ORGANOMETALLICS

Solid-State ^{45}Sc NMR Studies of Cp*$_2$Sc−OR (R = CMe$_2$CF$_3$, CMe(CF$_3$)$_2$, C(CF$_3$)$_3$, SiPh$_3$) and Relationship to the Structure of Cp*$_2$Sc-Sites Supported on Partially Dehydroxylated Silica

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ABSTRACT: Cp*$_2$Sc−OR (R = CMe$_2$CF$_3$, CMe(CF$_3$)$_2$, C(CF$_3$)$_3$, SiPh$_3$) was synthesized to determine how the alkoxide affects the quadrupole coupling (C$_Q$) obtained from solid-state ^{45}Sc{^{1}H} NMR spectroscopy. These alkoxides are characterized by large (>29 MHz) C$_Q$ values, which are similar to C$_Q$ values obtained for Cp*$_2$Sc−R (R = Me, Et, Ph) and Cp*$_2$Sc−X (X = F, Cl, Br, I) but significantly larger than C$_Q$ values obtained for Cp*$_2$ScX(THF). The NMR properties from these alkoxides were used to understand the NMR properties of Cp*$_2$Sc-supported on silica partially dehydroxylated at 700 °C. This material contains two species from the solid-state ^{45}Sc{^{1}H} NMR spectra assigned to Cp*$_2$ScOSi≡ (**5a**) and Cp*$_2$Sc(OSi≡)O(SiO$_x$)$_2$ (**5b**). The solid-state ^{45}Sc{^{1}H} NMR spectrum of **5a** is considerably broader than **5b**, which relates to the magnitude of the quadrupolar coupling (C$_Q$) in these two different sites. Density functional theory (DFT) optimized structures of Cp*$_2$Sc−OR and small cluster approximations of **5a** and **5b** follow similar trends as the experimental C$_Q$ values for this family of organoscandium complexes. Analysis of the origin of C$_Q$ using DFT methods shows that σ- and π-bonding orbitals from the Sc−O bond in Cp*$_2$Sc−OR and **5a** are major contributors to C$_Q$, whereas different orbitals contribute to C$_Q$ in **5b**. These studies show that quadrupolar solid-state NMR spectroscopy can distinguish between surface sites on partially dehydroxylated silica.
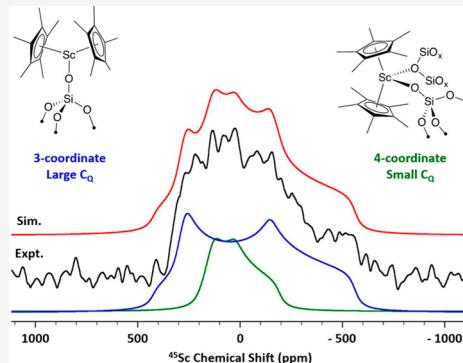
INTRODUCTION

Many of the largest scale catalytic reactions in industry use heterogeneous catalysts. These catalysts are usually thought to contain organometallic intermediates, either on a metal or an oxide surface.[1] Understanding these catalysts at a molecular level is challenging because these complex materials often have very low active site loadings, which complicates analysis of spectroscopic data when attempting to determine active site structure. For these reasons, introducing molecular precision on oxides surfaces is a long-term interdisciplinary challenge. One of the most familiar ways to address this challenge is to incorporate organometallic complexes onto a partially dehydroxylated support, Scheme 1.[2−9]

The proton transfer reaction in Scheme 1 results in formation of alkane and a well-defined supported organometallic that can form a covalent M−O$_x$ (O$_x$ = surface oxygen)

or an electrophilic M---O$_x$ ion pair. The nature of the support controls the formation of M−O$_x$ or M---O$_x$ ion pairs. Neutral supports (SiO$_2$, Al$_2$O$_3$) used in this reaction tend to form M−O$_x$. More Bronsted acidic supports, such as zeolites or sulfated oxides, usually form M---O$_x$ ion pairs.[10−21]

The most common method to determine structure in well-defined organometallics supported on oxides is solid-state NMR spectroscopy.[22,23] Magic angle spinning (MAS) is now a common technique, and moderate spinning speeds (∼10 kHz) are sufficient to suppress some of the anisotropic interactions in the solid state that can complicate analysis of NMR spectra. At these spinning speeds, the spectra of typical spin 1/2 nuclei (^{31}P, ^{13}C, ^{29}Si, etc) usually show isotropic chemical shift values that can be interpreted in similar ways to signals obtained from solution NMR spectra.

A few representative examples showing how analysis of isotropic NMR chemical shift can give information about the structure of surface species are shown in Figure 1. The isotropic ^{29}Si NMR chemical shift is sensitive to the nature of

Scheme 1. Reaction of Generic Organometallic with Oxide Surface To Form Either M−O$_x$ or M---O$_x$ Ion Pairs
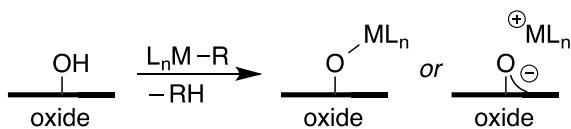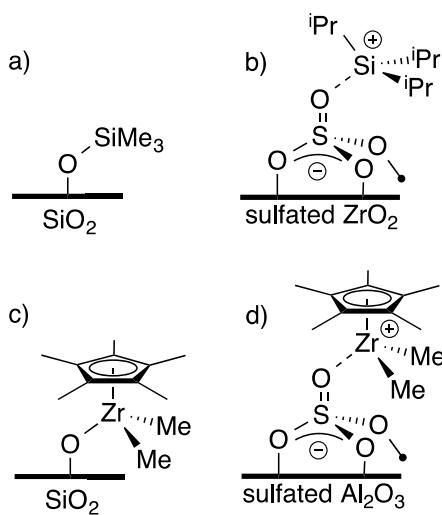
Figure 1. Representative examples of well-defined surface species that show pronounced differences in the isotropic ^{29}Si chemical shift (a,b) or ^{13}C chemical shift (c, d).

Figure 2. Two products of the reaction between partially dehydroxylated silica and $Ta(=CH^tBu)(CH_2{}^tBu)_3$; $\equiv SiO-Ta(=CH^tBu)(CH_2{}^tBu)_2$ shown on the left and $\equiv SiO-Ta(=CH^tBu)$-$(CH_2{}^tBu)_2(O(SiO_x)_2)$ is shown on the right in (a). The reaction of partially dehydroxylated silica and Cp*$_2$ScMe, the objective of this study (b).

the substituents connected to silicon.[24] Alkylsilanes have ^{29}Si NMR chemical shifts at ∼0 ppm, while silylium ions (R_3Si^+) paired to weakly coordinating anions have chemical shifts between ∼90 and 140 ppm.[25−27] This trend also applies to organosilanes supported on oxides. Alkylsilanes react with silica to form $\equiv SiO-SiR_3$ (Figure 1a).[28] The ^{29}Si cross-polarization magic angle spinning (CPMAS) NMR spectrum of $\equiv SiO-SiR_3$ contains signals at ∼14 ppm.[29−31] This chemical shift is close to the ^{29}Si NMR chemical shift of silylethers in solution, and is consistent with formation of $\equiv SiO-SiR_3$, and the observation that weakly acidic supports do not form ion pairs. Sulfated zirconium oxide reacts with allyltriisopropylsilane to form $[^iPr_3Si][\textbf{SZO}]$ ion pairs (Figure 1b).[32] The ^{29}Si CPMAS NMR spectrum of $[^iPr_3Si][\textbf{SZO}]$ contains a major signal at 53 ppm, which is ∼10 ppm downfield from the ^{29}Si NMR chemical shift of $^iPrSiOTf$ and is consistent with the formation of a surface ion pair. Recent reports of $^iPr_3Si$−sites supported on silica surfaces containing weakly coordinating anions contained a ^{29}Si NMR signal at 70 ppm, to date the most deshielded ^{29}Si NMR signal for a R_3Si-site supported on an oxide.[33]

Similar conclusions are supported by analysis of ^{13}C NMR chemical shifts. $\equiv SiO-ZrCp*(Me)_2$, shown in Figure 1c, contains a signal at 39 ppm for the Zr−Me.[34] Cp*$ZrMe_3$ supported on sulfated alumina forms $[Cp*ZrMe_2][\text{oxide}]$ ion pairs (Figure 1d), which is supported by a downfield shift of the Zr−Me signal (δ = 49) and extended X-ray adsorption fine structure (EXAFS) studies.[21]

Though solid-sate NMR is an indispensable technique in studies of surface species, there are certain ambiguities that cannot be resolved using this method. For example, $Ta(=CH^tBu)(CH_2{}^tBu)_3$ supported on silica partially dehydroxylated at 700 °C $(SiO_{2−700})$ forms $\equiv SiO-Ta(=CH^tBu)(CH_2{}^tBu)_2$, results supported by extensive solid-state NMR studies.[35] However, EXAFS analysis showed that a significant fraction of $\equiv SiO-Ta(=CH^tBu)(CH_2{}^tBu)_2$ also contains a siloxane bridge ligand, Figure 2a. Several early transition metal or lanthanide complexes supported on silica show similar behavior[36−39] and in NMR data of spin 1/2 nuclei usually

cannot distinguish between the presence or absence of a siloxane bridge ligand.[40]

This paper describes the reaction of Cp*$_2$ScMe, a monomeric C_{2v} bent metallocene,[41] with partially dehydroxylated silica (Figure 2b), and the application of solid-state ^{45}Sc{^{1}H} NMR spectroscopy to determine the structures of surface sites. Scandium has one NMR active nucleus (^{45}Sc, I = 7/2, γ = 6.5081 × 10^7 rad T^{-1} s^{-1}, 100% abundant) and is quadrupolar. Quadrupolar solid-state NMR of solids is a powerful technique to obtain information about structure[42] and is also useful in studying supported organometallics.[43−47] Given these characteristics, ^{45}Sc NMR may be able to distinguish between products that coordinate to siloxane bridges and those that do not coordinate to siloxane bridges.

Quadrupolar nuclei contain nonspherically symmetric distributions of positive charge. From a practical perspective, this is most commonly manifested as broad signals in solution NMR spectra. In solution, molecules tumble, which averages NMR interactions that depend on the orientation of the nuclear spins with respect to the external magnetic field ($\textbf{B}_0$). This is not the case in the solid-state, and spatially dependent NMR interactions can often be measured directly, provided that dynamics are slow on the NMR time scale. In quadrupolar nuclei, the dominant spatially dependent NMR interaction is between the electric field gradient (EFG) tensor and the quadrupole moment of the nucleus. The EFG is a traceless second-rank tensor (V, eq 1). The three principal components of the EFG tensor are ordered $|V_{33}| \geq |V_{22}| \geq |V_{11}|$. The quadrupolar coupling constant (C_Q) describes the magnitude of V_{33}, eq 2, where e = fundamental charge; Q = nuclear quadrupole moment; h = Planck's constant. Experimental C_Q can be extracted from solid-state NMR data. The magnitude of C_Q is usually much larger than typical MAS speeds (∼10 kHz), which can complicate analysis of NMR spectra under MAS unless very fast spinning speeds are accessible (>50 kHz). Acquisition of static NMR spectra using low RF fields in combination with frequency steps,[48] or pulse sequences containing echo-trains,[49] results in powder patterns whose properties can be simulated using commercially available software to extract C_Q from experimental data:

$$\mathbf{V} = \begin{vmatrix} V_{11} & 0 & 0 \\ 0 & V_{22} & 0 \\ 0 & 0 & V_{33} \end{vmatrix} \quad (1)$$

$$C_Q = \frac{e^2 Q V_{33}}{h} \quad (2)$$

C_Q is sensitive to symmetry, perturbations of core orbitals, and population of valence bonding orbitals.[42,50,51] A summary of C_Q values for available Cp*$_2$Sc-complexes is shown in Figure 3. The base-free Cp*$_2$Sc−X (X = F, Cl, Br, I) and
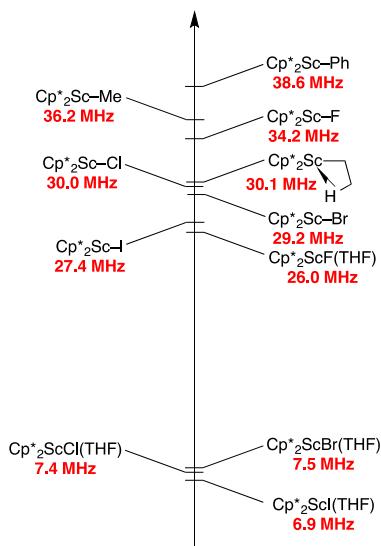
Figure 3. Summary of available C_Q values for Cp*$_2$Sc-complexes.

Cp*$_2$Sc−R (R = Me, Et, Ph) are characterized by relatively large C_Q values >27 MHz. These values are larger than scandium complexes that have higher symmetry than these metallocenes[52] or crystalline porous materials[53] but smaller than the C_3 Sc[N(SiMe$_3$)]$_3$ amide (C_Q = 66.2 MHz).[54] Figure 3 shows how subtle changes in the Cp*$_2$Sc-structure affect C_Q. For example, Cp*$_2$Sc−Me has a larger C_Q than Cp*$_2$Sc−Et because the latter contains a β-agostic structure (Figure 3).[55] More dramatic differences in C_Q were observed in studies of Cp*$_2$Sc−X and Cp*$_2$ScX(THF) (X = F, Cl, Br, I). The base-free halides have much larger C_Q values than the THF adducts.[56] Density functional theory (DFT) studies of these compounds showed that the smaller C_Q values for the THF adducts are due to the higher symmetry at Sc, which results in some degree of π-bonding from the halide to scandium.

The solid-state ^{45}Sc{^{1}H} NMR data shown in Figure 3 is a rough empirical aid for the interpretation of ^{45}Sc{^{1}H} NMR data of Cp*$_2$ScMe supported on partially dehydroxylated silica. Formation of Cp*$_2$ScOSi≡, a terminal siloxy surface species, should result in a large C_Q. Coordination of a siloxane bridge, which is reasonable based on the well-defined organometallics mentioned above, would form Cp*$_2$Sc(OSi≡)O(SiO$_x$)$_2$, which is expected to have a smaller C_Q than the terminal siloxy surface species.

DFT methods accurately predict C_Q and can decompose the C_Q into individual natural localized molecular orbitals to give insights into the origin of this spectroscopic observable.[50,51,57] DFT descriptions of amorphous supports, such as SiO$_2$, are complex.[58] However, several studies showed that C_Q depends

only on the first coordination sphere and that small cluster models give predicted C_Q values close to experimental values for a given coordination environment.[43,59,60] Simple approximations of a silica surface, such as the −OSi(OMe)$_3$ ligand or related simple siloxy models, also predict reactivity patterns and spectroscopic properties of organometallics supported on silica.[61−64] This article shows that the reaction of Cp*$_2$ScMe on silica dehydroxylated at 700 °C (SiO$_{2-700}$) generates two surface species by solid-state ^{45}Sc{^{1}H}NMR spectroscopy. Analysis of solid-state ^{45}Sc{^{1}H} NMR data for terminal alkoxide complexes, formed in the reaction of Cp*$_2$ScMe and ROH, shows that these complexes have similar C_Q values as the base free scandocene complexes in Figure 3. DFT calculations of these molecular alkoxides reproduce the structures of these complexes and predict scandium C_Q values close to experimental values. This benchmarks the DFT studies of the small cluster models for Cp*$_2$ScOSi≡ and Cp*$_2$Sc-(OSi≡)O(SiO$_x$)$_2$ shown in Figure 4. This study shows that
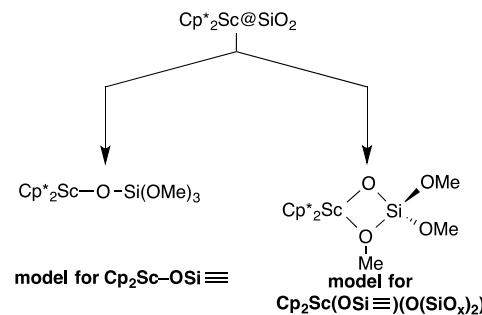
Figure 4. DFT models for Cp*$_2$ScOSi≡ and Cp*$_2$Sc(OSi≡)O-(SiO$_x$)$_2$.

the two reaction products in Cp*$_2$Sc@SiO$_2$ are Cp*$_2$ScOSi≡ and Cp*$_2$Sc(OSi≡)O(SiO$_x$)$_2$ from solid-state ^{45}Sc{^{1}H} NMR spectroscopy. NLMO decomposition of the origins of C_Q in these two clusters shows that the geometry differences in the $κ^1$- and $κ^2$-coordination modes of −OSi(OMe)$_3$ result in different bonding orbital contributions to V_{33}.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an inert atmosphere of dinitrogen or argon. Benzene-d_6 and cyclohexane-d_{12} were purchased from Cambridge Isotope laboratories and dried over sodium/benzophenone, distilled under vacuum, and stored inside an inert atmosphere glovebox. Pentane and toluene were dried over sodium/benzophenone, degassed, and distilled under vacuum. Nonafluorotertbutanol, 1,1,1,-trifluoro-2-methyl-2-propanol, and 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol were purchased from standard suppliers, dried over calcium hydride, and distilled under vacuum prior to use. Triphenylsilanol was sublimed under vacuum prior to use. Methyllithium in Et$_2$O was purchased from Sigma-Aldrich. Synthesis of Cp*$_2$ScCl and Cp*$_2$ScMe was reported previously.[41]

Aerosil-200 was obtained from Degussa. Aerosil-200 dehydroxylated at 700 °C (SiO$_{2-700}$) was prepared by suspending the silica in excess water and drying the slurry under static air at 120 °C in an oven for 1 day. The resulting monolith was crushed and sieved to give 250−425 μM size silica aggregates. This material was loaded into a quartz tube containing an adapter with a Teflon stopcock to attach to a high vacuum line, placed in a tube furnace, heated under static air at 500 °C (5 °C min^{-1}) for 4 h, and placed under vacuum on a diffusion pump vacuum line for 12 h. While under vacuum, the temperature was increased to 700 °C (5 °C min^{-1}) and its temperature maintained for 4 h. After this time, the Teflon stopcock was sealed, and the tube

Table 1. ^{45}Sc NMR Parameters for 1−5 Extracted from Simulations in Figures 6 and 7^a

	δ_{iso} (ppm)	C_Q (MHz)	η	Ω (ppm)	κ	α (deg)	β (deg)	γ (deg)
1	65(5)	31.6(1)	0.80(1)	290(20)	0.50(1)	95(5)	90(1)	90(1)
2	99(1)	30.5(1)	0.63(2)	270(10)	0.19(4)	106(4)	88(2)	88(3)
3	133(1)	29.2(2)	0.33(1)	375(3)	0.25(5)	103(2)	96(6)	78(3)
4	94(2)	35.1(1)	0.77(1)	239(3)	0.5(1)	108(5)	89(2)	90(1)
5a	135(15)	35.4(4)	0.60(5)	315(20)	0.90(8)	90(1)	90(1)	90(1)
5b	95(5)	21.9(3)	0.77(3)	150(15)	0.65(9)	90(1)	90(1)	90(1)

^{a}Values reported in the table are averages from simulations of experimental NMR data acquired at 9.4 and 14.1 T. Numbers in parentheses give the deviation from the average from these data.

was cooled to ambient temperature. The partially dehydroxylated silica was stored in an Ar filled glovebox and contains 0.26 mmol OH g^{-1}.

NMR Spectroscopy. Solution phase ^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{45}Sc{^{1}H} NMR spectroscopy were acquired on a Bruker 300 Avance spectrometer, Varian 500, or Bruker 600 Avance spectrometer. ^{1}H and ^{13}C NMR spectra were referenced to the NMR solvent residual peak. ^{19}F NMR spectra were referenced to C_6F_6 (−163.9 ppm) external standard. ^{45}Sc NMR spectra were referenced to 0.11 M $ScCl_3$ in 0.1 M aqueous HCl solution (0.0 ppm).

Solid state NMR spectra were recorded in 4 mm zirconia rotors packed inside an inert atmosphere glovebox, and acquired on a Bruker 400 Avance III or a Bruker Neo-600 NMR spectrometer. The ^{13}C CPMAS NMR spectra were recorded with a 2 ms contact time and a 2 s relaxation delay. Static ^{45}Sc{^{1}H} NMR spectra were recorded with a Hahn-echo pulse sequence, with full echo detection ($\pi/2 - \tau - \pi -$ acq). Echo delays (τ) were 100−150 μs. All analytical simulations of solid state spectra were performed in Topspin using Sola line shape analysis.

General Synthesis of Cp*$_2$Sc−OR. Cp*$_2$ScMe (200−500 mg, 0.6− 1.5 mmol) was dissolved in toluene (5−15 mL) and cooled to 0 °C. The alcohol (1.05−1.1 equiv) was added dropwise to the solution by syringe. After addition, the reaction was stirred at 0 °C for 10 min, then 20 min at room temperature. The volatiles were removed under vacuum, and a minimal amount of pentane was added by cannula to dissolve the residue. Recrystallization from pentane at −20 °C results in yellow crystals for compounds **1 − 3**. Yields and analytical data for the individual compounds are given below. The solid-state ^{45}Sc NMR data are given in below and summarized in Table 1. Results for C,H elemental analyses of **1−4** did not yield satisfactory results, possibly due to the sensitivity of these compounds. Elemental analysis data are given in the Supporting Information (Table S1).

Cp*$_2$Sc−OCMe$_2$CF$_3$ (1). Yield: 62%. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 1.89 (s, 30 H, Cp*Me*), 1.56 (q, $^4J_{HF}$ = 1 Hz, 6 H, OC*Me$_2$*CF$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_{12}$, 151 MHz): 129.4 (q, $^1J_{CF}$ = 289 Hz, OCMe$_2$*C*F$_3$), 122.5 (*Cp*Me), 78.7 (q, $^2J_{CF}$ = 27 Hz, *C*CF$_3$Me$_2$), 29.2 (OC*Me$_2$*CF$_3$), 12.6 (Cp*Me*). ^{19}F{^{1}H} NMR (C$_6$D$_6$, 282 MHz): δ −82.0 (s). ^{45}Sc NMR (C$_6$D$_6$, 73 MHz): δ 70 (br s).

Cp*$_2$Sc−OCMe(CF$_3$)$_2$ (2). Yield: 10%. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 1.83 (s, 30 H, Cp*Me*), 1.78 (sept, $^4J_{HF}$ = 1.5 Hz, 6 H, OC*Me*(CF$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_{12}$, 126 MHz): 126.3 (q, $^1J_{CF}$ = 289 Hz, OCMe(*C*F$_3$)$_2$), 123.8 (*Cp*Me), 82.9 (m, *C*CF$_3$Me$_2$), 23.2 (OC*Me*(CF$_3$)$_2$), 12.7 (bs, Cp*Me*). ^{19}F{^{1}H} NMR (C$_6$D$_6$, 282 MHz): δ −77.5 (s). ^{45}Sc{^{1}H} NMR (C$_6$D$_6$, 73 MHz): δ 89.

Cp*$_2$Sc−OC(CF$_3$)$_3$ (3). Yield: 26%. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 1.79 (s, 30 H, Cp*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_{12}$, 151 MHz): δ 125.6 (s, *Cp*Me), 123.7 (q, $^1J_{CF}$ = 295 Hz, OC(*C*F$_3$)$_3$), 86.6 (br m, O*C*(CF$_3$)$_3$), 12.4 (s, Cp*Me*). ^{19}F{^{1}H} NMR (C$_6$D$_6$, 282 MHz): δ −73.2 (s). ^{45}Sc{^{1}H} NMR (C$_6$D$_6$, 73 MHz): δ 118 (br s).

Cp*$_2$Sc−OSiPh$_3$ (4). This compound was synthesized with a slight modification of the generally synthesis. Triphenylsilanol (1.05 equiv) was dissolved in toluene and added to Cp*$_2$ScMe by syringe. Yield: 48%. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 7.28−7.31 (m, 6 H, ArH), 7.89− 7.92 (m, 9 H, ArH), 1.82 (s, 30 H, Cp*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 151 MHz): δ 142.1 (s, Ph), 137.2 (s, Ph), 129.7 (s, Ph), 128.3 (s, Ph),

122.7 (s, Cp*Me*), 12.5 (s, Cp*Me*). ^{45}Sc{^{1}H} NMR (C$_6$D$_6$, 73 MHz): δ 289 (br s).

Synthesis of 5. SiO$_{2−700}$ (0.2 g, 0.052 mmol OH) and Cp*$_2$ScMe (18 mg, 0.055 mmol) were loaded into a double Schlenk in an argon filled glovebox. The double Schlenk was connected to a high vacuum line, evacuated, and pentane (5 mL) was condensed onto the solids at 77 K. The slurry was warmed to room temperature and gently stirred for 1 h. Then the solution was filtered to the other arm of the double Schlenk. The derivatized silica was washed by condensing solvent from the other arm of the double Schlenk at 77 K, warming to room temperature, stirring for 2 min, and filtering the solvent back to the other side of the flask. This was repeated two times. The volatiles were transferred to a flask containing a Teflon stopcock at 77 K. Analysis of the volatiles by gas chromatography shows that 0.23 mmol/g of CH_4 are released during the reaction. The pale yellow solid was dried under diffusion pump vacuum for 1 h and was stored in a glovebox freezer at −20 °C. Solid state NMR: ^{1}H MAS NMR (600 MHz): δ 2.9−2.5 (Cp*Me*). ^{13}C{^{1}H} CPMAS NMR (151 MHz): δ 121.5 (*Cp*Me), 9.6 (Cp*Me*); and ^{29}Si{^{1}H} CPMAS NMR (119 MHz): δ −106 (*Si*O$_2$) ppm. Elemental analysis for **5**: C 5.61, H 0.49. ^{45}Sc NMR data are shown below and summarized in Table 1.

Computational Details. The geometries of **1−4**, **6a**, and **6b** were optimized with Gaussian 09 using the B3LYP functional and the 6-311G** basis set on scandium and the 6-31G** basis set on all other atoms. Frequency calculations at the same level of theory produced no imaginary frequencies, indicating an energy minimum equilibrium structure. The NMR parameters of **1−4**, **6a**, and **6b** were modeled in the Amsterdam Density Functional suite of programs at the B3LYP/ DZ, Si(DZP) level of theory using the GIAO method. The calculated isotropic chemical shift was referenced to geometry-optimized Sc(H$_2$O)$_6$$^{3+}$ at the same level of theory, which was used previously to reference ^{45}Sc chemical shift calculations.[52] Contributions of each natural localized molecular orbital (NLMO) to the C_Q were calculated at the same level of theory.[50] The EFG tensor plots were plotted using TensorView.[65]

■ RESULTS AND DISCUSSION

Synthesis of Cp*$_2$Sc−OR (R = CMe$_2$CF$_3$, CMe(CF$_3$)$_2$, C(CF$_3$)$_3$, SiPh$_3$) and Cp*$_2$ScOSi≡. The reaction of Cp*$_2$Sc− Me with fluorinated alcohols and triphenylsilanol form methane and Cp*$_2$Sc−OR (R = CMe$_2$CF$_3$ (**1**), CMe(CF$_3$)$_2$ (**2**), C(CF$_3$)$_3$ (**3**), SiPh$_3$ (**4**)), Scheme 2. The products were isolated as crystalline (**1** and **3**) or microcrystalline (**2** and **4**) solids in moderate yields.

The solid-state structures of **1** and **3** are shown in Figure 5. **3** crystallizes with three nearly identical molecules in the unit cell. **1** and **3** adopt bent C_{2v} structures that are typical for d^0 metallocenes. The Sc−O distance in **1** is 1.9481(8) Å, which is shorter than the average Sc−O distance in **3** (2.033(1) Å). In both cases, the Sc−O−C bond angle is nearly linear (175.16(7)° in **1** and 173.5(1)° in **3**). The Cp*−Sc bond distances in **1** are 2.2031(6) and 2.2088(6) Å, and the Cp*-Sc-Cp* angle is 135.26(2)°. In **3**, the average Cp*-Sc-Cp* angle is 133.9(1)°, and the average Cp*−Sc bond distances are

Scheme 2. Synthesis of Cp*₂Sc—OR

R = CMe₂CF₃ (**1**)
CMe(CF₃)₂ (**2**)
C(CF₃)₃ (**3**)
SiPh₃ (**4**)
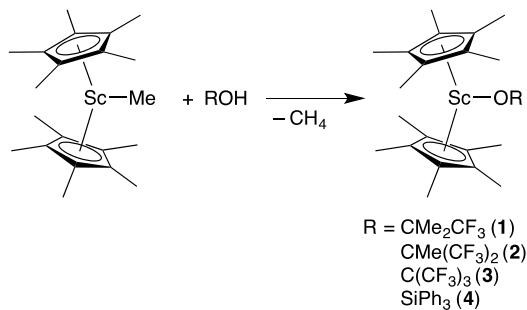
Scheme 3. Synthesis of Cp*₂Sc—OR

Cp*₂Sc–Me
+
SiO₂₋₇₀₀
− CH₄

5a   **5b**
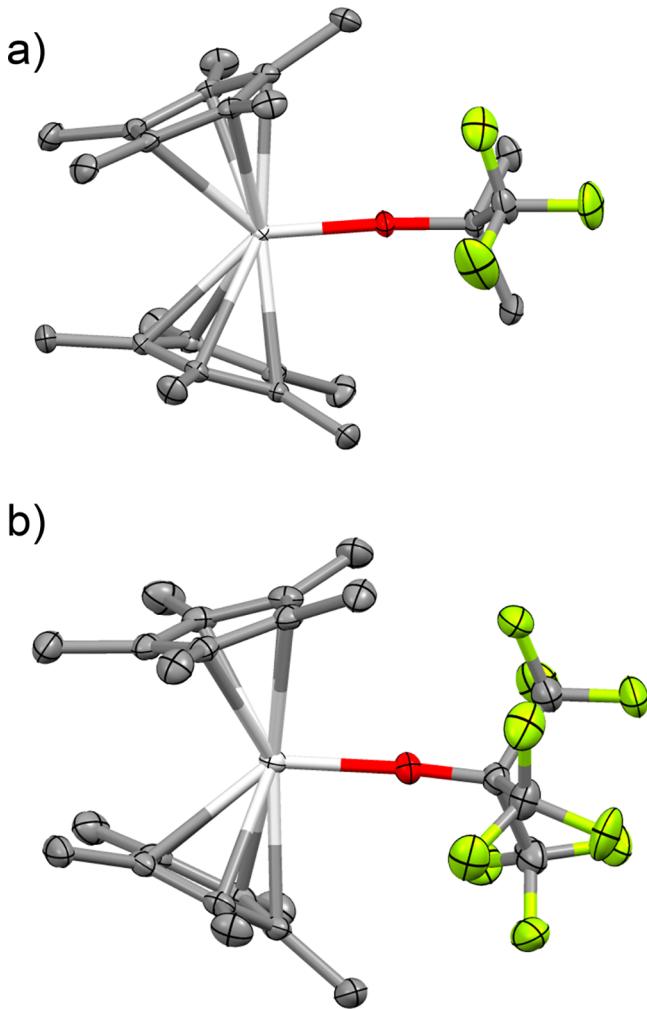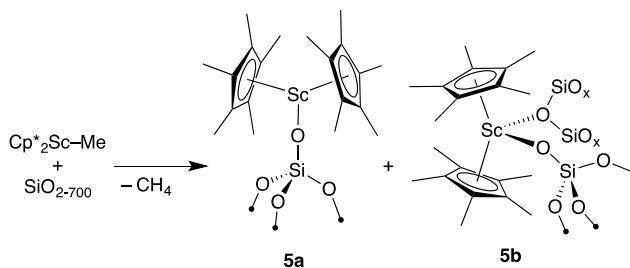
Figure 5. ORTEP drawing of **1** and **3**. Hydrogen atoms omitted for clarity. Refer to the Supporting Information for bond distances and angles.

2.199(1) and 2.205(1) Å. These values are similar to known permethylscandocene complexes.

The reaction of SiO_{2-700} and Cp*₂ScMe results in the formation of methane and Cp*₂ScOSi≡ (**5a**) and Cp*₂Sc-(OSi≡)O(SiO$_x$)₂ (**5b**), Scheme 3. This reaction forms 0.23 mmol g^{-1} methane, which is close to the −OH loading of SiO_{2-700} (0.26 mmol g^{-1}). The FTIR of **5** contains sp^3 ν_{CH} and sp^2 ν_{CC} bands from the Cp* fragment (Figure S9). In addition, this spectrum shows a significant decrease in the ν_{OH} band associated with isolated and geminal silanols on the partially dehydroxylated silica surface. The ^{13}C CPMAS spectrum of **5**

contains signals at 121.5 and 9.5 ppm that are signatures of the Cp* ligands in **5** (Figure S10). The ^{29}Si CPMAS spectrum of **5** contains only signals for bulk SiO_2 and does not contain signals for alkylsilanes (Figure S11). This result indicates that only HOSi≡ sites on the partially dehydroxylated silica surface react with Cp*₂ScMe to form **5** and that side reactions associated with strained siloxane bridges or geminal silanols do not occur under these conditions.[66] These spectroscopic data do not distinguish between **5a** and **5b**, which is typical of these particular techniques. However, the examples mentioned above and results showing that Cp*₂ScX(THF) complexes (X = H, alkyl, halide) are isolable,[41,56] suggest that **5b** would be present on partially dehydroxylated silica surfaces.

Solid-State ^{45}Sc{^{1}H} NMR of 1−4 and Cp*₂ScOSi≡. The static ^{45}Sc{^{1}H} NMR spectra of **1−4** recorded on a 14.1 T NMR spectrometer are shown in Figure 6. NMR data acquired at 9.4 T are given in the Supporting Information (Figure S12). These spectra show characteristic broad second order quadrupolar powder patterns associated with solid-state ^{45}Sc NMR spectra of Cp*₂Sc−X complexes (X = alkyl, halide).[56] Simulations of these spectra are shown in red in Figure 6, and the NMR parameters associated with these simulations are summarized in Table 1. The C_Q values decrease following the trend **4** > **1** > **2** > **3**.

The static ^{45}Sc{^{1}H} NMR spectrum of **5** recorded on a 14.1 and 9.4 T spectrometers is shown in Figure 7. The ^{45}Sc{^{1}H} NMR spectrum of **5** is more complicated than the ^{45}Sc{^{1}H} NMR spectra of **1−4**. There are clear discontinuities in these spectra at both fields indicating that **5** simulates as two sites, which is consistent with the presumption that Cp*₂ScMe reacts with partially dehydroxylated silica to form **5a** and **5b**. Importantly, the simulated spectral parameters given in Table 1 are reproduced at both fields, which support simulating this spectrum with two sites. On the basis of the data obtained for **1−4**, all of which have C_Q values >29 MHz, the broad ^{45}Sc{^{1}H} NMR signal that simulates with an average C_Q of 35.4(4) MHz is assigned to **5a**. The narrower signal that simulates with an average C_Q of 21.9(3) MHz is assigned to **5b**. Below DFT calculations of **1−4**, and small models of **5a** and **5b**, will be described to support these assignments.

DFT Studies of 1−5. Crystallographically characterized **1** and **3** show typical structural features associated with C_{2v} bent metallocenes, and are useful reference points to calibrate DFT studies. The structures of **1−4** were optimized with the B3LYP functional at the 6-311G**(Sc)/6-31G*(C, H, O, F, Si) level of theory. The bond angles and distances obtained from these optimizations are given in Table 2. The bond distances and angles of **1** and **3** agree well with the values obtained from the DFT structures. The structures of **2** and **4** are qualitatively similar to **1** and **3**; these structures also adopt C_{2v} structures with Sc−O−C or Sc−O−Si bond angles that are nearly linear.
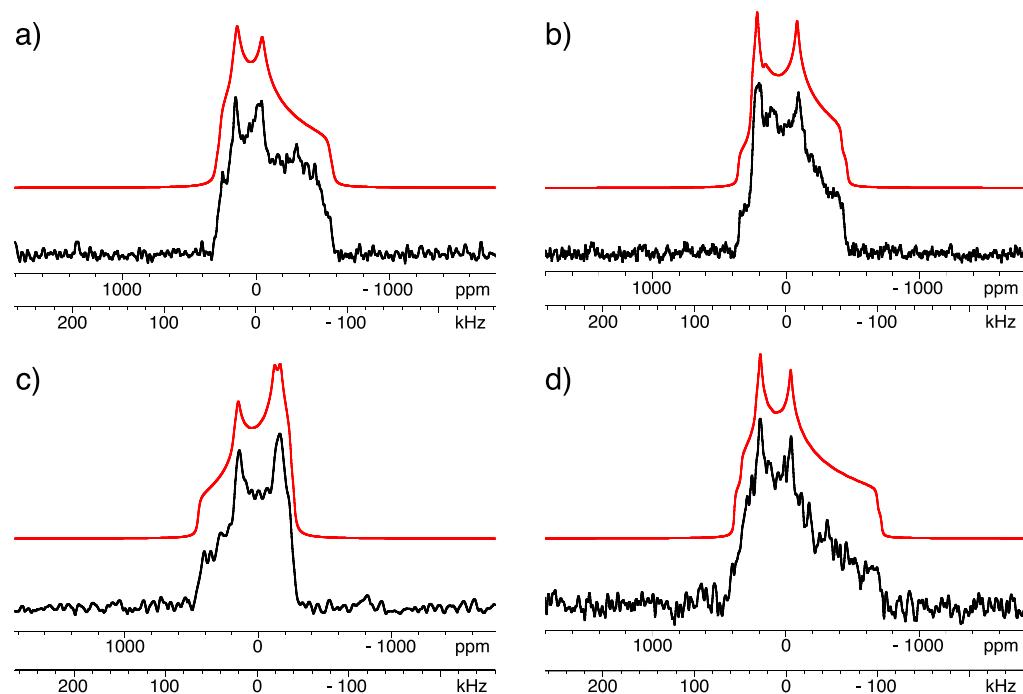
Figure 6. Static solid-state $^{45}\text{Sc}\{^1\text{H}\}$ NMR spectra of **1** (a), **2** (b), **3** (c), and **4** (d) acquired at 14.1 T. The experimental spectra are shown in black and simulations are shown in red.
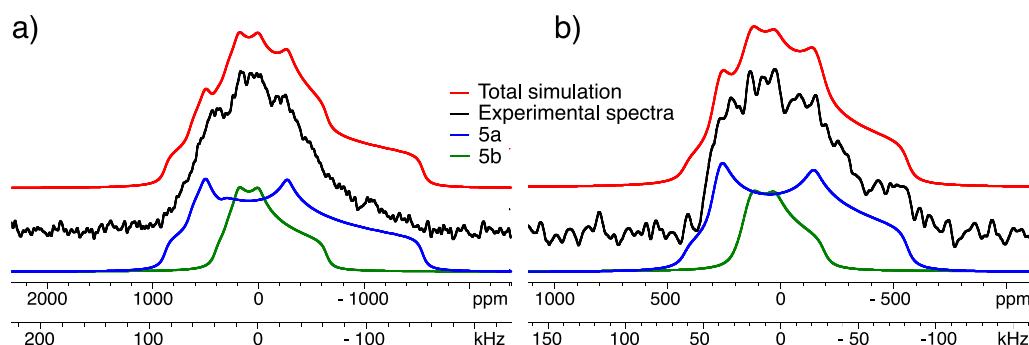

Figure 7. Static $^{45}\text{Sc}\{^1\text{H}\}$ NMR spectrum of **5** at 9.4 T (a) and 14.1 T (b). The experimental spectra are shown in black. Simulations of **5a** are shown in blue, simulations of **5a** are shown in green, and the total simulation is shown in red.

Table 2. Geometrical Parameters from DFT Optimized Structures of Cp*$_2$Sc−OR

compound	Cp*$_a$-Sc (Å)	Cp*$_b$-Sc (Å)	Cp*$_a$-Sc-Cp*$_b$ (deg)	Sc−O (Å)	Cp*$_a$−Sc-O (deg)	Cp*$_b$−Sc-O (deg)	Sc−O−C (deg)
2	2.23	2.23	135.0	1.94	111.9	113.1	175.5
1	2.22	2.23	134.3	1.98	111.4	114.4	172.3
3	2.21	2.22	134.4	2.02	111.5	114.1	175.4
4	2.21	2.21	137.8	1.96	110.2	112.0	174.0
6a	2.20	2.20	140.5	1.97	109.3	110.2	160.7
6b	2.24	2.24	138.4	2.04	106.9	109.0	106.1

Two models for **5a** and **5b**, Cp*$_2$Sc (κ^1-OSi(OMe)$_3$) (**6a**) and Cp*$_2$Sc(κ^2-OSi(OMe)$_3$) (**6b**), were optimized at the same level of theory and are shown in Figure 8. Similar to **1−4**, **6a** and **6b** adopt bent metallocene structures. The Sc−O distance in **6a** is 1.97 Å, which is shorter than the Sc−O distance in **6b** (2.04 Å). The Sc−O−Si bond angle in **6a** is 160.7°, which is smaller than the Sc−O−C or Sc−O−Si bond angle for **1−4**. The κ^2 structure in **6b** has a Sc−O−Si bond angle of 106.1°, which is expected.

The $^{45}\text{Sc}\{^1\text{H}\}$ NMR results described above show that Cp*$_2$Sc−OR complexes are characterized by fairly large C_Q values. The NMR parameters of **1−4** and **6** were calculated at the B3LYP/DZ level of theory, with silicon described with the DZP basis set. The results from these calculations are summarized in Table 3. Trends in C_Q and chemical shift (δ) are similar to those obtained experimentally. At this level of theory, the span values (Ω) are predicted to follow **4 > 1 > 2 > 3**. However, the experimental Ω values do not follow an
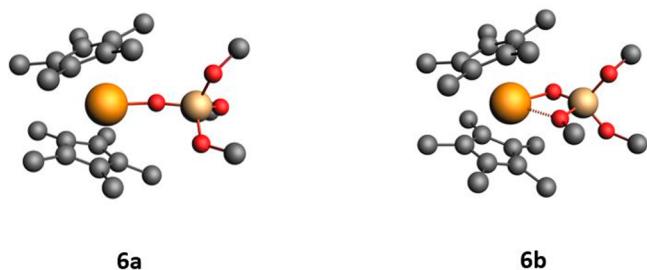
**Figure 8.** Structures of **6a** and **6b** from DFT calculations.

Figure 9. EFG Tensor plots of **1** (a) and **6b** (c). Calculated LUMO of **1** (b) and **6b** (d) calculated at B3LYP/DZ, Si(DZP); isovalue = 0.04.

obvious trend. The calculated Euler angles, which are defined as the angles between the shielding and EFG tensors, are close to those needed to simulate the experimental spectra shown in Figures 6−7 and summarized in Table 1. The calculated C_Q for **6a** is −36.6 MHz, and is close to the C_Q value for **5a**. This value is also close to the experimental and predicted values for **4**. The calculated C_Q for **6b** is 25.8 MHz, significantly smaller than the calculated C_Q for **6a**. This result is consistent with a large C_Q value for **5a**, corresponding to Cp*$_2$Sc(κ^1-OSi≡), and a smaller C_Q value for **5b**, which contains an additional interaction with a nearby siloxane bridge to form Cp*$_2$Sc-(OSi≡)O(SiO$_x$)$_2$. These results indicate that C_Q derived from [45]Sc NMR measurements can distinguish between κ^1 or κ^2 geometries in **5a** and **5b**.

The smaller C_Q for **5b** and **6b** than in **5a** and **6a** is reminiscent of similar trends observed in Cp*$_2$Sc−X and Cp*$_2$ScX(THF) (X = F, Cl, Br, I).[56] In this study the THF adducts consistently show smaller C_Q values than the base free compounds. This is a consequence of the more tetrahedral geometry at scandium in Cp*$_2$ScX(THF), which results in π-overlap between group fragment orbitals in these compounds. This interaction is absent in the THF free Cp*$_2$Sc−X compounds. This suggests that similar electronic consequences would emerge from analysis of the origin of the C_Q in **6a** and **6b**.

The orientation of the EFG tensor for **1** is shown in Figure 9a. The orientation of **2−4** and **6a** have similar orientations, and are shown in Figure S13. The magnitude of C_Q is determined by eq 2, and depends on V_{33}, the largest contributor to the EFG tensor (eq 1). In **1**, the orientation of V_{33} is perpendicular to the Sc−O bond, which aligns V_{33} with the LUMO of **1**, shown in Figure 9b. The orientation of the EFG tensor in **6b** is shown in Figure 9c. In this case, V_{33} orients along the Sc−O bond (Figure 9c). The calculated LUMO in **6b** is shown in Figure 5d, and corresponds to a π*-bonding orbital between an oxygen lone pair and the empty orbital on scandium. The LUMO and EFG tensor orientation in **1**, as well as **2−4** and **6a**, is similar to Cp*$_2$Sc−X, while the LUMO and EFG tensor orientation in **6b** is similar to Cp*$_2$ScX(THF) (X = F, Cl, Br, I).[56]

The C_Q originates from the interaction of the quadrupolar moment of the scandium nucleus and the EFG tensor, which is sensitive to local structure. This coupling is electric in origin, indicating that the magnitude of V_{33} will be related to core and valence scandium orbitals. DFT methods decompose the contributions of V_{33} into Natural Localized Molecular Orbitals (NLMO).[57] This method is particularly valuable to distinguish how certain geometries, which relate to bonding characteristics, affect V_{33}.[50,51,57] The NLMO decomposition of V_{33} for **1−4** and **6** is shown in Figure 10a. Consistent with the
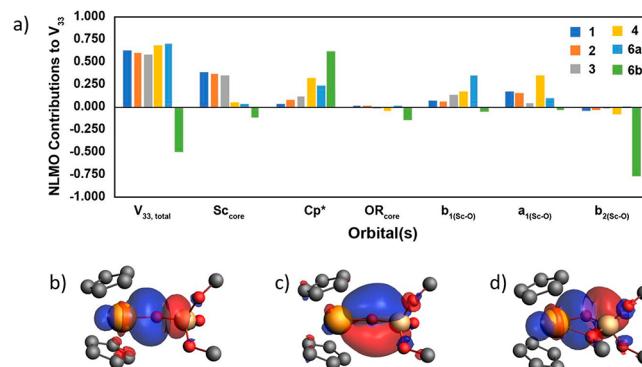

Figure 10. NLMO contributions to V_{33} calculated at B3LYP/DZ, Si(DZP) for **1−4** and **6** (a); plots of valence NLMO for the Sc−O σ-bond in **6a** (b); for the Sc−O π-bond in **6a** (c); and the Sc−O bond in **6b** (c); isovalue = 0.01.

electronic argument, the major contributors to V_{33} are bonding orbitals between scandium and the Cp* ligand, as well as σ- and π-bonding orbitals that describe the Sc−O bond, shown if Figure 10b and c for **6a** and Figure 10d for **6b**.

In **1−3**, the scandium core orbitals are significant contributors to V_{33}. Filled core scandium orbitals are spherically symmetrical and should not contribute to V_{33}.

Table 3. Calculated NMR Parameters for 1−4 and 6

R	δ_{iso} (ppm)	C_Q (MHz)	η	Ω (ppm)	κ	α (deg)	β (deg)	γ (deg)
1	81	−32.8	1.0	288	0.09	90.9	89.0	87.5
2	108	−31.2	0.75	395	0.06	90.1	88.6	90.0
3	139	−30.3	0.46	520	0.11	89.1	90.3	86.5
4	93	35.4	0.99	270	0.05	89.1	90.3	86.5
6a	90	−36.6	0.93	342	0.07	104.2	88.5	90.4
6b	48	25.8	0.84	238	0.70	89.4	90.8	86.6

Nonzero contributions to C_Q from core orbitals is a result of Sternheimer shielding,[67] which relates to the anisotropic shielding of nuclear charge by outer core orbitals from bonding partners and polarizability.[50] However, the electronics of the alkoxide also clearly play a role in the contributions to V_{33}. As the alkoxide becomes more electron withdrawing the σ-bonding Sc−O orbital (a_1) contributes less to V_{33}.

Figure 10a shows that the contributors to V_{33} in **4** and **6a**, closely related molecular structures to **5a**, are rather different than the contributions to V_{33} in **6b**, which is the model for **5b**. In **4** and **6a**, the major valence contributions are from the Cp*−Sc, of roughly equal magnitude, and the Sc−OSiR$_3$ σ- and π-bonds (a_1 and b_1). In **6b**, the Cp*−Sc orbitals are major contributors, but the a_1 and b_1 orbitals are minor contributors to V_{33} because this compound adopts a κ^2-OSi(OMe)$_3$ ligand geometry. Rather the b_2 orbital is the major contributor to V_{33} in **6b**. These results show that the magnitude of C_Q for these complexes can differentiate between κ^1- and κ^2-geometries and that the origin of the C_Q in these geometries is related to different valence orbitals.

■ CONCLUSIONS

This study was motivated by the application of ^{45}Sc{^{1}H} NMR parameters to determine the structure of surface organo-scandium sites supported on partially dehydroxylated silica. The reaction of Cp*$_2$ScMe and SiO$_{2−700}$ was chosen because the supported Cp*$_2$Sc-fragment contains bulky Cp* ligands to enforce monomeric speciation in solution. This avoids complications associated with formation of aggregates during the grafting reaction, which can complicate analysis of the solid-state NMR data in some cases.[43,59,60] The bent metallocene C_{2v} geometry of the Cp*$_2$Sc-fragment allows access to only two possible conformations of the organo-scandium species on the silica surface (Cp*$_2$ScOSi≡ (**5a**) and Cp*$_2$Sc(OSi≡)O(SiO$_x$)$_2$ (**5b**)). Consistent with this hypothesis, two sites were needed to accurately fit the solid-state ^{45}Sc{^{1}H} NMR data of **5**. One of the sites had a large C_Q, assigned to **5a**, and the other site had a significantly smaller C_Q, assigned to **5b**.

The ^{45}Sc{^{1}H} NMR parameters of Cp*$_2$Sc-OR (**1−4**) were important benchmarks that were necessary to relate to the ^{45}Sc{^{1}H} NMR parameters of **5a** and **5b**. These compounds were prepared by straightforward reactions of Cp*$_2$ScMe with alcohols to yield Cp*$_2$Sc-OR and methane. Diffraction studies of Cp*$_2$Sc−OCMe$_2$CF$_3$ (**1**) and Cp*$_2$Sc−O(CF$_3$)$_3$ (**3**) are typical of monomeric C_{2v} bent metallocenes. **1−4** all show broad quadrupolar powder patterns typical of Cp*$_2$Sc−X (X = halide, alkyl).[55,56] These compounds also have similar C_Q values to those obtained for **5a**. DFT studies showed that the EFG tensor in Cp*$_2$Sc-OR, and a small cluster Cp*$_2$Sc(κ^1-OSi(OMe)$_3$) (**6a**) to approximate the primary coordination sphere in **5a**, orient the V_{33} component of the EFG tensor perpendicular to the Sc−O bond. This aligns V_{33} with the LUMO of these compounds. NLMO calculations showed that the Sc−O σ- and π-bonding orbitals are contributors to V_{33} in these terminal alkoxides.

These results are in contrast to those for Cp*$_2$Sc(κ^2-OSi(OMe)$_3$) (**6b**). This compound is a small cluster model of Cp*$_2$Sc(OSi≡)O(SiO$_x$)$_2$ (**5b**). Though this is a rather dramatic truncation of a silica surface, the calculated C_Q for **6** (25.8 MHz) is rather close to the C_Q of **5b** (C_Q = 21.9(3) MHz) derived from simulations of experimental NMR data.

This result shows that C_Q is sensitive to the primary coordination sphere of scandium, which is typically encountered when modeling NMR properties of quadrupolar nuclei. In **6b**, the V_{33} component of the EFG tensor is not aligned perpendicular to the Sc−O bond, as in the terminal alkoxides **1−4** and **6a**, but rather along the Sc−O bond. NLMO decomposition of V_{33} in **6b** is also quite different from the terminal alkoxides. The Sc−O σ- and π-bonding orbitals are minor contributors to V_{33}. In **6b**, the b_2 orbital is the major contributor to V_{33} because this compound adopts a κ^2-geometry with the siloxide. These results establish that the magnitude of C_Q and the origin of V_{33} are very sensitive to local structure, in this case the coordination of a − OSi(OMe)$_3$ ligand in κ^1- or κ^2 geometries, and support the assignments of **5a** and **5b**. These studies show that quadrupolar NMR properties of surface organoscandium species, when coupled with relevant molecular models and supplemented by DFT studies, can provide valuable information about the structure of these supported organometallic sites.

■ ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00840.

Chemical structure (XYZ)
Chemical structure (XYZ)
Chemical structure (XYZ)
Chemical structure (XYZ)
Chemical structure (XYZ)
Chemical structure (XYZ)
NMR spectra, elemental analysis results, IR spectra, coordinates for computations, EFG orientation plots, NLMO tables (PDF)

Accession Codes

CCDC 1971453−1971454 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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