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Published on Web 09/12/2006

Solid-State ^{139}La and ^{15}N NMR Spectroscopy of Lanthanum-Containing Metallocenes

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Lanthanide-containing metallocenes date back to the early 1950s, when Wilkinson reported the synthesis of compounds of the form $(C_5H_5)_3Ln$ (Ln = Sc, Y, La, Ce, etc.).[1] Initial development in this area was slow, due to the instability of these species; however, more recently, this area has shown spectacular growth, largely due to the unique structural and physical properties of these complexes, along with their novel reactivity and potential applications in catalytic processes.[2] X-ray crystallography has been the primary means of structural characterization for these systems. Solid-state NMR has been utilized less frequently since many of these metallocenes are paramagnetic; however, there are some reports of solid-state NMR of the metal nuclei in these systems (e.g., ^{171}Yb and ^{89}Y).[3]

Despite the high natural abundance (99.91%) of ^{139}La, solid-state ^{139}La NMR spectroscopy is a challenging endeavor since it is a quadrupolar nucleus (spin $I = 7/2$) with a reasonably large quadrupole moment (0.21 b) and low gyromagnetic ratio ($\gamma = 3.8085 \times 10^7$ rad T^{-1} s^{-1}), similar to ^{17}O. Central transition powder patterns can extend over hundreds of kHz, making routine MAS acquisitions impossible and static NMR experiments challenging.[4] Additionally, rapid quadrupolar relaxation and broad peak widths associated with ^{139}La nuclei in asymmetric environments make solution ^{139}La NMR experiments problematic.[5] Recently, the quadrupolar Carr−Purcell Meiboom−Gill (QCPMG) pulse sequence was reintroduced as a means of enhancing S/N for quadrupolar nuclei in solids.[6] QCPMG experiments can be used to acquire piecewise frequency-stepped sub-spectra, which are co-added or projected to form the complete ultra-wide-line (UW) spectrum, from which NMR parameters can be obtained.[7]

Herein we present the first solid-state ^{139}La NMR spectra of lanthanum-containing metallocenes, including Cp_3La, $Cp^{\dagger}_3La$, $[Cp^*_2La]^+[BPh_4]^-$, and ^{15}N-enriched $[Cp^{\dagger}_2La(THF)]_2{}^{15}N_2$,[8] where $Cp = C_5H_5^-$, $Cp^{\dagger} = C_5Me_4H^-$, and $Cp^* = C_5Me_5^-$. Broad spectra, with breadths ranging from 600 kHz to 2.5 MHz, are acquired with QCPMG techniques at 9.4 T. The spectra show remarkable sensitivity to changes in metallocene structure. In addition, we report the first NMR measurement of a nitrogen chemical shift (CS) tensor for dinitrogen bound side-on to a metal atom, via ^{15}N CP/MAS NMR of $[Cp^{\dagger}_2La(THF)]_2{}^{15}N_2$. Preliminary calculations of ^{139}La electric field gradient (EFG) and nitrogen CS tensors are used to rationalize the origin of the NMR parameters.

Experimental UW−QCPMG ^{139}La NMR spectra and simulated manifolds[9] (Figure 1A) for Cp_3La reveal $C_Q = 44(3)$ MHz, $\eta_Q = 0.45(5)$, and $\delta_{iso} = -500(50)$ ppm (Table S1, Supporting Information). The large C_Q arises from the nonspherical environment about the central La atom, which is located in a "flattened" pyramidal environment (i.e., the sum of $Cp_{cent}-La-Cp_{cent}$ angles is 348°).[10] The largest component of the EFG tensor, V_{33}, should be directed along the 3-fold molecular axis.[11] The value of η_Q indicates that the EFG tensor is not axially symmetric since one of the Cp rings forms a weak η^1-coordination with a neighboring Cp_3La molecule. Single-crystal XRD (Supporting Information) confirms that there are two crystallographically distinct La sites[10] ($Cp_{cent}-La$ distances are 2.572, 2.579, and 2.601 Å and 2.551, 2.576, and 2.626 Å for sites 1 and 2, respectively), which can give rise to distinct EFG tensor parameters. First-principles calculations confirm this, along with the proposed EFG tensor orientation (Figure 2A); however, theoretical EFG tensors are close to axial symmetry since calculations are only conducted upon a single Cp_3La unit. The ^{139}La NMR spectrum undoubtedly arises from two unresolvable overlapping patterns with slightly differing values of C_Q and η_Q, as well as similar chemical shifts (Figure S1). Lanthanum chemical shift anisotropy (CSA) is not considered, as its effects on spectral appearance are minimal in all cases at 9.4 T (Figures S2 and S3).

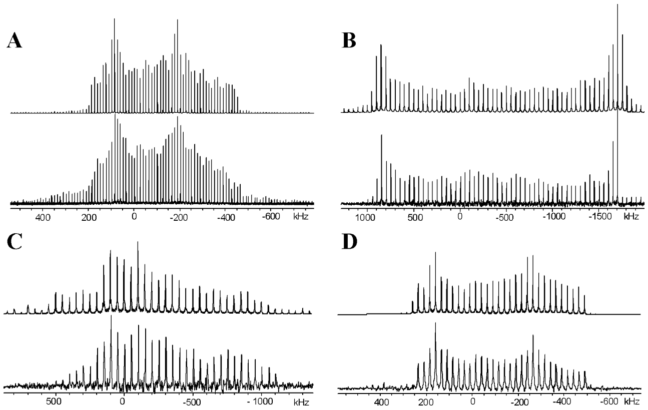

Figure 1. Experimental (bottom) and numerically simulated (top) solid-state ^{139}La UW−QCPMG NMR spectra of (A) Cp_3La, (B) $Cp^{\dagger}_3La$, (C) $[Cp^*_2La]^+[BPh_4]^-$, and (D) $[Cp^{\dagger}_2La(THF)]_2{}^{15}N_2$. Satellite transitions are partially observed at the edges of the central transition pattern in (A).

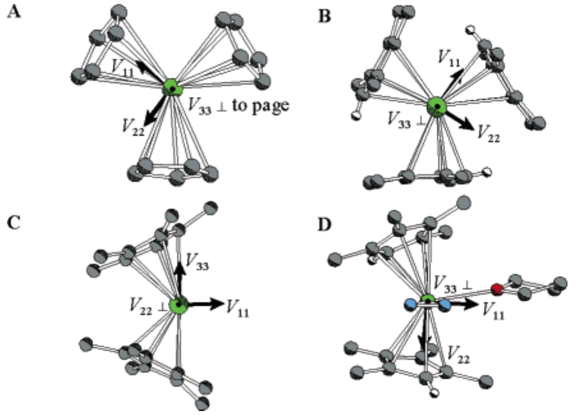

Figure 2. Theoretically predicted ^{139}La EFG tensor orientations, compounds as denoted in Figure 1. EFG tensor components are defined as $|V_{11}| \leq |V_{22}| \leq |V_{33}|$, where the quadrupolar coupling constant is $C_Q = eQV_{33}/h$, $\eta_Q = (V_{11} - V_{22})/V_{33}$, and eQ is the nuclear quadrupolar moment.

The ^{139}La NMR spectrum of $Cp^{\dagger}_3La$ (which has one La site) reveals the largest known $C_Q(^{139}La)$ to date ($C_Q = 105(2)$ MHz) and an axially symmetric EFG tensor (Figure 1B). The increase in

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10.1021/ja0645180 CCC: $33.50

C_Q compared to that of Cp_3La results largely from the perfectly trigonal planar arrangement of Cp′ ring centroids about La in the former (the sum of $Cp^\dagger_{cent}$−La−$Cp^\dagger_{cent}$ angles is 360°) and pyramidal arrangement in the latter.[12] The $Cp^\dagger_{cent}$−La distances are all 2.575 Å, similar to those of $LaCp_3$. Further, the location of the La atom results in higher magnetic shielding of the ^{139}La nucleus ($\delta_{iso} = -1100(100)$ ppm). DFT EFG calculations are in qualitative agreement with experiment, again predicting the orientation of V_{33} along the 3-fold molecular axis.

The ^{139}La NMR spectrum of $[Cp^*{}_2La]^+[BPh_4]^-$ is distinct in appearance from the tris-Cp′ systems (Figure 1C). The C_Q (61(2) MHz) is larger than that in Cp_3La; however, $\eta_Q = 0.8(1)$, meaning that the EFG tensor has nonaxial symmetry, and that its smallest component, V_{11}, should be oriented in a unique environment. In addition, the chemical shift is higher ($\delta_{iso} = +100(50)$ ppm), indicating that the ^{139}La nucleus is deshielded compared to both tris-Cp′ species. At the time of these experiments, there was no reported crystal structure; thus, the NMR parameters and ab initio calculations were used to hypothesize a molecular structure: the C_Q indicates an increasingly nonspherically symmetric environment compared to that of Cp_3La, with only two Cp* rings η^5-coordinated. The η_Q suggests a bent, nonaxial structure, with V_{11} oriented away from the Cp* rings, possibly along a 2-fold rotational axis. The "open face" of the molecule is consistent with the higher frequency chemical shift. The recently acquired crystal structure for this species (Table S2) is congruent with this structural interpretation. Preliminary theoretical parameters for the lone $[Cp^*{}_2La]^+$ cation are not in good agreement with experiment, though this may be improved with larger scale calculations including the $[BPh_4]^-$ anion. However, the predicted tensor orientation (Figure 2C) is in agreement with our earlier hypothesis.

Simulation of the ^{139}La NMR spectrum of $[Cp^\dagger{}_2La(THF)]_2{}^{15}N_2$ (Figure 1D) reveals NMR parameters intermediate to those of $Cp^\dagger{}_3$-La and $[Cp^*{}_2La]^+[BPh_4]^-$, with $C_Q = 50(1)$ MHz, $\eta_Q = 0.32(3)$, and $\delta_{iso} = -150(50)$ ppm. A single crystallographically distinct La site is coordinated by two η^5-$Cp^\dagger$ rings and a proximate THF solvent molecule. The nonaxial η_Q indicates that the three EFG tensor components are distinct and, therefore, oriented in dissimilar environments. The chemical shift indicates that the ^{139}La nucleus is not as shielded as in the planar tris-Cp′ species, but also not as deshielded as the bis-Cp* cation, consistent with a bent molecule undergoing "side-on" interactions with the dinitrogen. The theoretical EFG tensors have V_{33} oriented such that it almost bisects the dinitrogen, and V_{11} oriented near (ca. 20°) a La−O bond of the THF (Figure 2D—note, the second metallocene unit is not shown for clarity).

Solid-state NMR is very useful for probing the hapticity of bonding interactions between metal nuclei and a variety of ligands.[13] The ^{15}N CP/MAS NMR spectra of $[Cp^\dagger{}_2La(THF)]_2{}^{15}N_2$ (Figure 3A) reveal $\delta_{iso} = +877(5)$ ppm, $\Omega = 1598(50)$ ppm, and $\kappa = -0.4(1)$, with the span, $\Omega = \delta_{11} - \delta_{33}$, and the skew, $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$. The CS tensor is very different from that of solid dinitrogen ($\delta_{iso} = +450$ ppm, $\Omega = 603$ ppm, and $\kappa = +1.0$),[14] where with the most shielded component, δ_{33}, is directed along the molecular axis, and $\delta_{11} = \delta_{22}$ due to axial symmetry (Figure 3B). The increased span, high-frequency isotropic shift, and the nonaxial symmetry of the CS tensor all arise from bridging η^2-bonding between the La atoms and N_2 (lengthening of the N≡N bond from 1.1 Å in N_2(s) to 1.24 Å in this complex also has a minor effect on tensor parameters). Theoretical nitrogen CS tensors reveal that δ_{33} is still directed along the N≡N axis, with δ_{11} oriented in the LaNLaN plane. The component that changes the most is δ_{11}, which is the direction of the side-on N_2 bonding interaction. Detailed calculations of CS tensors and analysis of contributing MOs are underway, which will enable the correlation of bonding with the nuclear magnetic shielding properties.

The preliminary data presented herein represent the first direct acquisitions of NMR tensor parameters of quadrupolar metal lanthanide nuclei in organometallic complexes. The ^{139}La EFG tensors and chemical shifts are extremely sensitive to molecular symmetry and the nature of the surrounding ligands and can be interpreted in a chemically intuitive manner. The nitrogen CS tensor of dinitrogen bound side-on to a metal center holds much diagnostic promise for probing the existence and nature of such bonding in molecules capable of fixing N_2. Future experimental and theoretical investigations will shed much light on the molecular structure of analogous systems for which crystal structures are unavailable (e.g., noncrystalline or disordered).

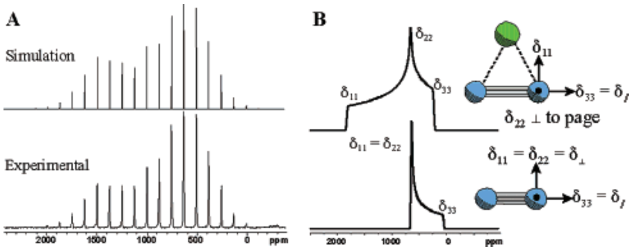

Figure 3. (A) ^{15}N CP/MAS NMR spectrum of $[Cp^\dagger{}_2La(THF)]_2{}^{15}N_2$. (B) Nitrogen CS tensors in $[Cp^\dagger{}_2La(THF)]_2{}^{15}N_2$ (top) and dinitrogen (bottom).

Acknowledgment. R.W.S. thanks Imperial Oil and NSERC (Canada) for funding, as well as the Canadian Foundation for Innovation (CFI), the Ontario Innovation Trust (OIT), and the University of Windsor. W.J.E. thanks the NSF (U.S.) for support. Charles L. B. Macdonald and Cory M. Widdifield (Windsor) are acknowledged for technical support. Kevin A. Miller and Joseph W. Ziller are thanked for crystal data of $[Cp^*{}_2La]^+[BPh_4]^-$.

Supporting Information Available: Additional spectra and simulations, ab initio data, and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0645180