parameters are presented. The theoretical EFG and CS tensor orientations are utilized to relate the anisotropic NMR tensor parameters to the molecular and electronic structures of the complexes.

SECTION Kinetics, Spectroscopy

Early transition-metal metallocene complexes are highly active catalysts for olefin polymerization, affording better control over the stereospecificity and molecular weight distributions of resulting polymers than the traditional heterogeneous TiCl\textsubscript{4}/MgCl\textsubscript{2} Ziegler–Natta system.\textsuperscript{1–4} While certain metalloccenes can be dissolved in polymerization media and used as homogeneous catalysts, they are also employed as heterogeneous catalysts on support materials such as alumina and silica.\textsuperscript{2,3} The solubilized homogeneous catalysts are amenable to traditional structural, kinetic, and mechanistic studies; however, the active sites of supported catalysts are often difficult to characterize.\textsuperscript{2,5} One intriguing possibility for characterizing heterogeneous catalysts is solid-state NMR (SSNMR) spectroscopy of quadrupolar nuclei.\textsuperscript{6–10} We have demonstrated that SSNMR spectra of metal quadrupolar nuclei that lie at the “hearts” of metalloccenes can act as sensitive probes of molecular structure and dynamics\textsuperscript{11–14} and could therefore find use for characterizing heterogeneous catalysts. In this regard, \textsuperscript{47/49} Ti SSNMR could potentially serve as a powerful probe of molecular structure for titanocene-based heterogeneous catalysts.

Titanium possesses two NMR-active nuclei, \textsuperscript{47} Ti (I = 5/2) and \textsuperscript{49} Ti (I = 7/2),\textsuperscript{15} both of which are unreactive owing to their low natural abundances [n.a. (\textsuperscript{47} Ti) = 7.44\%, n.a. (\textsuperscript{49} Ti) = 5.41\%], moderate quadrupole moments [Q (\textsuperscript{47} Ti) = 29.0 fm\textsuperscript{2}, Q (\textsuperscript{49} Ti) = 24.0 fm\textsuperscript{2}], and low gyromagnetic ratios [\(\gamma\) (\textsuperscript{47} Ti) = \(-1.5105 \times 10^{7}\) rad s\textsuperscript{-1} T\textsuperscript{-1}, \(\gamma\) (\textsuperscript{49} Ti) = \(-1.51095 \times 10^{7}\) rad s\textsuperscript{-1} T\textsuperscript{-1}].\textsuperscript{15} \textsuperscript{49} Ti is preferred for SSNMR experiments as the central transition (CT) powder patterns are significantly narrower due to its slightly smaller quadrupolar moment and higher nuclear spin. However, the similarity of the gyromagnetic ratios of \textsuperscript{47} Ti and \textsuperscript{49} Ti complicates the acquisition and analysis of SSNMR spectra; the difference of the Larmor frequencies is so small that the \textsuperscript{49} Ti and \textsuperscript{47} Ti resonances are located \(-267\) ppm apart, which often results in overlapping CT powder patterns. Despite these difficulties, there are numerous examples of \textsuperscript{47/49} Ti solution\textsuperscript{16–30} and solid-state\textsuperscript{31–53} NMR found in the literature, reflecting the myriad number of important systems containing titanium. To date, most \textsuperscript{47/49} Ti SSNMR studies have been restricted to oxides and other extended solids. In this work, we report the first application of \textsuperscript{47/49} Ti SSNMR for the structural characterization of molecular titanium-containing complexes. Before complex solid catalysts can be investigated by SSNMR of quadrupolar nuclei such as \textsuperscript{47/49} Ti, fundamental studies on well-characterized crystalline species are required. To this end, we have acquired MAS and static \textsuperscript{47/49} Ti SSNMR spectra of the titanocenes, 1–4. Quantum chemical calculations of NMR tensor parameters are also presented.

Magic angle spinning (MAS) \textsuperscript{47/49} Ti SSNMR spectra of compounds 1–4 acquired at 21.1 T are shown in Figure 1. At 21.1 T, spectra of 1, 3, and 4 could be acquired in relatively short experimental times (<1.5 h). The spectrum of 2 required \(-32000\) scans (1 day) due to the increased breadth of its MAS powder pattern and the reduced Ti content. The \textsuperscript{49} Ti MAS spectra of 1 and 2 display characteristic second-order quadrupolar CT powder patterns, indicative of sizable quadrupolar interactions. From the simulations of these patterns, it is possible to obtain \(C_Q\), \(\eta_Q\), and \(\delta_{iso}\) (Table 1). For both 1 and 2, the \textsuperscript{47} Ti powder patterns are obscured due to their comparable larger breadths and subsequently lower signal-to-noise ratios. Simulations of the \textsuperscript{47} Ti powder patterns, which utilize a \(C_Q(\textsuperscript{47} Ti)\) that has been scaled by the ratio of \textsuperscript{47} Ti and \textsuperscript{49} Ti quadrupole moments, indicate that much faster sample spinning speeds are necessary to prevent sideband overlap. For this reason, the reported \textsuperscript{47/49} Ti NMR tensor parameters are based on simulations of the MAS \textsuperscript{49} Ti CT powder patterns, with the MAS \textsuperscript{47} Ti CT patterns providing additional constraints on these parameters. It should be noted.

Received Date: August 24, 2010
Accepted Date: September 16, 2010
Published on Web Date: September 24, 2010
**Figure 1.** Experimental MAS $^{47/49}$Ti SSNMR spectra (black traces) of 1 (Cp$_2$TiCl$_2$), 2 (Cp$_2$TiCl$_3$), 3 (CpTiCl$_3$), and 4 (Cp*TiCl$_3$) acquired at 21.1 T [ν$_0$(47Ti) = 50.75 MHz] and spectra of 3 and 4 acquired at 9.4 T [ν$_0$(47Ti) = 22.53 MHz]. Sample spinning speeds are given in the figure. Analytical simulations are overlaid on the experimental spectra (red traces). All spectra at 21.1 T were acquired with a standard rotor synchronized 90°–180° echo pulse sequence. Asterisks denote spinning sidebands. The inset of the spectrum of 4 shows the $^{47}$Ti and $^{49}$Ti isotropic peaks that are obtained when the spinning sidebands are added onto the isotropic peak. Spectra at 9.4 T were acquired with the DFS−echo sequence, while the DFS−QCPMG (4) pulse sequences. The spectrum of 4 at 9.4 T was formed by co-adding the QCPMG echoes in the time domain, followed by Fourier transformation of the resultant echo.

that the crystal structure of 1 contains two crystallographically distinct titanium sites with similar local environments. As a result, the $^{47/49}$Ti NMR spectrum of 1 is composed of two very similar powder patterns which can be simulated with a single set of quadrupolar and chemical shift parameters. Quantum chemical calculations also confirm the similarities between the sites (vide infra).

In comparison to 1 and 2, the MAS $^{47/49}$Ti CT powder patterns of the trichloride species, 3 and 4, are relatively narrow, and at 21.1 T, it is difficult to accurately extract values of $C_Q$ and η$_Q$. The $^{47}$Ti powder patterns of 3 and 4 are slightly broader and can be used to estimate $C_Q$ and η$_Q$, although with large uncertainties. In order to obtain accurate measurements of $C_Q$ and η$_Q$ for 3 and 4, additional MAS spectra were recorded at 9.4 T (Figure 1, bottom). The CT powder patterns are considerably broader than those obtained at 21.1 T and exhibit features typical of a strong second-order quadrupolar interaction. From these spectra, EFG tensor parameters of $C_Q$ = 1.6 MHz and η$_Q$ = 0.95 and $C_Q$ = 3.0 MHz and η$_Q$ = 0.35 were obtained for 3 and 4, respectively, comparable to the small $C_Q$(Mo) values observed for a similar “piano-stool” complex, (Me$_3$C$_6$H$_3$)$_2$Mo(CO)$_6$. $^{55}$ Experimental times at 9.4 T were significantly greater than those at 21.1 T. The MAS $^{47/49}$Ti SSNMR spectrum of 3 was acquired in 2 h (5680 scans, 2 s pulse delay) with a DFS−echo pulse sequence, while the spectrum of 4 was acquired in ~21 h (25000 scans, 3 s pulse delay) with a DFS−QCPMG sequence.

Complex 4 possesses a relatively large $^{47/49}$Ti chemical shift anisotropy (CSA, vide infra), which further disperses spectral intensity into the spinning sidebands and affects the shape of the isotropic CT pattern; therefore, it is necessary to add the sideband intensity into the isotropic position to obtain an undistorted CT pattern (inset, Figure 1). $^{56}$ The spectrum of 4 at 9.4 T does not require the addition of spinning sidebands into the isotropic pattern due to an increase in the relative magnitude of the quadrupolar interaction with respect to the CSA.

The trends in the titanium isotropic chemical shifts mirror those observed in previous solution NMR studies. $^{17,19,35–36,30}$ An increase in δ$_{iso}$ is observed for the Cp* complexes in comparison to the analogous Cp complexes, and the mono-Cp’ species possess higher chemical shifts than the bis-Cp’ species (Cp’ refers to a Cp ligand of any substitution pattern). The differences in δ$_{iso}$ of 3 and 4 have previously been correlated with the absorption maxima (λ$_{max}$) of UV–visible spectra, which are 380 and 437 nm for 3 and 4, respectively. $^{26,30}$ It is well known that smaller energy separations between occupied and virtual orbitals give rise to larger paramagnetic shielding interactions and hence more positive chemical shifts (increased deshielding). $^{57–65}$ Thus, correlations between δ$_{iso}$ and λ$_{max}$ are observed when the MoS that make large contributions to the nuclear magnetic shielding are the same MOs involved in optical transitions.

A comparison of the $^{47/49}$Ti EFG tensor parameters obtained from solid-state and solution $^{47/49}$Ti NMR experiments is not as straightforward. In solution, the values of $C_Q$ are estimated from the full widths at half-height (FWHH) of the $^{47/49}$Ti peaks, under the approximation of the extreme narrowing limit. Furthermore, the values of η$_Q$ cannot be accurately determined from solution NMR spectra (many instances of predicting $C_Q$ values from FWHHS rely on the assumption that η$_Q$ = 0, which is most often not the case). Nonetheless, the previously measured FWHH values from solution $^{47/49}$Ti NMR spectra of 1–3 correlate well with the relative magnitudes of $C_Q$ obtained from the corresponding SSNMR spectra, and the values of $C_Q$(47Ti) are slightly larger for the bis-Cp’ species in comparison to those of the mono-Cp species. $^{18,26,30}$ However, FWHH values obtained from solution NMR spectra of 4 suggest that it possesses a smaller $C_Q$ than that of 3, $^{18,30}$ which is not the case in the solid state. Both 3 and 4 possess very small quadrupolar coupling constants; therefore, the differences in the magnitude of $C_Q$ may be a result of subtle structure deviations and/or long-range intermolecular electrostatic interactions. We note that our research group has previously observed that substituted selenocenes and niobocene complexes possess larger values of $C_Q$(23Na) and $C_Q$(97Nb), respectively, than the corresponding unsubstituted Cp complexes. $^{12,64}$ However, given the limitations of the
Table 1. Experimental and Calculated $^{47/49}$Ti EFG and CS Tensor Parameters

<table>
<thead>
<tr>
<th>complex/method/structure</th>
<th>$\delta_{\text{obs}}^{(49)}$Ti (ppm)$^a$</th>
<th>$Q_{\text{C}}^{(49)}$Ti (MHz)$^b$</th>
<th>$\eta_Q$</th>
<th>$\Omega$ (ppm)$^c$</th>
<th>$\kappa$</th>
<th>$\alpha$ ($)$^d$</th>
<th>$\beta$ ($)</th>
<th>$\gamma$ ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp$^+$TiCl$_2$(1)/experiment</td>
<td>$-732(5)$</td>
<td>$4.2(4)$</td>
<td>$0.45(30)$</td>
<td>$275(50)$</td>
<td>$0.65(30)$</td>
<td>$20(70)$</td>
<td>$20(20)$</td>
<td>$-10(90)$</td>
</tr>
<tr>
<td>1/RHF/site 1 ideal Cp</td>
<td>$-689$</td>
<td>$-6.1$</td>
<td>$0.21$</td>
<td>$166$</td>
<td>$0.7$</td>
<td>$65$</td>
<td>$82$</td>
<td>$9$</td>
</tr>
<tr>
<td>1/RHF/site 1 X-ray$^c$</td>
<td>$-737$</td>
<td>$-2.0$</td>
<td>$0.55$</td>
<td>$252$</td>
<td>$0.2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/RHF/site 2 ideal Cp</td>
<td>$-692$</td>
<td>$-6.0$</td>
<td>$0.16$</td>
<td>$168$</td>
<td>$0.7$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/RHF/site 2 X-ray</td>
<td>$-715$</td>
<td>$4.2$</td>
<td>$0.95$</td>
<td>$230$</td>
<td>$0.3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/BSLYP/site 1 ideal Cp</td>
<td>$-678$</td>
<td>$3.8$</td>
<td>$0.16$</td>
<td>$526$</td>
<td>$-0.3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/BSLYP/site 1 X-ray</td>
<td>$-729$</td>
<td>$7.8$</td>
<td>$0.07$</td>
<td>$588$</td>
<td>$-0.4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/BSLYP/site 2 ideal Cp</td>
<td>$-680$</td>
<td>$3.8$</td>
<td>$0.12$</td>
<td>$530$</td>
<td>$-0.3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/BSLYP/site 2 X-ray</td>
<td>$-708$</td>
<td>$8.3$</td>
<td>$0.04$</td>
<td>$576$</td>
<td>$-0.3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp$^+$TiCl$_2$(2)/experiment</td>
<td>$-449(4)$</td>
<td>$5.5(3)$</td>
<td>$0.72(10)$</td>
<td>$165(60)$</td>
<td>$-0.1(8)$</td>
<td>$80(40)$</td>
<td>$90(30)$</td>
<td>$-5(60)$</td>
</tr>
<tr>
<td>2/RHF/ideal Cp</td>
<td>$-478$</td>
<td>$-5.9$</td>
<td>$0.40$</td>
<td>$101$</td>
<td>$-0.1$</td>
<td>$154$</td>
<td>$19$</td>
<td>$37$</td>
</tr>
<tr>
<td>2/RHF/X-ray</td>
<td>$-479$</td>
<td>$-6.5$</td>
<td>$0.42$</td>
<td>$138$</td>
<td>$-0.4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2/BSLYP/ideal Cp</td>
<td>$-399$</td>
<td>$-4.0$</td>
<td>$0.67$</td>
<td>$327$</td>
<td>$-0.1$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2/BSLYP/X-ray</td>
<td>$-401$</td>
<td>$6.4$</td>
<td>$0.83$</td>
<td>$317$</td>
<td>$0.1$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpTiCl$_3$(3)/experiment</td>
<td>$-341(2)$</td>
<td>$1.6(2)$</td>
<td>$0.95(10)$</td>
<td>$85(10)$</td>
<td>$0.8(2)$</td>
<td>$50(30)$</td>
<td>$12(12)$</td>
<td>$10(40)$</td>
</tr>
<tr>
<td>3/RHF/ideal Cp</td>
<td>$-200$</td>
<td>$3.8$</td>
<td>$0.46$</td>
<td>$44$</td>
<td>$-0.5$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/RHF/X-ray</td>
<td>$-214$</td>
<td>$3.8$</td>
<td>$0.60$</td>
<td>$43$</td>
<td>$-0.2$</td>
<td>$71$</td>
<td>$86$</td>
<td>$171$</td>
</tr>
<tr>
<td>3/BSLYP/ideal Cp</td>
<td>$-239$</td>
<td>$8.5$</td>
<td>$0.19$</td>
<td>$375$</td>
<td>$-0.8$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/BSLYP/X-ray</td>
<td>$-253$</td>
<td>$8.5$</td>
<td>$0.24$</td>
<td>$369$</td>
<td>$-0.8$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp$^+$TiCl$_3$(4)/experiment</td>
<td>$-333(3)$</td>
<td>$3.0(3)$</td>
<td>$0.35(10)$</td>
<td>$650(75)$</td>
<td>$0.9(3)$</td>
<td>$50(90)$</td>
<td>$0(10)$</td>
<td>$0(90)$</td>
</tr>
<tr>
<td>4/RHF/ideal Cp</td>
<td>$-33$</td>
<td>$1.2$</td>
<td>$0.62$</td>
<td>$394$</td>
<td>$0.9$</td>
<td>$45$</td>
<td>$63$</td>
<td>$26$</td>
</tr>
<tr>
<td>4/RHF/X-ray</td>
<td>$-33$</td>
<td>$1.4$</td>
<td>$0.57$</td>
<td>$414$</td>
<td>$1.0$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4/BSLYP/ideal Cp</td>
<td>$-33$</td>
<td>$2.6$</td>
<td>$0.77$</td>
<td>$102$</td>
<td>$0.7$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4/BSLYP/X-ray</td>
<td>$-33$</td>
<td>$2.1$</td>
<td>$0.62$</td>
<td>$138$</td>
<td>$0.7$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp$^+$TiMe$_2$(5)/experiment</td>
<td>$-218$</td>
<td>$22.5$</td>
<td>$0.79$</td>
<td>$1809$</td>
<td>$-1.0$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp$^+$TiMe$_2$/RHF/ideal Cp</td>
<td>$-254$</td>
<td>$25.5$</td>
<td>$0.84$</td>
<td>$1811$</td>
<td>$-1.0$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The shifts are referenced to neat TiCl$_4$($\delta_{\text{obs}}^{(47)}$Ti = 0.0 ppm) via a secondary external standard of solid SrTiO$_3$, for which $\delta_{\text{obs}}^{(47)}$Ti = −845 ppm. The value is $\delta_{\text{obs}}^{(49)}$Ti = $\delta_{\text{obs}}^{(47)}$Ti − 267 ppm. Calculated isotropic magnetic shielding (MS) values ($\eta_{\text{CS}}$) were converted to $\delta_{\text{obs}}^{(49)}$Ti values by subtracting the calculated MS values from those calculated for 4, $\delta_{\text{obs}} = \delta_{\text{ins}}^{(49)}$Ti − 33 ppm. The EFG tensor is defined by three principal components ordered such that $|V_{11}| \leq |V_{22}| \leq |V_{33}|$, where $C_{Q} = eQV/\hbar$ and 0 $\leq \eta_Q = (V_{11} - V_{22})/V_{33} \leq 1.0$. The value is $C_{Q}^{(47)}$Ti = 1.21$C_{Q}^{(49)}$Ti. The CS tensor is described by three principal components ordered such that $\kappa_1 \geq \kappa_2 \geq \kappa_3$, where $\kappa_{\text{ins}} = (\kappa_1 + \kappa_2 + \kappa_3)/3$. $\kappa$ = $\kappa_1 - \kappa_3$, and $\kappa = 3(\kappa_2 - \kappa_3)/2$. The Rose convention is used to describe the Euler angles. Uncertainties associated with the last digits of the experimental NMR parameters are given in parentheses. Quantum chemical calculations employed atomic coordinates obtained from single-crystal X-ray diffractions structures. The “X-ray” and “ideal Cp” labels indicate whether XRD coordinates of the Cp carbon atoms were employed or whether idealized Cp rings were employed (see main text).

approximations described above, it is more likely that the solid-state measurement of $C_Q$ is simply more accurate. For complexes 1, 2, and 4, $\eta_Q$ values are not close to either 0 or 1, indicating that all of the components are distinct from one another. For 3, $\eta_Q$ is close to 1, indicating that $V_{11}$ is the distinct component of the EFG tensor and $V_{22}$ is not.

The values of $C_Q^{(49)}$Ti obtained for 1–4 are on the smaller end of the range previously measured from SSNMR spectra of non-cubic oxides and other extended solids, where $C_Q^{(49)}$Ti is found to range from 2.6 to 24.0 MHz. Similarly, in our $^{91}$Zr SSNMR study of bis-Cp zirconocene dihalide complexes, we found that $C_Q^{(91)}$Zr was relatively small compared to those of oxides and related systems (unpublished results; publication forthcoming). This indicates that the ground-state electronic environment at the metal atoms in d$^0$ metalloocene halide complexes is of comparatively higher spherical symmetry than that of the metal oxides.

Titanium CSA has previously been observed for several titanates ($\Omega = 22–180$ ppm) and the rutile phase of TiO$_2$ ($\Omega = 30$ ppm). Furthermore, our previous $^{91}$Zr SSNMR studies of zirconocenes, $^{115}$Sc SSNMR study of coordination complexes, and extensive $^{51}$V SSNMR studies of Polenova et al. have indicated that CSAs are substantial for the nuclei of the elements directly adjacent to Ti in the periodic table. In order to measure the CS tensor parameters, the span ($\Omega$), and skew ($\kappa$), static $^{47/49}$Ti SSNMR spectra of 1–4 were acquired at 21.1 and 9.4 T (Figure 2). The static spectra also serve to confirm EFG tensor parameters isolated from MAS spectra and allow for the determination of the Euler angles which describe the relative orientation of the EFG and CS tensors in each complex.

The appearance of the static spectra is indicative of the presence of substantial titanium CSA (Figure 2); it is not possible to simulate the static powder patterns using only the quadrupolar interaction (Figure S1, Supporting Information).
For all static spectra, the $^{47}\text{Ti}$ and $^{49}\text{Ti}$ powder patterns are observed to overlap, except for the spectrum of 3 acquired at 21.1 T. Overlap of the patterns can complicate simulations of the static spectra; however, with spectra from two magnetic fields, it is possible to obtain reasonably accurate measurements of the CS tensors. If more accurate measurements of the CS tensors and Euler angles are desired, QCPMG experiments which employ pulses with nutation angles designed to give a spectrum with only one of the $^{47/49}\text{Ti}$ nuclei may be employed. However, acquisition times for the static spectra were significantly longer than those for the MAS spectra due to much wider dispersion of the signal intensity in the former. At 21.1 T, static echo spectra were acquired in 3−20 h, while at 9.4 T, DFS−echo and DFS−QCPMG pulse sequences were used, with experiment times on the order of days.

From the static spectra, $\Omega$ is found to range from 85 (3) to 650 ppm (4). The $\Omega$ of 1 is greater than that of 2 (Cp vs Cp*), while for 3 and 4, the opposite is observed. The value of $\Omega$ for
4 is substantially larger than those of the other complexes, as well as those previously reported for other systems \( (\Omega \leq 180 \text{ ppm}) \). As mentioned above, the MAS spectrum of 4 possesses a number of intense spinning sidebands not observed in any of the other MAS spectra, consistent with this large CSA. SIMPSON simulations of the \(^{47/49}\text{Ti}\) MAS spectra with variable values of \( \Omega \) confirm the unusually large value of \( \Omega = 650 \text{ ppm} \) (Figure S2, Supporting Information).

The values of \( \kappa \) are close to \(+1\) for 1, 3, and 4, indicating that the CS tensors are all nearly axially symmetric (i.e., \( \delta_{11} \approx \delta_{22} \), and \( \delta_{33} \) is the distinct component of each CS tensor). Axial symmetry of the CS tensor is expected for \( \kappa \) calculations yield accurate values of \( \delta_{iso} \), and correctly predicting the symmetry of the CS tensor \( \kappa \) for 1, 2, and 4. While the calculations do not accurately predict the values of \( \Omega \), they do correctly predict the relative values for complexes 1–4 (i.e., \( \Omega \) for 4 > 1 > 2 > 3). B3LYP calculations yield accurate values of \( \delta_{iso} \), however, calculated values of \( \Omega \) and \( \kappa \) show poor agreement with experimental values.

Both RHF and B3LYP calculations yield \( C_Q \) and \( \eta_Q \) values which show relatively poor agreement with the experimental data. The calculations are able to correctly predict that \( C_Q \) is relatively small for 1–4; however, they are unable to predict the relative magnitudes of \( C_Q \) within the series. Accurate calculations of \(^{45}\text{Sc}\) and \(^{51}\text{V}\) EFG tensor parameters have previously been demonstrated \(^{65–67,69,73}\) and Ti is a relatively light element for which relativistic effects should be minimal. This suggests that calculations of titanium EFG tensors should be straightforward. It may be that because \( C_Q \) is relatively small for 1–4, minor errors in the calculated EFG tensor principal components \( (V_i) \) lead to substantial errors in both \( C_Q \) and \( \eta_Q \). Periodic plane-wave DFT calculations were also attempted for 1–4 (Table S5, Supporting Information); however, the calculated NMR tensor parameters also show poor agreement with experiment. All of this data suggest that more quantum chemical methods and functionals should be tested in the future in order to identify suitable methods for calculations of \(^{47/49}\text{Ti}\) NMR tensor parameters.

Finally, we present calculated EFG and MS tensor orientations for 1–4 (Figure 5). The tensor orientations provide insight into the origin of the observed anisotropic NMR interactions and allow for correlations between the NMR interaction tensors.
and molecular symmetry and structure. The orientation of the calculated EFG tensors in 1 and 2 are similar. The orientation of V_{33} perpendicular to the Cl–Ti–Cl plane arises because the electric field is large in the direction of the chloride ligands but small along the direction of the Cp ligands, giving rise to the large gradient. We have previously calculated that the magnitude of V_{33} significantly increases as the Zr–Cl bond lengths of Cp₂ZrCl₂ are shortened (unpublished results). In fact, the EFG and MS tensor orientations calculated for 1 are similar to those previously calculated for Cp₂ZrCl₂. At this time, we do not comment on the orientation of the EFG tensors for 3 and 4 as the calculated values of C₉ and η₉ show relatively poor agreement with experiment, though they are shown for reference in Figure 3.

For the Cp complexes 1 and 3, α₁₁, the least-shielded components of the MS tensors, are oriented toward the Cp ring carbon atom which lies above the Ti atom. For 1, α₁₁ is oriented such that it is approximately perpendicular to the Cl–Ti–Cl plane. Deshielding along this direction likely arises from mixing of high-energy occupied Ti–Cl bonding molecular orbitals with low-lying unoccupied d orbitals, both of which are located in the Cl–Ti–Cl plane. It is known that paramagnetic deshielding arises due to magnetic-field-induced mixing of occupied and virtual molecular orbitals, and deshielding contributions are largest in the direction perpendicular to the plane of mixing. In this regard, Hoffman has previously presented Hückel calculations which demonstrate that the valence molecular orbitals in titanocenes correspond to Cl–Ti–Cl bonding and π-bonding orbitals.

In 2, the most shielded component of the MS tensor, α₂₂, is directed toward a Cp* carbon atom which lies above the Ti atom, while in 4, α₂₂ is directed toward the centroid of the Cp* ligand. The distinct orientations of the MS tensors for 2 and 4 compared to 1 and 3 suggest that the energies and symmetries of the molecular orbitals are undoubtedly influenced by the increased basicity of the Cp* ligand in comparison to the Cp ligands. The orientations of α₁₁ and α₂₂ for both 2 and 4 suggest that deshielding primarily arises due to mixing of high-energy occupied or low-lying virtual orbitals of Ti–Cp* bonding character, which is also consistent with the observations of more positive δ_{iso} values for the Cp* complexes. As noted above, previous UV–vis measurements on 3 and 4 have found that λ_{max} occurs at longer wavelengths in the latter. If the MOs that make large anisotropic contributions to the nuclear magnetic shielding are the same MOs involved in optical transitions, then it is anticipated that decreased energy separations between these MOs will lead to a larger titanium CSA in 4 than that in 3.

Finally, EFG and CS tensor calculations were also performed for Cp₂TiMe₂ (5), which is a species important to catalytic processes involving titanocenes. In order to obtain active metallocene olefin polymerization catalysts, it is necessary to treat them with an activator or cocatalyst, such as methylaluminoxane (MAO). MAO abstracts the chloride ligands, replaces them with methyl ligands, and subsequently abstracts a methyl group to generate a catalytically active, coordinatively unsaturated, cationic metallocene. We have previously observed that Cp₂ZrMe₂ possesses relatively large values of C₀(⁴⁷/⁴⁹Ti) = 28.0 MHz and Ω(⁴⁷/⁴⁹Ti) = 1750 ppm (unpublished results). Consistent with these findings, quantum chemical calculations indicate that 5 has a very large C₀ (ca. 22–25 MHz) and CSA (Ω > 1800 ppm). From these calculations, it is clear that ⁴⁷/⁴⁹Ti SSNMR spectra very distinct from those of 1 and 2 would be observed for methyl titanocenes. However, due to the large C₀ and Ω values, 5 would be expected to possess a wide-line ⁴⁷/⁴⁹Ti SSNMR spectrum of ~300–400 kHz in breadth at 21.1 T, the acquisition of which would be difficult and beyond the scope of the current work.

MAS and static ⁴⁷/⁴⁹Ti SSNMR spectra were acquired for complexes 1–4, each yielding unique sets of EFG and CS tensor parameters. C₀ values for these complexes are small with respect to the known range of C₀ values. All of the complexes possess significant titanium CSAs, affording another set of NMR parameters which can be used to provide insight into their molecular and electronic structures. Quantum chemical calculations can accurately predict δ_{iso} for 1–4; however, further computational methods and basis sets must be evaluated in order to obtain better agreement between experimental and theoretical anisotropic ⁴⁷/⁴⁹Ti NMR parameters.

At an ultrahigh magnetic field of 21.1 T, it is possible to acquire MAS and static ⁴⁷/⁴⁹Ti SSNMR spectra in several hours with standard echo techniques. However, at a moderate magnetic field of 9.4 T, signal-enhancement techniques are required for the acquisition of ⁴⁷/⁴⁹Ti SSNMR spectra, and acquisition times remain on the order of days. The lengthy experiment times required to obtain adequate signal-to-noise ratios suggest that ⁴⁷/⁴⁹Ti SSNMR experiments on systems with low Ti contents, such as heterogeneous catalysts, would be very challenging. However, isotopic labeling in conjunction with cross-polarization (CP)-CPMG experiments at cryogenic temperatures could enable the acquisition of ⁴⁷/⁴⁹Ti spectra of heterogeneous catalysts. Ellis and Lipton have extensively utilized this approach to acquire SSNMR spectra of metalloproteins, which contain dilute concentrations of low-γ nuclei such as ²⁵Mg and ⁶⁷Zn. From ¹H could be especially beneficial for ⁴⁷/⁴⁹Ti, given that the maximum theoretical signal enhancement is γ₁H/γ₁⁴⁷Ti = −17.7. In addition, the differences in CP Hartmann–Hahn matching conditions which arise from the different spins of ⁴⁷Ti and ⁴⁹Ti could be useful for selectively exciting only one of the isotopes.

In an analogous manner to CP experiments, the development of dynamic nuclear polarization (DNP) experiments may also be very beneficial for SSNMR studies of unreactive nuclei such as ⁴⁷/⁴⁹Ti as the maximum signal enhancement is γ₁d/γ₁⁴⁷Ti = 11654. These signal-enhancing methods and the sensitivity of ⁴⁷/⁴⁹Ti NMR parameters to differences in molecular structure make ⁴⁷/⁴⁹Ti SSNMR very appealing for continued study of such systems.

**EXPERIMENTAL METHODS**

Samples of 1–4 were purchased from Strem Chemicals Inc. and used without further purification. All samples were finely ground into powders and packed into zirconia rotors or shortened glass NMR tubes under an inert N₂ atmosphere. ⁴⁷/⁴⁹Ti SSNMR spectra were acquired on a 21.1 T Bruker
Avance II NMR spectrometer at the Canadian National Ultra-high-Field Facility and a 9.4 T Varian InfinityPlus. A complete listing of experimental details is given in the Supporting Information (Tables S6–S9). Experiments at 9.4 T were conducted with Chemagnetics 5 mm HXY MAS, 4 mm HXY, and 5 mm static probes equipped with a Chemagnetics low-y tuning box. Experiments at 21.1 T were acquired with a Bruker 4 mm HX MAS probe and home-built single-channel static 5 mm and 7 mm probes. Pulse width calibrations were performed on saturated solutions of 1 dissolved in CH₂Cl₂. Chemical shifts were referenced to neat TiCl₄ [δiso(⁴⁹Ti) = 0.0 ppm] via an external standard of powdered SrTiO₃ [δiso(⁴⁹Ti) = −843 ppm].³³ Experiments at 21.1 T employed standard echo sequences for acquisition. Experiments at 9.4 T employed DFS–echo,⁸⁴,⁸⁵ or DFS–QCPMG,⁸⁶,⁸⁷ pulse sequences for signal enhancement. The Rose convention is used to describe the direction and order of the Euler angles which describe the CS and EFG tensor orientation.⁸⁸,⁸⁹ Analytical simulations of MAS and static ⁴⁹/⁵¹Ti SSNMR spectra were performed with the WSoilds program.⁹⁰ The SIMPSON program was employed for numerical simulations of the MAS ⁴⁹Ti SSNMR spectrum of 4 (Figure S2, Supporting Information).⁹¹

Quantum chemical calculations of NMR tensor parameters were performed with the Gaussian 03 software package and employed molecular coordinates for isolated molecules resolved from single-crystal X-ray diffraction structures.⁵⁴,⁹⁵–⁹⁵ In all cases, the hydrogen atoms were fixed to idealized positions prior to calculations. Both restricted Hartree–Fock (RHF) and hybrid density functional theory (B3LYP) calculations were performed.⁹⁶–⁹⁸ Several Ti basis sets were tested, and results from these calculations are given in the Supporting Information. The double-ζ basis set of Dunning was employed for Cl, and the 6-311G** basis set was employed for C and H. Additional ab initio plane-wave density functional calculations were performed using the CASTEP NMR program (Table S5, Supporting Information).¹⁰⁰,¹⁰¹

SUPPORTING INFORMATION AVAILABLE Additional quantum chemical calculation results, NMR experiment details, additional simulations of ⁴⁹/⁵¹Ti SSNMR spectra, and a complete author list for Gaussian 03. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author:
*To whom correspondence should be addressed. Fax: (519) 973-7098. E-mail: tschurko@u windsor.ca.

Present Addresses:
† Center of Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, FL 32310, U.S.A.

ACKNOWLEDGMENT A.J.R. thanks the Natural Science and Engineering Research Council (NSERC, Canada) for a graduate scholarship. R.W.S. thanks NSERC for research funding and also acknowledges the Canadian Foundation for Innovation (CFI), the Ontario Innovation Trust (OIT), and the University of Windsor for funding the solid-state NMR facility. R.W.S. also thanks the Ontario Ministry of Research and Innovation for an Early Researcher Award. Mr Ryan W. Mills is thanked for running preliminary Gaussian 03 calculations. This work was made possible by the facilities of the Shared Hierarchical Academic Research Computing Network (SHARCNET: www.sharcnet.ca). Dr. Victor Terskikh and Dr. Shane Pawsey are thanked for assistance with experiments conducted at 21.1 T at the Canadian National Ultrahigh-Field Facility. Access to the 900 MHz NMR spectrometer was provided by the National Ultrahigh-Field NMR Facility for Solids (Ottawa, Canada), a national research facility funded by the Canada Foundation for Innovation, the Ontario Innovation Trust, Recherche Quebec, the National Research Council Canada, and Bruker BioSpin and managed by the University of Ottawa (www.nmr900.ca). NSERC is acknowledged for a Major Resources Support grant.

REFERENCES


