Ultrahigh-field NMR Spectroscopy

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Application of Ultrahigh-Field ^{59}Co Solid-State NMR Spectroscopy in the Investigation of the 1,2-Polybutadiene Catalyst $[Co(C_8H_{13})(C_4H_6)]$**

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Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

Syndiotactic 1,2-polybutadiene (sPBD) is an important industrial polymer with a wide variety of uses;[1] however, there is only a very limited number of catalysts currently capable of producing this polymer with a high degree of syndiotacticity.[2] Only one such catalyst has been structurally characterized, when in 1967 Natta et al. published a low-resolution crystal structure of the cobalt complex $[Co(\eta^3{:}\eta^2\text{-}C_8H_{13})(\eta^4\text{-}C_4H_6)]$ (**1**).[3] Since then, no spectroscopic data have been published on this or any other sPBD catalyst, a fact which frustrates discussions on the mechanism of the reaction, though the mechanism of syndiotactic formation of the larger 1,3-dienes is quite well understood.[4]

This is especially unfortunate in the case of **1**, which requires the addition of CS_2 to increase the formation of syndiotactic polymer,[5,6] as there are many possibilities as to how this molecule may be altering the catalyst behavior.[7] In sharp contrast to the sPBD systems, the formation of 1,4-polybutadiene has been fully explored by Taube and Tobisch,[8] and recent work has experimentally confirmed the mechanism.[9] Thus, the application of spectroscopic tools to **1** will greatly aid in our understanding of this and other catalysts. Solution-state NMR studies would provide the best insights into the mechanism of the homogeneous catalyst **1**; however, information garnered from solid-state studies may also provide crucial insights into the activity of this unique system. ^{59}Co solid-state NMR (SSNMR) spectroscopy has been used in the past to investigate various small molecules, biological model systems, and homogeneous catalysts;[10–14] only recently has the potential of ultrahigh-field ^{59}Co SSNMR spectroscopy of powdered samples been demonstrated in cases where the cobalt nucleus experiences a very large electric field gradient (EFG).[15] Most of these previous SSNMR studies, however, focussed on the +III oxidation state of Co. It is clear that this technique has the potential to become a valuable new tool for the investigation of catalytically important Co complexes with diamagnetic electron configurations.

Following a modified literature procedure,[6] single crystals of **1** were isolated and an X-ray structure determination was carried out. The structure of **1** is in agreement with the original Natta formulation, in which the Co^I center is located in a distorted square-pyramidal coordination environment (Figure 1). The basal plane comprises an η^4-bound butadiene molecule [C(1)–C(2) and C(3)–C(4)] and the allylic portion

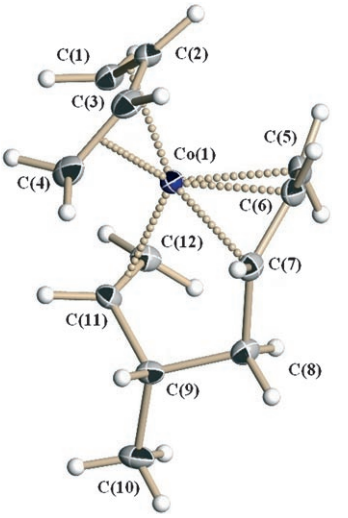

Figure 1. Crystal structure of **1** with 30% thermal ellipsoids. Selected bond lengths [Å]: Co(1)–C(1) 2.096(3), Co(1)–C(2) 2.027(3), Co(1)–C(3) 2.028(3), Co(1)–C(4) 2.119(3), Co(1)–C(11) 2.126(3), Co(1)–C(12) 2.116(3), Co(1)–C(5) 2.104(3), Co(1)–C(6) 2.010(3), Co(1)–C(7) 2.105(3).

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[C(5)−C(7)] of a dimerized butadiene, whereas the apical position is filled by an η^2-bound alkene [C(11)−C(12)] of the same dimerized butadiene. The ^{13}C CPMAS NMR spectrum of solid **1** is consistent with the molecular structure determined by X-ray diffraction (see Supporting Information). The formal oxidation state of the cobalt center, for which zero had also been proposed,[16] is clearly +I. When single crystals of **1** were dissolved in common NMR solvents, even at −80 °C, poorly resolved NMR spectra invariably resulted, likely as a result of accelerated relaxation owing to paramagnetic species (Figure 2 top).

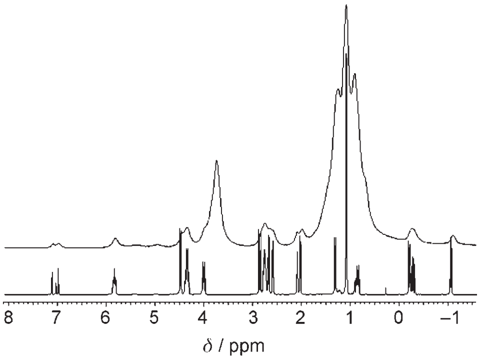

Figure 2. Comparison of a typical paramagnetically broadened ^{1}H NMR spectrum (top) and a spectrum of purified **1** (bottom).

Recrystallization of **1** from pentane at −35 °C resulted in the formation of a small quantity of X-ray quality crystals of the Co^{II} complex [Co(EtOH)$_6$][CoCl$_4$] (**2**), which is isostructural to the previously reported [CoBr$_4$]$^{2-}$ derivative.[17] It was thus apparent that small amounts of the paramagnetic Co^{II} complex were interfering with the solution NMR analysis of **1**. It was found that **1** was stable on silica for very short periods of time if kept under an inert atmosphere and at a reduced temperature. Therefore, purification of **1** was performed by flash column chromatography at −40 °C over a minimal amount of silica. The resulting single crystals of **1** produced identical X-ray structural data, but more importantly, led to fully diamagnetic NMR spectra (Figure 2 bottom). Although the spectra were somewhat complex, since all hydrogen atoms except those of the CH$_3$ group are in asymmetric environments, a full assignment was nevertheless possible using common NMR experiments. These assignments were corroborated by quantum-chemical calculations (see Supporting Information). Complex **1** is stable for several hours at −10 °C in solution; however, it degrades rapidly in a matter of minutes at room temperature to give paramagnetically broadened NMR spectra.

Given the need for detailed spectroscopic information for **1**, we characterized it by ^{59}Co solid-state NMR spectroscopy. Although ^{59}Co ($I = 7/2$) is a relatively receptive NMR nucleus, large EFGs in compounds lacking high symmetry at cobalt result in large second-order quadrupolar broadenings of the central transition (CT, $+1/2 \leftrightarrow -1/2$).[10] These broadenings can be on the order of megahertz, rendering NMR studies in moderate magnetic fields challenging. However, when the strength of the external magnetic field is increased, the role which the quadrupolar interaction plays in determining the resulting isotropic frequency associated with the CT, as well as the orientation-dependent broadening of the CT, is reduced.[18] Therefore the study of **1** necessitated the highest possible available field strength.

The ^{59}Co NMR spectra of solid powdered **1** acquired in a magnetic field of 21.1 T (^{1}H frequency of 900 MHz) are shown in Figure 3. We were able to acquire both quadrupolar-echo and quadrupolar Carr–Purcell–Meiboom–Gill (QCPMG) spectra.[19] Both spectra required a stepped-frequency approach given that the breadth of the spectrum of the CT is 1.14 MHz. The fact that we were able to obtain a QCPMG spectrum speaks for the relatively long T_2 in this sample, which in turn supports the conclusion that a pure sample of **1** free of paramagnetic impurities was indeed prepared. Although the quadrupolar-echo spectrum provides a more well-defined powder pattern, it should be noted that the QCPMG spectrum was acquired in considerably less time (i.e., 80 min vs. several hours). Given that a relatively large ^{59}Co chemical shift anisotropy (CSA) was anticipated for **1**, care was exercised in the simulation of the experimental spectrum. Since there are no symmetry elements to enforce particular relative tensor orientations (as was the case in the work of Ooms et al.),[15] we combined our experimental spectrum with DFT calculations of the EFG and nuclear magnetic shielding tensors to reliably determine the experimental tensor information. Bühl and co-workers have recently demonstrated the utility of GIAO-B3LYP computational studies of the ^{59}Co magnetic shieldings and chemical

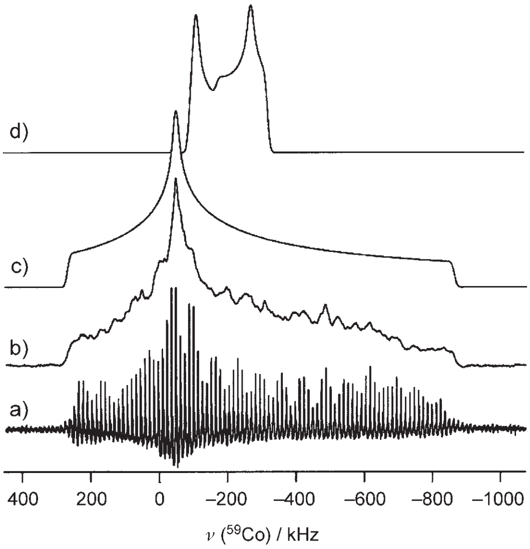

Figure 3. a) Experimental QCPMG spikelet-echo solid-state ^{59}Co NMR spectrum of **1** acquired at 21.1 T and 5 °C. The spectrum was acquired under static conditions and is the sum of ten frequency-stepped spectra. b) Quadrupolar-echo ^{59}Co NMR spectrum acquired under the same conditions as (a); this spectrum is the sum of two frequency-stepped spectra. c) Best-fit simulated spectrum generated by using the "experimental" parameters given in Table 1. d) Same as (c) but under the assumption of no cobalt CSA ($\Omega = 0$).

Table 1: Experimental and calculated ^{59}Co quadrupolar and chemical shift (and magnetic shielding) interaction tensors for **1**.[a]

	C_Q [MHz]	η_Q	σ_{iso} [ppm]	σ_{iso} (ref) [ppm]	δ_{iso} [ppm]	Ω [ppm]	κ [ppm]	α [°]	β [°]	γ [°]
B3LYP/6-31G*	−72.7	0.12	−4624.7	−7087.2	−2445.2	6151.5	0.07	265	57	2
B3LYP/6-311G*	−81.5	0.19	−4783.5	−7136.7	−2336.5	6002.5	0.11	261	62	1
B3LYP/6-311+G*	−81.2	0.21	−4697.2	−7039.4	−2325.8	5790.0	0.13	263	63	1
B3LYP/6-311++G**	−81.0	0.21	−4729.2	−7039.4	−2294.1	5829.1	0.13	262	63	1
PBEPBE/6-31G*	−54.4	0.16	−3245.9	−4687.6	−1435.0	4605.3	0.24	277	45	1
PBEPBE/6-311G*	−56.1	0.19	−3353.9	−4781.9	−1421.2	4441.7	0.30	270	49	−1
PBEPBE/6-311+G*	−55.1	0.20	−3258.9	−4743.5	−1477.6	4224.3	0.33	268	51	−1
PBEPBE/6-311++G**	−54.9	0.19	−3283.3	−4743.5	−1453.3	4254.9	0.33	267	51	−1
ADF/TZP	−55.5	0.12	−3193.3	−4529.4	−1330.1	4220.4	0.31	267	52	0
ADF/TZ2P	−55.2	0.12	−3179.2	−4542.5	−1357.1	4212.0	0.32	264	51	0
Experiment	±(56±5)	0.20±0.15	–	–	−807±100	5260±500	0.12±0.10	272	60	0

[a] Conventions are as follows: $C_Q = eV_{33}Q/h$ and $\eta_Q = (V_{11} - V_{22})/V_{33}$, where $|V_{33}| \geq |V_{22}| \geq |V_{11}|$; $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$ where $\delta_{11} \geq \delta_{22} \geq \delta_{33}$; $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ where $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$; $\Omega = \sigma_{33} - \sigma_{11}$; $\kappa = 3(\sigma_{iso} - \sigma_{22})/\Omega$; $\delta_{iso}(\text{calcd}) = [\sigma_{iso}(\text{ref}) - \sigma_{iso}(\text{calcd})]/[1 - \sigma_{iso}(\text{ref})]$. See reference [28] for an explanation of the Euler angles.

shifts in a series of small cobalt-containing molecules.[20] Our calculated data as well as our experimental values are summarized in Table 1.

The tensor information from the calculations reproduces the experimental spectra particularly well, and only small adjustments of the DFT-computed values were required to obtain the best-fit to the experiment (Figure 3c). The experimental values reported in Table 1 are the result of a novel combined experimental–theoretical analysis, since there are not enough experimental data to uniquely determine all of the tensor parameters. The analysis therefore nicely demonstrates the utility of the DFT methods in the interpretation of experimental NMR spectra. The spectrum is dominated by the CSA of the cobalt center, and the spectral simulations are indeed most sensitive to the CS principal components and to the Euler angles α and β. According to the calculations, the largest component of the EFG tensor lies approximately along the Co–H(6a) internuclear vector, whereas the largest component of the shielding tensor (σ_{33}) lies approximately perpendicular to the basal plane formed by the C(1)–C(4) atoms.

It is informative to discuss the ^{59}Co quadrupolar and chemical shift data for **1** in the context of existing data for Co^{III} complexes.[10,11] Much of the quadrupolar coupling constant (C_Q) data originates from nuclear quadrupole resonance (NQR) studies;[21] however, recent work using SSNMR spectroscopy has also yielded several values. For relatively symmetric complexes, C_Q can be less than 1 MHz,[10] whereas NQR studies have revealed values well in excess of 100 MHz. The value obtained herein for **1**, ±(56±5) MHz, is therefore intermediate in magnitude compared to all known values of C_Q(^{59}Co). With some exceptions, for example, the value of 163(2) MHz for cobalt dicarbollide complexes[15] and the value of 45.0(3) MHz for [(Py)$_2$Co-phthalocyanine]Br (Py = pyridyl),[12] however, the value obtained for **1** is particularly large relative to those measured previously by powder SSNMR spectroscopy. The span of the CS tensor for **1** is also quite large with respect to that for other cobalt compounds, and comparable to the value of 5650(100) ppm reported for [CoCp$_2$][PF$_6$] (Cp = cyclopentadienyl).[15]

The large paramagnetic deshielding of the σ_{11} component of the cobalt shielding tensor in **1** is well explained upon examination of the calculated frontier MOs (Figure 4). According to Jameson and Gutowsky[22] and Schreckenbach,[23] application of the magnetic operator M_s to the HOMO results in favorable overlap with the LUMO+2; the energy gap is only 2.2 eV (PBEPBE/6-311++G** level). The σ_{22} component is dominated by contributions from a similar pair of occupied and virtual orbitals with an associated energy gap of 2.8 eV. Previous work has demonstrated the utility of a similar orbital analysis of the isotropic chemical shifts for Co^I and Co^{III} complexes.[24] The present analysis demonstrates the additional insight into the electronic structure about Co^I as a result of an analysis of the complete orientation-dependent shielding tensor.

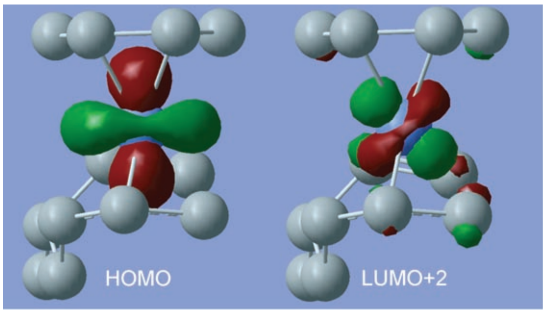

Figure 4. Calculated (PBEPBE/6-311++G**) isosurfaces for the orbitals most strongly responsible for the large deshielding of the σ_{11} component of the ^{59}Co magnetic shielding tensor. Shown here are the HOMO and the LUMO+2, separated by 2.2 eV; the view is along the direction of the eigenvector corresponding to σ_{11}. The action of the magnetic operator M_s on the HOMO results in an orbital with favorable overlap with the LUMO+2, resulting in paramagnetic deshielding.

It is important to point out the pioneering single-crystal work by Spiess and Sheline on trigonal cobalt carbonyls in which cobalt is in the +I oxidation state,[25] and Hirschinger and co-workers' powder NMR studies of mixed-metal clusters.[26] Interestingly, Spiess et al. noted a linear correlation between the value of $C_Q(^{59}\text{Co})$ and the value of $\sigma_{zz}-\sigma_{iso}$ in a series of closely related pseudo-octahedral Co^{III} complexes.[27] On the basis of the limited data now available for Co^{I} complexes, no such correlation appears to exist; however, this is not surprising given the large structural and symmetry differences between **1** and the trigonal cobalt carbonyls $(X_3M)[Co(CO)_4]$, $MX_3 = GeI_3, SnBr_3, Sn(C_6H_5)_3)$.

In conclusion, the purification of the Natta complex **1** has for the first time in 40 years allowed spectroscopic data to be collected that can be directly used in structure determination studies. We have demonstrated that ultrahigh-field ^{59}Co solid-state NMR spectroscopy and complementary quantum-chemical calculations can be used as tools for investigating highly relevant organometallic complexes such as thermally sensitive compounds as in the present case. To our knowledge this study represents the first powder NMR spectroscopic characterization of the EFG and CS tensors for a solid Co^{I} complex. The present work will allow meaningful investigations into the mechanism by which syndiotactic 1,2-polybutadiene is produced by this system. Work is currently underway to explore the interaction of CS_2 with the cobalt complex **1**.

Experimental Section

The synthesis of **1** and accompanying characterization data along with the details for the solid-state NMR experiments and quantum-chemical calculations are given in the Supporting Information.

Crystal data for **1**: $C_{12}H_{19}Co$, $M_r = 222.20\ \text{g mol}^{-1}$, orthorhombic, space group $P2(1)2(1)2(1)$, $a = 7.27940(10)$, $b = 11.3268(2)$, $c = 13.1054(3)$ Å, $V = 1080.57(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.366\ \text{Mg m}^{-3}$; 10599 reflections were collected, of which 2475 were unique ($R_{int} = 0.0705$), $R_1[I>2\sigma(I)] = 0.0361$, $wR_2 = 0.0702$, $\mu(\text{Mo}_{K\alpha}) = 1.540\ \text{mm}^{-1}$, GOF = 1.074.

Crystal data for **2**: $C_{12}H_{36}Cl_4O_6Co$, $M_r = 536.07\ \text{g mol}^{-1}$, orthorhombic, space group *Pbca*, $a = 14.1033(2)$, $b = 14.46230(10)$, $c = 20.2906(3)$ Å, $V = 4997.09(11)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.425\ \text{Mg m}^{-3}$; 28471 reflections were collected, of which 3054 were unique ($R_{int} = 0.1095$), $R_1[I>2\sigma(I)] = 0.0587$, $wR_2 = 0.1146$, $\mu(\text{Mo}_{K\alpha}) = 1.775\ \text{mm}^{-1}$, GOF = 1.087.

CCDC-660516 (**1**) and CCDC-660592 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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