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The Molecular and Electronic Structure of Isolated Platinum Sites Enabled by Expedient Measurement of ^{195}Pt Chemical Shift Anisotropy

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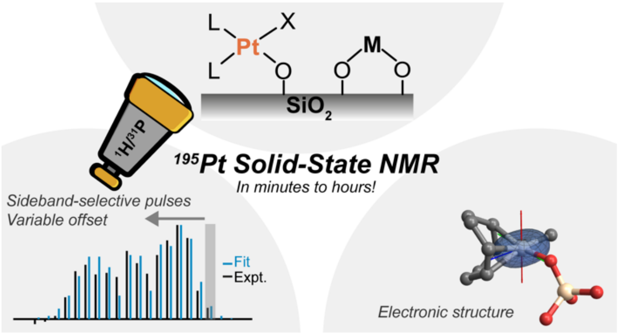
Abstract

Techniques that can characterize the molecular structures of dilute surface species are required to facilitate the rational synthesis and improvement of Pt-based heterogeneous catalysts. ^{195}Pt solid-state NMR spectroscopy could be an ideal tool for this task because ^{195}Pt isotropic chemical shifts and chemical shift anisotropy (CSA) are highly sensitive probes of the local chemical environment and electronic structure. However, characterization of Pt surface-sites is complicated by the typical low Pt loadings that are between 0.2 to 5 wt.% and broadening of ^{195}Pt solid-state NMR spectra by CSA. Here, we introduce a set of solid-state NMR methods that exploit fast MAS and indirect detection using a sensitive spy nucleus (^{1}H or ^{31}P) to enable rapid acquisition of ^{195}Pt MAS NMR spectra. We demonstrate that high-resolution wideline ^{195}Pt MAS NMR spectra can be acquired in minutes to a few hours for a series of molecular and single-site Pt species grafted on silica with Pt loading of only 3-5 wt.%. Low-power, long-duration, sideband-selective excitation and saturation pulses are incorporated into t_1-noise eliminated (TONE) dipolar heteronuclear multiple quantum coherence (D-HMQC), perfect echo resonance echo saturation pulse double resonance (PE RESPDOR) or *J*-resolved pulse sequences. The complete ^{195}Pt MAS NMR spectrum is then reconstructed by recording a series of 1D NMR spectra where the offset of the ^{195}Pt pulses is varied. Analysis of the ^{195}Pt MAS NMR spectra yields the ^{195}Pt chemical shift tensor parameters. Zeroth order approximation (ZORA) DFT calculations accurately predict ^{195}Pt CS tensor parameters. Simple and predictive orbital models relate the CS tensor parameters to the Pt electronic structure and coordination environment. The methodology developed here paves the way for the detailed structural and electronic analysis of dilute platinum surface-sites.

TOC Graphic


L
X
Pt
L
O
M
O
O
SiO$_2$
^{1}H/^{31}P
^{195}Pt Solid-State NMR
In minutes to hours!
Sideband-selective pulses
Variable offset
Fit
Expt.
Electronic structure

Introduction

Heterogeneous catalysis is widely used in industrial chemistry and is vital to sustainable chemical processes.[1-5] Recently, single-site[6-7] and single-atom[8] catalysts have emerged as a distinct class of highly efficient heterogeneous catalysts that display unique reactivity, increased catalytic efficiency and improved precious metal utilization. The ultimate goal in catalysis science is to derive detailed structure-activity relationship for rational development. The search for single-site catalysts that comprise of a well-defined coordination environment has thus been an active field of research. In this context, Surface Organometallic Chemistry (SOMC) has emerged as a powerful approach that relies on the controlled reaction of tailored molecular precursors with the functionality of supports, such as the isolated OH groups of oxide materials.[9-11] These well-defined surface species can be used directly as single-site catalysts or as precursors to i) generate isolated metal sites with defined oxidation state and nuclearity, or ii) control the interface, growth and composition of supported nanoparticles.[12-16] A key aspect of SOMC is the need to obtain an atomic-level characterization of surface species, using in particular solid-state nuclear magnetic resonance (NMR) spectroscopy.[5, 17-23]

Solid-state NMR spectroscopy has been used to determine the three-dimensional structure of surface single-sites with a sub-angstrom precision.[24-25] The complete measurement of the NMR chemical shift tensor via determination of the isotropic chemical shift and the chemical shift anisotropy (CSA) provides a fingerprint of the electronic structure and symmetry of an atomic environment.[26-29] For example, differences in magnitude of the CSA (the span), determined experimentally, and the computed orientation of the chemical shift tensors can be traced back to specific molecular frontier orbitals and their relative energies in organometallic complexes; this has been used for instance to predict the reactivity of alkene and alkyne metathesis catalysts,[30-34] unravel the electronic structure of organo-tellurides[35] and understand the π-accepting abilities of carbenes.[36-38] Many metal-based catalysts have spin-1/2 isotopes which can be directly probed by solid-state NMR spectroscopy (^{89}Y, ^{103}Rh, ^{109}Ag, ^{113}Cd, ^{119}Sn, ^{183}W, ^{199}Hg, ^{195}Pt, ^{207}Pb, etc.). However, direct NMR experiments on the metal nucleus of supported catalysts are challenging because of the typically low metal loadings. Consequently, NMR experiments have traditionally been limited to highly receptive isotopes of metals such as aluminum,[39] scandium,[21] vanadium,[40-41] niobium[18] and/or isotopically enriched materials.[22, 42-43] Recently, sensitivity-enhancement by dynamic nuclear polarization (DNP) or proton detection has enabled NMR experiments on catalysts featuring unreceptive nuclei.[44-49]

The noble metal platinum is utilized in numerous catalytic processes.[8, 50-52] However, Pt(II) sites typically adopt a square-planar geometry, giving rise to very large ^{195}Pt CSA, reaching several thousand ppm and making acquisition of ^{195}Pt solid-state NMR spectra challenging.[53-55] Yet, measurement of ^{195}Pt isotropic chemical shifts and CSA provides invaluable information by providing direct insight into the identity and symmetry of atoms within the Pt coordination sphere as well as a full understanding of its electronic structure.[55-60] Towards this goal, various schemes have been proposed for the acquisition of wideline solid-state NMR spectra.[53, 61-63] DNP has been used to enhance further the sensitivity of wideline solid-state NMR experiments under static[46, 64-65] and moderate magic angle spinning (MAS) conditions.[49] However, these methods offer poor ^{195}Pt NMR resolution. Recently, we used static DNP experiments to characterize a model Pt single-site catalyst at 3.7 wt.% Pt loading, however even with DNP, six days of acquisition time was required to measure the ^{195}Pt CSA.[66] A rapidly developing approach to improve the sensitivity and resolution of solid-state NMR experiments, which can be readily applied with standard solid-state NMR spectrometers, is indirect detection of insensitive nuclei under fast MAS.[67-70]

In this work, we demonstrate that ^{195}Pt chemical shift tensors can be measured with high resolution in only minutes to hours for a series of molecular and single-site Pt species grafted on silica with Pt loading of only 3-5 wt.% (Figure 1). Our approach consists in the incorporation of long duration, low-power, sideband-selective pulses into indirect detection ^{1}H{^{195}Pt} t_1-noise eliminated heteronuclear multiple quantum coherence (TONE D-HMQC), perfect echo resonance echo saturation pulse double resonance (PE RESPDOR) and ^{31}P{^{195}Pt} *J*-resolved or *J*-HMQC pulse sequences all of which are performed with fast MAS ($\nu_{rot} \geq 25$ kHz). By varying the offset of the sideband-selective pulses across the ^{195}Pt spectrum and monitoring the 1D NMR signal intensity, complete ^{195}Pt NMR spectra can be obtained with sensitivity far exceeding that offered by traditional methods. These schemes, together with DFT computations, were applied to unravel the molecular and electronic signatures of surface Pt species. The large variations in experimental ^{195}Pt CSA can be related to simple orbital models, rationalizing the effect of different coordination environments on ^{195}Pt CSA patterns.

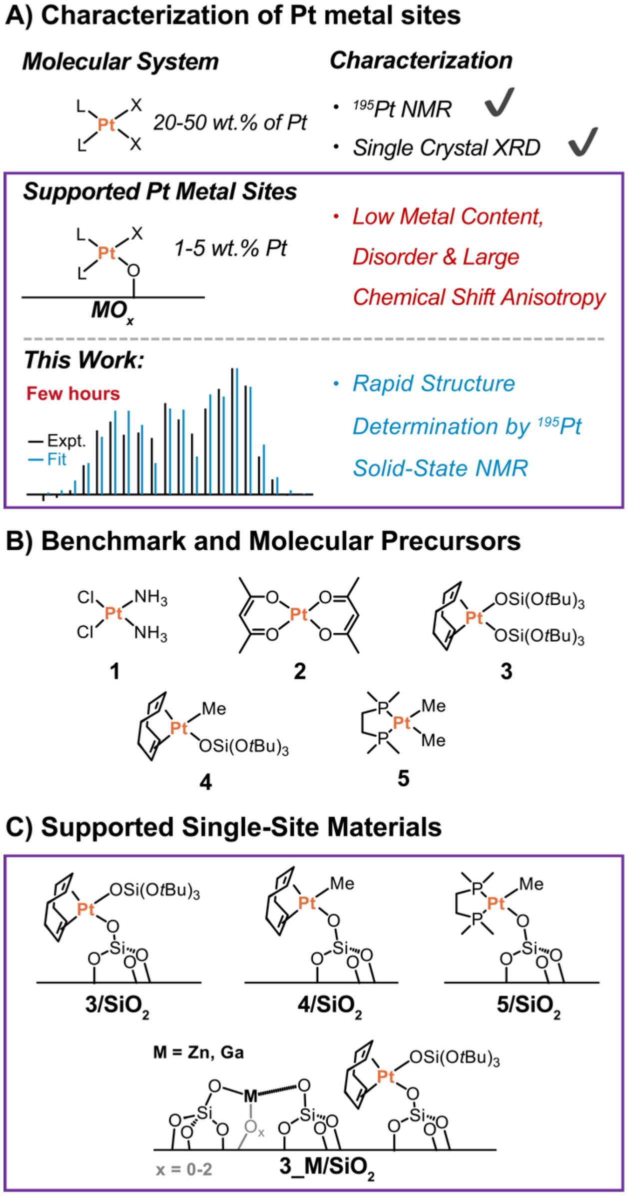


Figure 1. (A) Graphical summary of the characterization of molecular and supported Pt metal sites and the development of methodology for fast structure determination using ^{195}Pt solid-state NMR. Scheme showing the structures of the (B) molecular and (C) supported single-site Pt compound studied in this work. The Pt loadings of the supported compounds were 3.73 wt.% (**3/SiO$_2$**), 2.77 wt.% (**3_Zn/SiO$_2$**), 4.37 wt.% (**3_Ga/SiO$_2$**), 4.96 wt.% (**4/SiO$_2$**) and 4.39 wt.% (**5/SiO$_2$**).

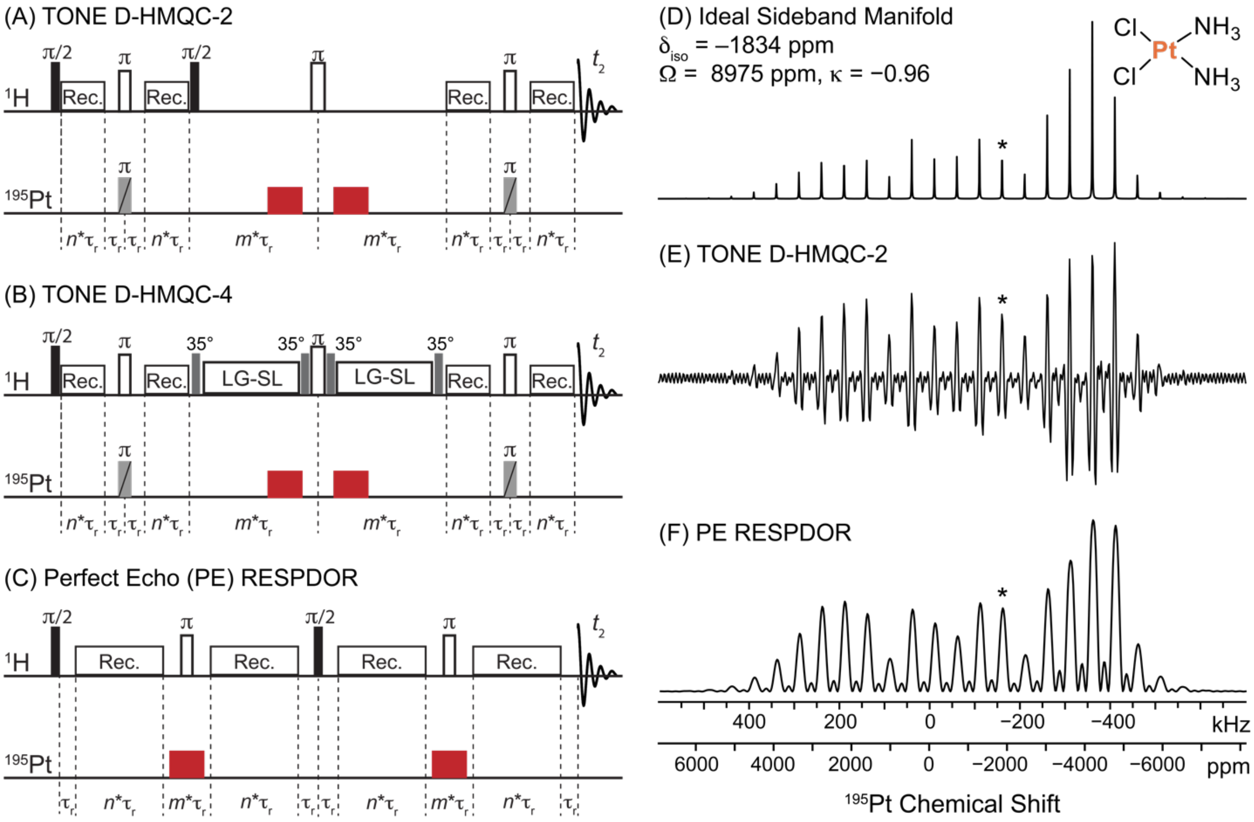


Figure 2. ^{1}H{^{195}Pt} (A) TONE D-HMQC-2, (B) TONE D-HMQC-4 and (C) Perfect echo (PE) RESPDOR pulse sequences with low-rf field, sideband-selective excitation/saturation pulses with durations of one or more rotor cycles on the ^{195}Pt channel denoted as red rectangles. m and n are positive integers and τ_r denotes a rotor period. (D-F) Simulations of MAS ^{195}Pt NMR spectra of cisplatin at 50 kHz MAS and B_0 = 9.4 T using the previously reported ^{195}Pt isotropic shift and CSA parameters (span (Ω) and skew (κ)). (D) Ideal simulation. Numerical SIMPSON simulations of sideband intensities obtained by varying the offset in steps of 1 kHz of 60 μs ^{195}Pt sideband-selective (9 kHz rf field) excitation or saturation pulses within (E) TONE D-HMQC or (F) PE RESPDOR pulse sequences, respectively. The isotropic shift is indicated by an asterisk.

Results and Discussion

Sideband-Selective ^{195}Pt NMR methods. Wideline ^{1}H{^{195}Pt} D-HMQC experiments[71-74] use microsecond duration, high-rf field (ν_1 > 150 kHz) excitation pulses to excite the broad ^{195}Pt NMR spectra. Small rotor-asynchronous t_1-increments (Δt_1 < 4 μs) are used to finely sample the indirect dimension time domain signal, allowing observation of the entire wideline ^{195}Pt MAS spectrum in the frequency domain after 2D Fourier transformation.[71-74] However, when the indirect dimension spectrum consists of a series of sidebands due to a significant CSA, the sensitivity of the wideline NMR experiment is significantly reduced (Figure S1), and further attenuated by t_1-noise. Recently Paluch *et al.* showed that the traditional microsecond duration, high-rf field excitation pulses used in ^{1}H{^{195}Pt} D-HMQC experiments on samples with large CSA can be replaced with low-rf field pulses (5-50 kHz) with durations of one rotor cycle or longer.[75] These multiple rotor cycle duration pulses have a narrow excitation bandwidth and must be applied on resonance with an isotropic peak or sideband; hence, we denote these pulses as being sideband-selective. Here, sideband-selective excitation or saturation ^{195}Pt pulses are incorporated into D-HMQC and RESPDOR pulse sequences. To obtain the MAS ^{195}Pt solid-state NMR spectra, a series of 1D sideband-selective D-HMQC or RESPDOR experiments are performed where the ^{195}Pt pulse offset frequency is stepped in increments equal to the MAS frequency. By plotting the 1D NMR signal intensities as a function of the ^{195}Pt pulse offset the MAS ^{195}Pt NMR spectrum can be reconstructed (Figure 2 and Figure S2-S4). This method is analogous to previous work that utilized indirect detection schemes such as TRAPDOR,[76-77] REAPDOR,[78] RESPDOR[79-80] or PROSPR[81] where the signal dephasing of the detected nucleus at different transmitter offsets was used to reconstruct the NMR spectrum of the indirectly detected spin.

Figure 2D shows the simulated ideal MAS ^{195}Pt NMR spectrum of cisplatin, based on the previously reported CSA parameters $\delta_{iso} = -1834$ ppm, $\Omega = 8975$ ppm and $\kappa = -0.96$,[60, 71] where δ_{iso}, Ω and κ denote the isotropic chemical shift, span and skew of the chemical shift tensor, respectively. Numerical SIMPSON[82-84] simulations show the effects of varying the offset of 60 μs, 9 kHz rf field ^{195}Pt pulses in 2 kHz steps for the TONE D-HMQC-2 and PE RESPDOR pulse sequences with $SR4_1^2$ recoupling[85] (Figure 2E and 2F). Most importantly, a comparison of Figure 2E and 2F with Figure 2D shows that the MAS ^{195}Pt NMR spectrum is essentially reproduced in both cases, with peak intensities obtained with the PE RESPDOR sequence being very similar to the ideal spectrum (Figure 2D). Further details on sideband-selective NMR experiments and simulations are found in the SI for the interested reader (Figure S5-S11, Note S1), and will be elaborated on in a forthcoming publication. Note that the simulations and experiments shown in Figure 2 and 3 used t_1-noise eliminated (TONE) D-HMQC[86] and the closely related perfect echo[87] (PE) RESPDOR pulse sequences (Figure 2). Both of these sequences give more reliable ^{1}H NMR signal intensities because they are designed to tolerate experimental MAS frequency fluctuations.[86, 88-89] The use of PE RESPDOR to accurately measure heteronuclear distances is discussed elsewhere.[90]

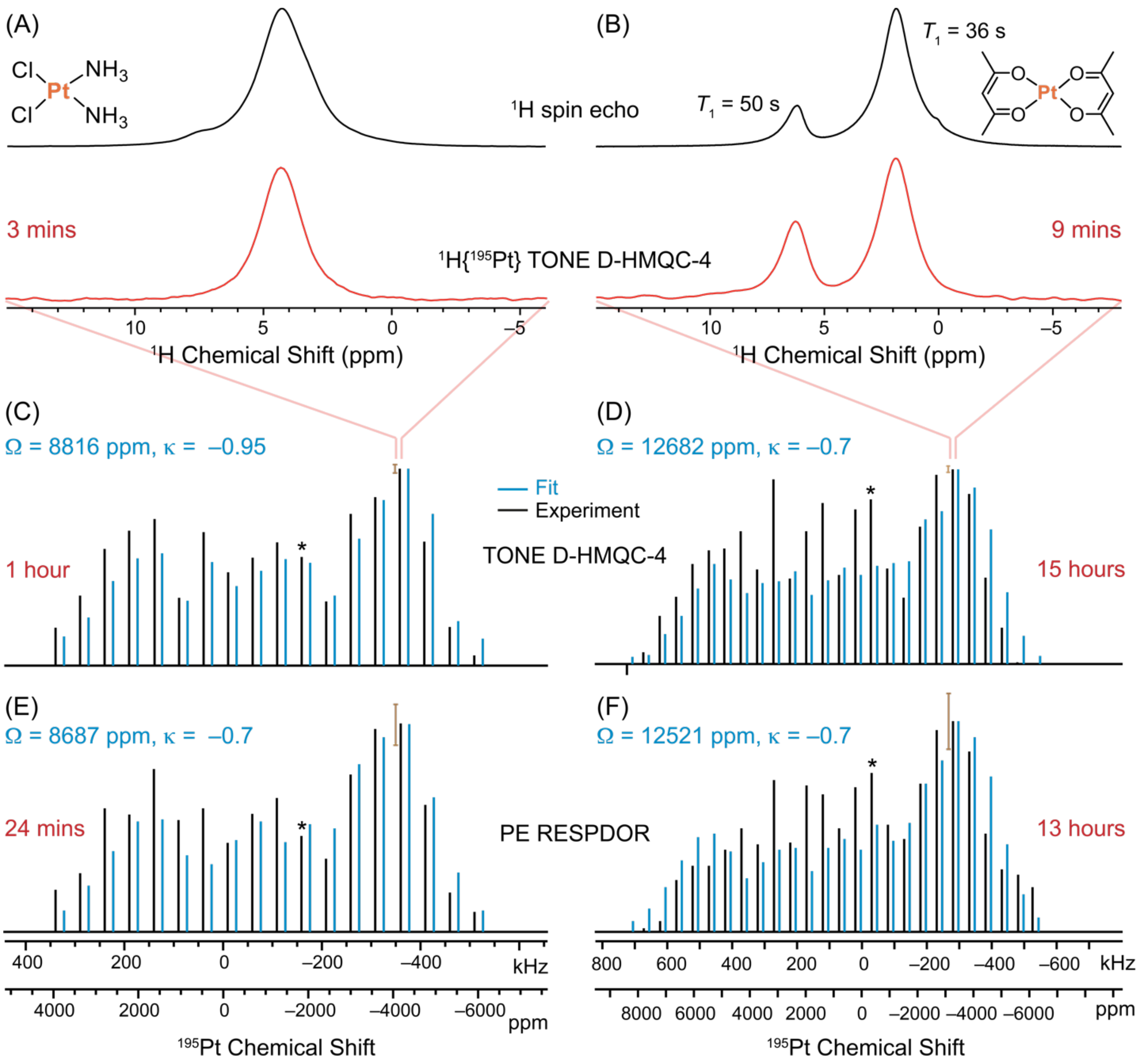


Figure 3. (A-B, upper traces) 1D ^{1}H spin echo spectra. (A-F) $^{1}H\{^{195}Pt\}$ sideband-selective solid-state NMR experiments on (A, C, E) cisplatin (**1**) and (B, D, F) $Pt(acac)_2$ (**2**) performed with a 50 kHz MAS frequency. (A-B, lower traces) 1D $^{1}H\{^{195}Pt\}$ sideband-selective TONE D-HMQC-4 with the ^{195}Pt transmitter applied at the most-intense sideband. (black traces) Sideband intensities from $^{1}H\{^{195}Pt\}$ (C-D) TONE D-HMQC-4 and (E-F) PE RESPDOR experiments using 60 μs, 9 kHz rf field sideband-selective ^{195}Pt pulses. For **2**, the signal intensities of the CH proton at 6.3 ppm are shown. (blue traces) SIMPSON simulated peak intensities corresponding to the indicated CS tensor parameters which gave the lowest RMSD. Error bars are provided only for the most intense sideband as the same magnitude of error applies to all sidebands (see SI for details on error bars). Total experiment times are indicated in red.

Experimental Demonstration of ^{195}Pt Sideband-Selective NMR Experiments on Molecular Precursors. We tested sideband-selective $^{1}H\{^{195}Pt\}$ TONE D-HMQC-4 and PE RESPDOR experiments with the two prototypical molecular compounds cisplatin (**1**) and $Pt(acac)_2$ (**2**) (Figure

3). The sideband-selective pulses must be applied precisely on-resonance with a ^{195}Pt NMR signal. The position of a sideband can be located using a high sensitivity rotor-synchronized D-HMQC experiment[66, 73, 75] or by varying the offset of the sideband-selective pulses in steps of 1-2 kHz, until the signal (or dephasing) is observed; the former approach was employed throughout this work. For both **1** and **2**, plots of the ^{1}H{^{195}Pt} TONE D-HMQC-4 signal or the PE RESPDOR dephasing as a function of the sideband-selective pulse offset yields the intensity of each sideband in the MAS ^{195}Pt NMR spectrum.

For both types of NMR experiments CSA parameters were determined by least-squares fitting of the sideband intensities using SIMPSON simulations (Figure S12). The resulting CSA parameters obtained with sideband-selective ^{1}H{^{195}Pt} TONE D-HMQC-4 for **1** ($\Omega = 8816$ ppm, $\kappa = –0.95$) are in close agreement with the known values ($\Omega = 8975$ ppm, $\kappa = -0.96$).[60, 71] Analysis of the sideband-selective PE RESPDOR data set yields $\Omega = 8687$ ppm and $\kappa = –0.7$, again in good agreement with the established CSA tensor parameters (Figure S11C).

^{1}H{^{195}Pt} sideband-selective NMR experiments were also applied to **2**, which has not previously been analyzed by ^{195}Pt solid-state NMR. The 1D ^{1}H solid-state NMR spectrum of **2** showed two signals at 1.9 and 6.3 ppm, corresponding to the methyl and CH hydrogen atoms of the acetylacetonate ligands, respectively (Figure 3B). A standard 1D ^{1}H{^{195}Pt} TONE D-HMQC-2 spectrum showing both ^{1}H NMR signals can be obtained in a few minutes (Figure 3B), despite the long ^{1}H T_1 (36 and 50 s for the methyl and methine ^{1}H, respectively) and small ^{1}H-^{195}Pt heteronuclear dipolar couplings of ca. 300 Hz (see ^{1}H{^{195}Pt} SHAP S-REDOR experiments[66, 74] in Figure S13A). Rotor-synchronized 2D TONE D-HMQC-4 experiments were performed with MAS frequencies of 50 and 52 kHz to measure the ^{195}Pt isotropic chemical shift of **2** (Figure S13B). Notably, two ^{195}Pt signals at –360 and –385 ppm were observed, suggesting that the sample studied here contains two crystallographically inequivalent sites, in disagreement with the currently known crystal structure of **2**.[91] A ^{13}C CPMAS spectrum of **2** also shows more peaks than expected, yet the experimental PXRD pattern closely matches that predicted from the 200 K X-ray structure (Figure S13). Hence, we conclude that the sample of **2** studied here was phase pure, but that the structure at room temperature may be slightly different from the reported 200 K single-crystal X-ray structure. A wideline ^{1}H{^{195}Pt} D-HMQC experiment on **2** takes 45 hours and it suffers from an incomplete excitation because of the large CSA (Figure S13C). The Ω was estimated to be 11800 ppm (Figure S13D, Note S2), in good agreement with a previous estimate of 10000 ppm from solution ^{195}Pt NMR relaxation experiments.[92] On the other hand, with sideband-selective TONE D-HMQC-4 and PE RESPDOR experiments, ^{195}Pt NMR spectra were obtained in only 15 and 13 hours, respectively (Figure 3). Fits of the ^{195}Pt NMR spectra obtained with TONE D-HMQC-4 or PE RESPDOR yielded a κ of -0.7 and similar Ω values of 12682 ppm or 12521 ppm (Figure S14), which agree with the parameters determined from the MAS ^{195}Pt NMR spectrum extracted from the ^{1}H{^{195}Pt} D-HMQC experiment (Figure S13D). Resolving the two CSA patterns for the two platinum sites of **2** is not possible under our experimental conditions because of their similar isotropic shifts (ca. 15 ppm and 2150 Hz isotropic shift difference).

In summary, the sideband-selective ^{1}H{^{195}Pt} TONE D-HMQC and PE RESPDOR experiments were performed with unprecedented sensitivity: the entire ^{195}Pt MAS NMR spectrum of cisplatin was obtained in only 1 hour with TONE D-HMQC-4 and 24 minutes with PE RESPDOR. For Pt(acac)$_2$ the ^{195}Pt MAS NMR spectrum was obtained within 15 hours, despite the unfavorable NMR properties of **2**. Given the high signal to noise ratios observed with cisplatin (Figure S15), preliminary ^{195}Pt MAS NMR spectra can typically be obtained in a few minutes for most pure compounds. With these remarkable first results on molecular compounds, sideband-selective $^1H\{^{195}Pt\}$ solid-state NMR experiments were then applied to examine silica-supported platinum compounds.

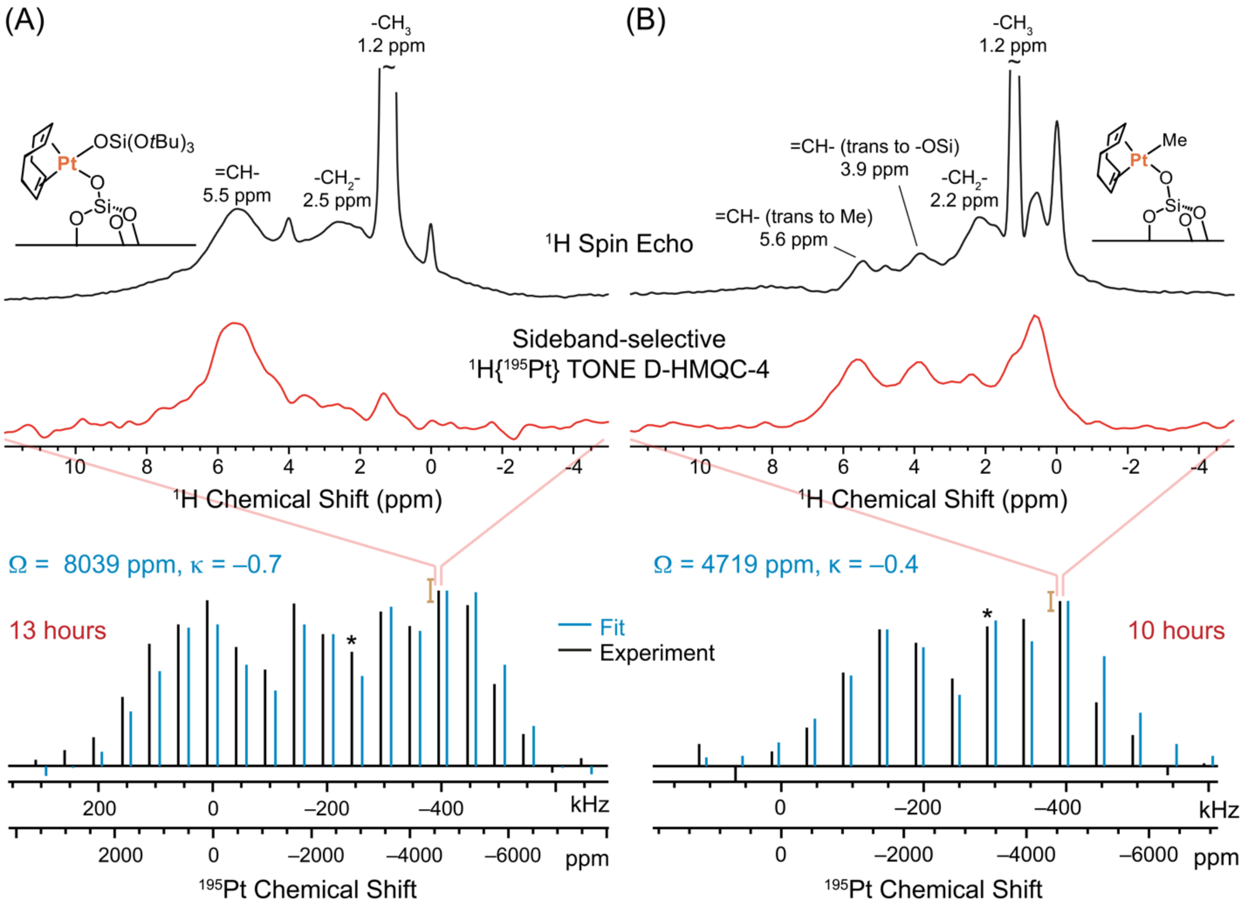


Figure 4. ^{195}Pt sideband-selective NMR experiments with silica-supported Pt compounds (A) **3/SiO$_2$** and (B) **4/SiO$_2$**. (top) 1D ^{1}H spin echo NMR spectra, (middle) sideband-selective $^1H\{^{195}Pt\}$ TONE D-HMQC-4 spectra at the indicated ^{195}Pt offset (corresponding to the most intense sidebands). (bottom, black trace) $^1H\{^{195}Pt\}$ sideband-selective TONE D-HMQC-4 spectra of (A) **3/SiO$_2$** and (B) **4/SiO$_2$**, obtained from the intensities of the CH ^{1}H NMR signal at ca. 5.5 ppm and the CH_3 ^{1}H NMR signal at 1.2 ppm, respectively. (blue trace) SIMPSON simulations with TONE D-HMQC-2 using ^{195}Pt (A) $\Omega = 8039$ ppm, $\kappa = -0.7$ and (B) $\Omega = 4719$ ppm, $\kappa = -0.4$, which correspond to the CS tensors parameters that give the lowest RMSD. The error bar accounting for SNR is shown for the most intense sideband. Intense *t*-butoxide methyl signals were truncated in the ^{1}H spin echo NMR spectra. All experiments were performed with a 50 kHz MAS frequency.

MAS ^{195}Pt Solid-State NMR of Surface Species. In order to investigate materials used in heterogeneous catalysis, we first measured the ^{195}Pt CSA of a model single-site compound prepared by grafting **3** [(COD)Pt(OSi(O*t*Bu)$_3$)] on partially dehydroxylated silica[12, 49, 93] which yields (**3/SiO₂**) with a surface Pt loading of 3.73 wt.% (ca. 1 Pt/nm^2). Recently, we determined the CS tensor parameters of **3/SiO₂** ($\delta_{iso} = -2819$ ppm, $\Omega = 8412$ ppm, $\kappa = -0.77$) using a combination of DNP-SENS $^1H \rightarrow ^{195}Pt$ BRAIN-CP WCPMG and isotropic fast MAS ^1H-^{195}Pt TONE D-HMQC experiments that required approximately five days and one day of spectrometer time, respectively.[66] As we showed previously, the ^{195}Pt isotropic peak and sidebands of the grafted compound are broad (ca. 8-10 kHz full width at half maximum) because of an inhomogeneous distribution of isotropic shifts likely related to slightly different local environments, a result from the amorphous character of silica.[66] To enable efficient excitation/saturation in the sideband-selective experiments, 40 μs excitation pulses with an optimal rf field of 16 kHz were used (Table S1, Figure S3-S4). The sideband-selective TONE D-HMQC-4 experiment yielded the MAS ^{195}Pt CSA pattern within 13 hours that could be fitted to $\Omega = 8039$ ppm, $\kappa = -0.7$, consistent with the reported values mentioned above (Figure 4A and Figure S16-S17). Although PE RESPDOR showed only a maximum dephasing of 5% (corresponding to an estimated error of ca. 20% of the dephasing difference signal intensities), a ^{195}Pt NMR spectrum was obtained in only 3.3 hours and fits of this spectrum gave $\Omega = 7876$ ppm, $\kappa = -0.8$ (Figure S17). The significant savings in time (few hours) compared to our previous report (6 days),[66] demonstrates the high sensitivity of the sideband-selective experiments for measurement of ^{195}Pt NMR spectra.

To probe if the sideband-selective experiments are suitable to detect differences in the ligand environment of supported compounds, we obtained ^{195}Pt NMR spectra of [(COD)PtMe]/SiO₂ (**4/SiO₂**) that has a surface Pt loading of 4.96 wt.%. In **4/SiO₂,** the –OSi(O*t*Bu)₃ ligand of **3/SiO₂** is replaced with a methyl ligand. Consequently, in **4/SiO₂** the two sets of olefinic protons in the COD ligand become inequivalent; the CH protons *trans* to the methyl and –OSi groups appear at 5.6 and 3.9 ppm, respectively, in close accordance with the solution ^1H NMR spectrum of **4** (δ_{iso} = 5.90 and 3.56 ppm, Figure S18).[12] As a result, the signal intensities of the olefinic protons is halved in comparison to **3/SiO$_2$** which will decrease the overall indirect detection sensitivity. However, the methyl group protons at 1.2 ppm are also in close proximity to the Pt center and can also be used as spy nuclei for the indirect detection experiments. Indeed, all of these ^{1}H NMR signals are clearly observed in rotor-synchronized 1D and 2D ^{1}H{^{195}Pt} TONE D-HMQC-2 spectra (Figure 4B, Figure S19), indicating that COD and methyl ligands remain coordinated to Pt after grafting on silica. For **4/SiO$_2$** δ_{iso} was determined to be –3327 ppm from the rotor-synchronized 2D ^{1}H{^{195}Pt} TONE D-HMQC-2 spectra (Figure S19). A single 1D sideband-selective ^{1}H{^{195}Pt} TONE D-HMQC-4 spectrum can be acquired in only 40 minutes with a SNR of 20 at the most intense sideband. Consequently, the entire ^{195}Pt MAS NMR spectrum of **4/SiO$_2$** was obtained in only 10 hours (Figure 4B). Least-squares fitting of the resulting pattern with SIMPSON simulations provides Ω = 4719 ppm, κ = −0.7 (Figure S20), which illustrates a significant lowering of the span in comparison to **3/SiO$_2$**. These results demonstrate that the new solid-state NMR experiments are well suited to capture differences in Pt environments of surface species.

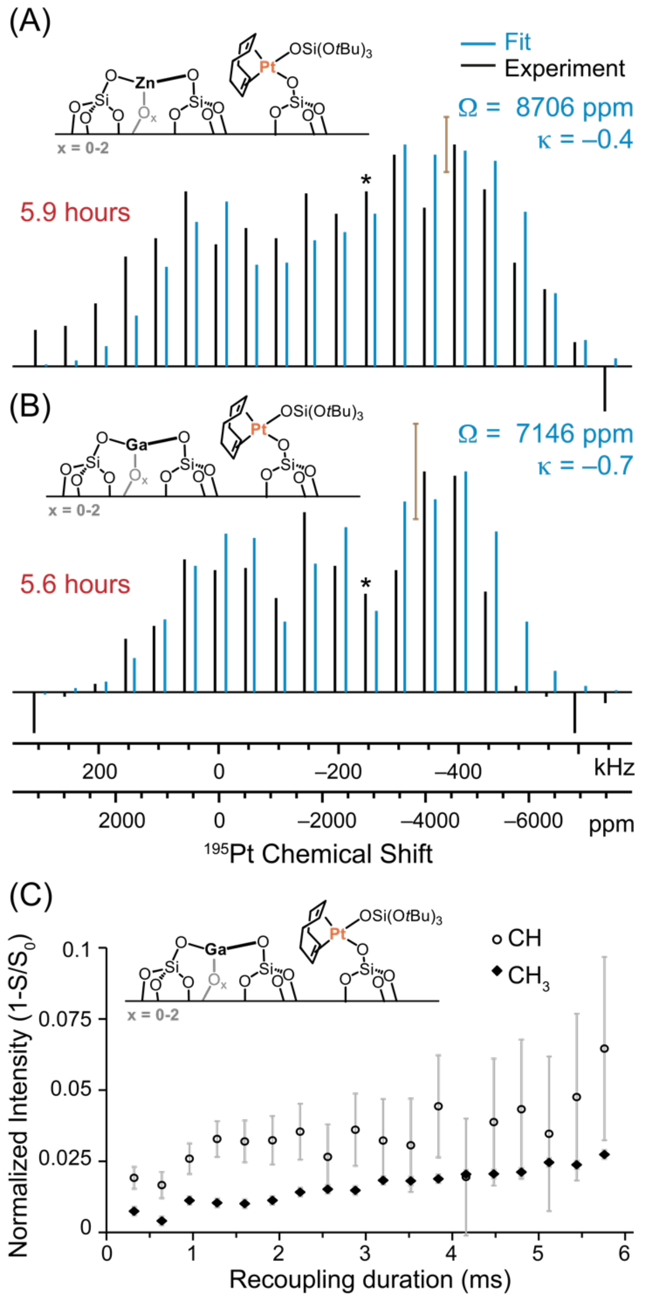


Figure 5. Sideband-selective $^{1}H\{^{195}Pt\}$ PE RESPDOR experiments on single-site Pt compounds (A) **3_Zn/SiO$_2$** and (B) **3_Ga/SiO$_2$**. (black) Experimental patterns and (blue) SIMPSON simulations performed using the indicated CS tensor parameters. A maximum experimental signal dephasing of (A) 6.4% and (B) 3.7% was observed. Error bars are shown for the most intense sidebands. (C) $^{1}H\{^{71}Ga\}$ PE RESPDOR build-up curves: plot showing normalized dephasing difference signal intensity ($1–S/S_0$) as a function of dipolar recoupling duration for (circles) CH and (diamonds) CH_3 groups in the grafted [(COD)Pt(OSi(O*t*Bu)$_3$)] complex.

In order to probe the sensitivity of these newly developed NMR experiments to modifications on the surface, we investigated the surface species of [(COD)Pt(OSi(O*t*Bu)$_3$)$_2$]

grafted on silica doped with different Lewis acids, namely Zn(II) and Ga(III), in order to probe the local environment around Pt and determine if there are any interactions of Pt with the adjacent Lewis acid sites. These systems, denoted **3_Zn/SiO$_2$** and **3_Ga/SiO$_2$**, were chosen because they are used as precursors to prepare highly active mixed-metal nanoparticle catalysts for the non-oxidative propane dehydrogenation.[13, 15-16] The 1D ^{1}H NMR spectra of both compounds clearly show signals corresponding to CH$_3$ (ca. 1.2 ppm), CH$_2$ (ca. 2.2 ppm) and the olefinic CH (ca. 5.6 ppm) protons (Figure S21), in good agreement with the chemical shift assignments of **3/SiO$_2$**.[66] The ligand structure was further confirmed by 2D ^{1}H single quantum-double quantum (SQ-DQ) correlation spectroscopy, and ^{13}C and ^{29}Si DNP-SENS (Figure S21-S23). Rotor-synchronized 2D ^{1}H{^{195}Pt} TONE D-HMQC spectra were used to measure the isotropic ^{195}Pt chemical shifts of –2844 and –2828 ppm for **3_Zn/SiO$_2$** and **3_Ga/SiO$_2$**, respectively (Figure S24). These isotropic shift values are entirely consistent with a similar Pt local environment as found in **3/SiO$_2$** (^{195}Pt δ_{iso} = –2819 ppm).

Figure 5A and 5B shows comparisons between experimental sideband patterns obtained with ^{1}H{^{195}Pt} PE RESPDOR and corresponding SIMPSON simulations using the best fit ^{195}Pt CS tensor parameters. Sideband-selective ^{1}H{^{195}Pt} PE RESPDOR was used to measure the ^{195}Pt MAS NMR spectra of **3_Zn/SiO$_2$** and **3_Ga/SiO$_2$** because it provided better sensitivity than TONE D-HMQC. We obtained Ω = 8706 ppm and κ = –0.4 for **3_Zn/SiO$_2$** and Ω = 7146 ppm, κ = –0.7 for **3_Ga/SiO$_2$**, from least-squares fitting (Figure S25). Notably, the ^{195}Pt NMR spectra obtained with the sideband-selective experiments are clearly superior to those obtained with DNP-SENS ^{1}H→^{195}Pt BRAIN-CP-WCPMG[62] NMR experiments, which provided only partial excitation of the ^{195}Pt shielding patterns, with greatly reduced intensity at the high-frequency side of the pattern

(Figure S26). Note that similar distortions of intensity were previously seen in the $^{1}H \rightarrow ^{195}Pt$ BRAIN-CP-WCPMG spectrum of **3/SiO$_2$**.[66]

Clearly, the structure of the grafted single-site [(COD)Pt(OSi(O*t*Bu)$_3$)] species in **3_Zn/SiO$_2$** is similar to **3/SiO$_2$**. In case of **3_Ga/SiO$_2$**, the observed ^{195}Pt sideband manifold indicates a span that is lower than that of **3/SiO$_2$** by ca. 1250 ppm, which could indicate differing interactions between the grafted Pt compounds and the co-grafted Ga^{3+} and Zn^{2+} ions, that in turn suggests slight average differences in the conformation and electronic structure. Note that the reduction in span of **3_Ga/SiO$_2$** could also be partially attributed to the error in intensities due to a low PE RESPDOR dephasing of ca. 3.7%. To confirm the proximity of the co-grafted Pt complex and the Ga^{3+} ions, we performed $^{1}H\{^{71}Ga\}$ PE RESPDOR experiments which show dephasing of the olefinic CH and the methyl groups of the siloxide ligand (Figure 5C). The slow build-up of the $^{1}H\{^{71}Ga\}$ PE RESPDOR curve is consistent with ^{1}H-^{71}Ga inter-nuclear distances on the order of several angstroms. Similar RESPDOR experiments could not be performed on **3_Zn/SiO$_2$** due to the low ^{67}Zn natural abundance of 4.1%.

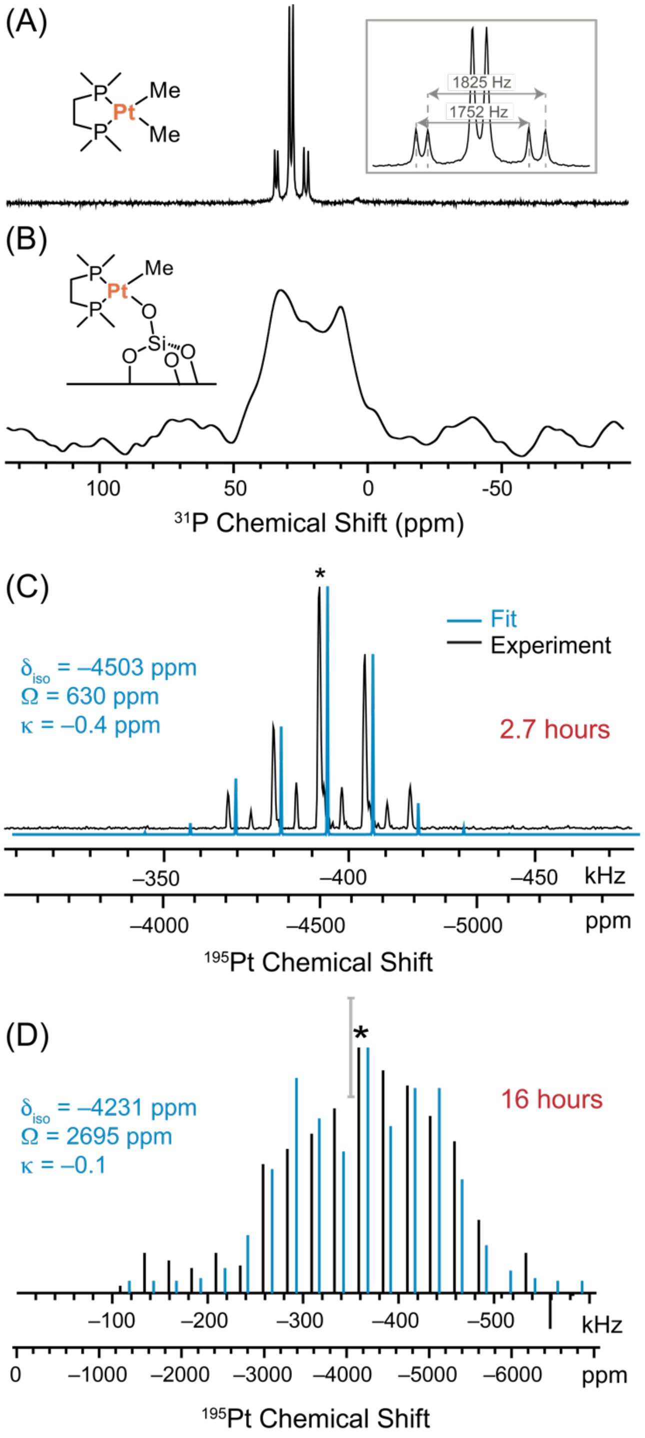


Figure 6. ^{31}P{^{195}Pt} NMR experiments on compounds **5** and **5/SiO$_2$**. ^{1}H→^{31}P CP-MAS spectra of (A) **5** and (B) **5/SiO$_2$** obtained with a 25 kHz MAS frequency. (C) 1D ^{195}Pt projection from a 2D ^{31}P{^{195}Pt} CP constant time *J*-HMQC spectrum of **5** acquired with a 12.5 kHz MAS frequency. (D) ^{195}Pt CSA pattern of **5/SiO$_2$** acquired with a sideband-selective ^{1}H-^{31}P{^{195}Pt} CP *J*-resolved pulse sequence using CPMG detection and a 25 kHz MAS frequency.

$^{31}P\{^{195}Pt\}$ J-HMQC and J-Resolved NMR Experiments. While ^{1}H spins near ^{195}Pt were used to indirectly observe ^{195}Pt CSA patterns and determine the local structure of single-site Pt compounds, many catalysts can contain alternative ligands, such as phosphines. ^{31}P can also serve as a spy nucleus for sideband-selective experiments as it offers good NMR sensitivity. We demonstrate this approach with [(DMPE)PtMe$_2$] (**5**) and the corresponding supported compound **5/SiO$_2$** (Figure 1) using *J*-based ^{1}H-^{31}P{^{195}Pt} solid-state NMR experiments performed with a triple-resonance 2.5 mm HXY probe and MAS frequencies of 12.5 and 25 kHz, respectively.

Figure 6A shows a ^{1}H→^{31}P CP-MAS spectrum of **5**, which can be obtained within a few minutes. Two ^{31}P sites are observed at 29.1 ppm and 30.4 ppm with $^{1}J_{\text{P-Pt}}$ values of 1825 and 1750 Hz, respectively. Both the chemical shifts and $^{1}J_{\text{P-Pt}}$ values agree closely with previous solution NMR measurements.[94] Note that small variations in bond angles/lengths in the solid-state can create inequivalence and cause two ^{31}P NMR signals to be observed instead of one. A ^{31}P{^{195}Pt} constant-time *J*-HMQC experiment was then performed on **5** (Figure S27A). The constant-time format of the HMQC experiment enables arbitrary and large F_1 spectral widths necessary for the indirect detection of ^{195}Pt spinning sideband manifolds.[71] The resulting ^{195}Pt NMR spectrum was fit to CS tensor parameters of $\delta_{\text{iso}} = -4503$ ppm, $\Omega = 630$ ppm and $\kappa = -0.4$ (Figure 6C).

The ^{31}P CP-MAS spectrum of **5/SiO$_2$** has a low SNR (ca. 9 after 3.5 hours of acquisition) because of the low Pt surface loading of 4.4 wt % and signal broadening due to surface disorder (Figure 6B). Additionally, the ^{31}P NMR spectrum of **5/SiO$_2$** shows two characteristic features at 35 and 10 ppm, consistent with the inequivalence of the two phosphines in the grafted species: one is *trans* to a methyl (35 ppm), while the other is *trans* to a siloxide group (10 ppm). CPMG detection was used to accelerate all ^{31}P{^{195}Pt} solid-state NMR experiments on **5/SiO$_2$**. Due to low sensitivity, it was not possible to perform a ^{31}P{^{195}Pt} wideline *J*-HMQC experiment on **5/SiO$_2$**.

However, a rotor-synchronized $^{31}P\{^{195}Pt\}$ *J*-HMQC spectrum showed that the ^{195}Pt isotropic chemical shift of **5/SiO₂** was –4231 ppm (Figure S27B, Figure S28). The ^{195}Pt CSA of **5/SiO₂** was then measured using a $^{31}P\{^{195}Pt\}$ CP *J*-resolved (heteronuclear spin echo) experiment with 40 μs ^{195}Pt sideband-selective saturation pulses at 22 kHz rf field (Figure 6D). The dephasing observed for CPMG spikelets at 36 and 29 ppm was averaged to improve the SNR (Figure S29). With this approach, the sideband manifold could be obtained in only 16 hours. Least-squares fitting of the sideband manifold yields $\Omega = 2695$ ppm and $\kappa = -0.1$ (Figure 6D, Figure S30). Interestingly, the values of δ_{iso} for **5** and **5/SiO₂** only differ by 272 ppm, a small difference with respect to the large chemical shift range of ^{195}Pt. However, the value of Ω for **5/SiO₂** is considerably larger than that measured for **5** (2695 *vs* 630 ppm), illustrating the importance of measuring CSA to probe the changes in the local Pt coordination environment upon grafting. The origin of the large difference in ^{195}Pt CSA is further discussed below. In conclusion, sideband-selective $^{31}P\{^{195}Pt\}$ *J*-resolved experiments enabled acquisition of the ^{195}Pt NMR spectrum of **5/SiO₂** in only 16 hours, demonstrating that NMR-active nuclei other than ^{1}H can be used for indirect detection of ^{195}Pt NMR spectra.

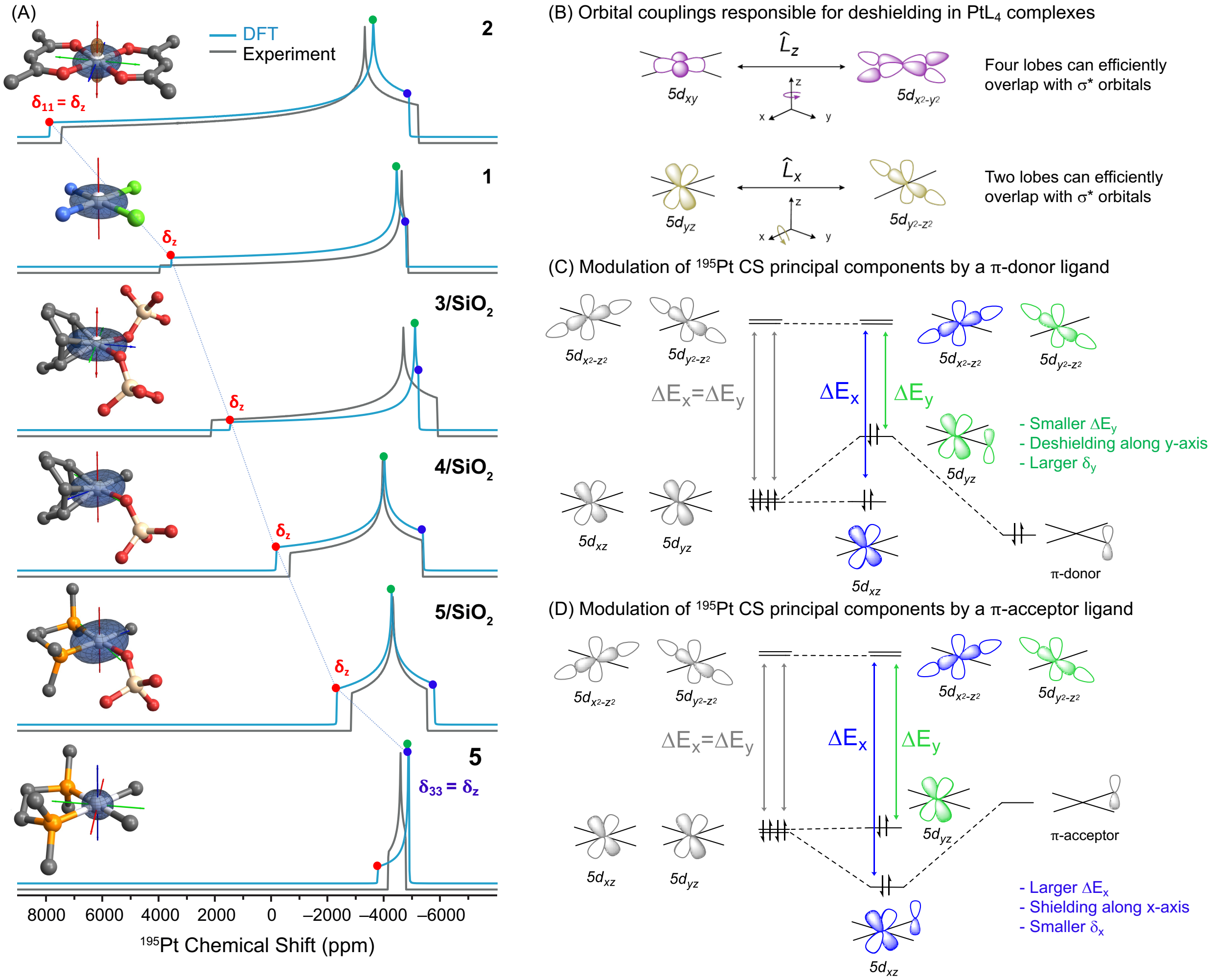


Figure 7. (A) Simulated static ^{195}Pt CSA parameters obtained using parameters from (black traces) sideband-selective NMR experiments and (blue traces) ZORA DFT calculations. The DFT optimized structures and the corresponding 3D representations of the calculated shielding tensors are shown for each compound. (B) Orbital couplings responsible for paramagnetic deshielding in square planar PtL$_4$ complexes. Modulation of orbital energies and Pt CS principal components in the plane by (C) a π-donor and (D) a π-acceptor ligand. In (A), blue and orange lobes indicate positive and negative shielding, respectively. The CSA principal components color code is: $\delta_{11} > \delta_{22} > \delta_{33}$. Plots of the shielding tensors are scaled to 0.002 pm/ppm. A summary of ^{195}Pt CSA parameters from different methods are provided in the Supporting Information in Table S2. NMR calculations of the supported species were performed using with *t*-butoxy siloxide groups in place of the silica surface. Hydrogen atoms are omitted for clarity. For the same reason, only the SiO$_4$ unit of the siloxide ligands is shown.

DFT Calculations of ^{195}Pt CS Tensors. Finally, we used spin-orbit ZORA DFT calculations to compute the ^{195}Pt CS tensor parameters of the molecular and supported Pt-species studied.[95-96] The differences in CSA parameters can be related to differences in the coordination environments using simple and powerful orbital models. Modern computational chemistry packages allow accurate prediction of NMR properties, including ^{195}Pt chemical shifts,[58-59, 97] which is useful for structure determination by NMR crystallography protocols.[55, 98-99] As demonstrated by Ziegler, the origin of the ^{195}Pt CSA can be traced back to electronic structure.[100] Autschbach subsequently demonstrated a localized molecular orbital analysis of ^{195}Pt CS tensors that provides a clear link between the energy and symmetry of orbitals in square planar Pt compounds and the observed CS tensor parameters:[55, 59] the deshielding for the CS component along the *z* direction of the molecular frame (denoted δ_z), originate from the coupling of the high-lying, filled d_{xy} orbital with the antibonding σ*(Pt-L) orbital by the $\hat{L}_z$ operator and, to a minor extent, from the filled d_{xz} and d_{yz} Pt orbitals coupling with the specific σ*(Pt-L) along the y or x axis, by $\hat{L}_y$ and $\hat{L}_x$ respectively (Figure 7B, details in experimental section below).

Standard gas-phase DFT calculations using the Gaussian09 program[101] were used to optimize atomic coordinates. Then, ZORA DFT calculations as implemented in the ADF program[102] were used to calculate ^{195}Pt CSA principal components ($\delta_{11} > \delta_{22} > \delta_{33}$) (for additional details, see the experimental section). The computed and experimental values of CSA are in good agreement, thus validating the computational approach (see Figure 7A and Table S2).

In all but one case, δ_{11}, the most deshielded component, lies perpendicular to the plane, along the natural *z*-axis of these square planar compounds ($\delta_{11} = \delta_z$). The exception is for compound **5**, where δ_{33} is aligned with the molecular *z*-axis. Across the series of square planar compounds studied here, the value of δ_z varies from +7873 to –4885 ppm, while the other components in the plane (δ_x/δ_z), varies only within ca. 2000 ppm. Note also that small changes in geometry significantly affect ^{195}Pt CS tensor parameters (Figure S31).

The (de)shielding across the series of Pt-species studied here is clearly affected by the energy of σ*(Pt-L) orbitals, which is determined by the σ-donating properties of the corresponding

L ligands (Note S3). Thus, it may not be so surprising that changes in the coordination sphere of $Pt^{II}L_4$ compounds dramatically affect the δ_z component, which varies from +7873 (**2**) to –4885 ppm (**5**) upon going from oxygen to carbon-based ligands. As discussed above, the compound **5** presents the most shielded value for δ_z that correspond to δ_{33} and not δ_{11} as for the other compounds discussed here. Using the orbital-rotation model (Figure 7B, details in SI), one can readily justify the much more shielded value for δ_z in **5** which contains four strong σ-donor ligands bound to Pt (two methyl and two phosphine), hence the increase of σ*(Pt-L) orbital energies and high shielding of the Pt nucleus. At the opposite end, the compound **2** with acac ligands has four weak σ-donor oxygen atoms bound to Pt, leading to a lower σ *(Pt-L) orbital energy and the more deshielding δ_z (larger positive value). Overall, the strength of the σ-donating ligands drives the value of δ_z and determine the overall anisotropy and isotropic CS.

The sensitivity of the CS tensor parameters to the types of coordinated ligands explains why **5** and the supported **5/SiO₂** have significantly different spans (Figure 7A). The replacement of one Pt-methyl bond in **5** by a Pt-siloxide bond in **5/SiO₂** upon grafting, leads to a more deshielded δ_z component, as a result of the lower σ-donating properties of the siloxide ligand. This analysis also proves suitable to understand the differences in spans among supported Pt sites. For the supported species **3/SiO₂** and **4/SiO₂** the latter has a more shielded δ_z component, resulting from the presence of a methyl group, a strong σ-donor ligand. A remarkable difference in δ_z can also be observed between **4/SiO₂** and **5/SiO₂**, where a more shielded δ_z in the latter can be related to the stronger σ-donating properties of DMPE with respect to the COD ligand.

Although CSA parameters in square planar $Pt^{II}L_4$ complexes are mostly affected by σ-interactions, the other principal components lying in the plane can be modulated through π-bonding interactions. These effects are observed upon comparison of **3/SiO₂** with the respective asymmetric complex **4/SiO₂**. While the symmetric molecular model for **3/SiO₂** (having two siloxide ligands) has an axially symmetric CS tensor ($\delta_{22} \approx \delta_{33} \approx -5150$ ppm), the asymmetric system **4/SiO₂**, with both a siloxide (weak π-donor) and a methyl ligand (mostly σ-donor) has δ_{22} (–4021 ppm) >> δ_{33} (–5400 ppm). In **4/SiO₂**, the most shielded component δ_{33} is aligned with the Pt-methyl bond, while δ_{22} is aligned with the Pt-siloxide bond. Specifically, the presence of a π-donor ligand causes an increase in energy of the overlapping filled Pt $5d_{yz}$ orbital through an antibonding interaction, which ultimately results in an increased energy of the $5d_{yz}$ orbital that allows for a more efficient coupling with σ*(Pt-L), hence the observed deshielding in the direction of the coupling (Figure 7C). On the contrary, a π-acceptor ligand can interact with the filled Pt $5d_{yz}$ orbital, stabilising it, and resulting in a less efficient orbital coupling due to increase in energy difference with the antibonding σ*(Pt-L) (Figure 7D). When combined, these orbital interactions lead to the observed effects in CSA of the asymmetric system **4/SiO₂**; analogous observations can be made for **5/SiO₂**. In summary, ^{195}Pt solid-state NMR spectra and CSA provide a signature of the metal sites, the types of ligands and the local symmetry of organometallic complexes and supported Pt species. Hence ^{195}Pt solid-state NMR spectroscopy is a powerful tool to characterize compounds and surface sites.

Conclusions

In conclusion, we have developed robust and expedient sideband-selective solid-state NMR methods to rapidly measure the ^{195}Pt NMR spectroscopic signatures of Pt-containing compounds and materials, including some having very large CSA such as Pt(acac)$_2$. The sideband-selective NMR experiments offer an enormous time saving in comparison to state-of-the-art static DNP SENS experiments.[66] Additionally, the sideband-selective NMR methods can be performed at room temperature and require only a few mg of material when performed with fast MAS probes and small diameter rotors. These methods are based on low-power pulses that are one or more rotor cycles in duration and provide sideband-selective excitation or saturation in fast MAS ^{1}H{^{195}Pt} TONE D-HMQC-4 and PE RESPDOR experiments, thus allowing the reconstruction of MAS ^{195}Pt sideband intensities from a series of 1D NMR spectra. This approach was also extended to sensitive spy nuclei such as ^{31}P for indirect detection in sideband-selective ^{31}P{^{195}Pt} *J*-resolved experiments, thus showing that, even in the absence of ^{1}H in the materials, other NMR active spy nuclei can be utilized to obtain valuable molecular-level information on metal sites. Furthermore, analysis of the CSA patterns down to the nature of the Pt-bonded ligands (σ-donor strength and π-donating/accepting ability) provides an understanding of the trends in NMR parameters and also demonstrates the potential of Pt NMR spectroscopy to distinguish subtle differences in the Pt-coordination sphere. With this methodology in hand, we are currently exploring structure-reactivity relationships in Pt-based single-atom catalysts, and are also investigating their applications to other high *Z* spin-1/2 nuclei with moderate isotopic abundance that exhibit large CSA. Finally, combining the sideband-selective NMR experiments with DNP should offer further gains in sensitivity that will be needed to study dilute single-atom catalysts or enable the use of nuclei such as natural abundance ^{13}C as a spy-nucleus.

Experimental Section

Synthesis of Materials. All experiments were conducted inside an Argon filled MBraun GloveBox or using standard Schlenk technique, using anhydrous reagents and distilled solvents, unless indicated otherwise. All solvents were stored over 4 Å molecular sieves after being transferred to a glove box. Silica (SiO_2, Aerosil 200®, 200 m^2 g^{-1}) was calcined in air at 500°C before subsequent dehydroxylation at 700°C under high vacuum as reported in literature.[10] The resulting dehydroxylated silica is referred to as SiO_{2-700}. Titration of the resulting SiO_{2-700} using $[Mg(CH_2Ph)_2(THF)_2]$ purified *via* sublimation prior to use,[103] yielded an Si−OH density of 0.3 mmol/g, corresponding to 0.9 accessible Si−OH groups per nm^2. $PtCl_2(NH_3)_2$ (**1**, 99 % purity, Alfa Aesar) and $Pt(acac)_2$ (**2**, 98 % purity, Strem Chemicals) were used as received. $[(COD)Pt(OSi(O^tBu)_3)_2]$ (**3**), $[(COD)PtMe(OSi(O^tBu)_3)]$ (**4**), $[(DMPE)PtMe_2]$ (**5**), $[Zn(OSi(OtBu)_3)_2]_2$ and $[Ga(THF)(OSi(OtBu)_3)_3]$ molecular precursors were synthesized *via* literature procedures with minor modifications.[12, 93, 104-106] $[(COD)Pt(OSi(OtBu)_3)]/SiO_2$ (**3/SiO₂**) was synthesized according to the previously described procedure.[66] The materials $[(COD)Pt(OSi(OtBu)_3)]\_Zn^{II}/SiO_2$ (**3_Zn/SiO₂**), $[(COD)Pt(OSi(OtBu)_3)]\_Ga^{III}/SiO_2$ (**3_Ga/SiO₂**) and $[(COD)PtMe]/SiO_{2-700}$ (**4/SiO₂**) were synthesized following adapted literature procedures.[12-13, 15]

$[(COD)Pt(OSi(OtBu)_3)]\_Zn^{II}/SiO_2$ (3_Zn/SiO₂): A colourless solution of $[Zn(OSi(OtBu)_3)_2]_2$ (0.234 g, 0.395 mmol) in benzene (10 ml) was added slowly to a suspension of SiO_{2-700} (1.517 g, 0.455 mmol -OH) in benzene (10 ml) while stirring (100 rpm). The resulting suspension was stirred for 5 h at room temperature. The supernatant was removed, and the material washed with benzene (10 ml) three times to wash off unreacted complex. The material was then washed with pentane and subsequently dried under high vacuum (10^{-5} mbar) for 3 h to remove residual solvent. The resulting white solid was then transferred to a tubular quartz reactor and treated under high vacuum (10^{-5} mbar) at high temperature (r.t. to 300 °C (5 °C/min) for 1 h, 400 °C (5 °C/min) for 1 h, 500 °C (5 °C/min) for 1 h, 600 °C (5 °C/min) for 8 h). Part of the resulting white solid (1.193 g, 0.358 mmol –OH assumed) was suspended in benzene (10 ml), and a colourless solution of **3** (0.258 g, 0.311 mmol) in benzene (10 ml) added to it slowly while stirring

(100 rpm). The resulting suspension was stirred for 4 h at room temperature. The supernatant was removed, and the material washed with benzene (10 ml) three times to wash off unreacted complex. The material was then washed with pentane and subsequently dried under high vacuum (10^{-5} mbar) for 3 h to remove residual solvent. **3_Zn/SiO$_2$** was obtained as a white solid. Elemental Analysis: 2.77 wt.% Pt, 1.48 wt.% Zn.

[(COD)Pt(OSi(OtBu)$_3$)]_Ga^{III}/SiO$_{2-700}$ (3_Ga/SiO$_2$): A colourless solution of [Ga(THF)(OSi(OtBu)$_3$)$_3$] (0.245 g, 0.263 mmol) in benzene (10 ml) was added slowly to a suspension of SiO$_{2-700}$ (1.009 g, 0.303 mmol -OH) in benzene (10 ml) while stirring (100 rpm). The resulting suspension was stirred for 12 h at room temperature. The supernatant was removed, and the material washed with benzene (10 ml) three times to wash off unreacted complex. The material was then washed with pentane and subsequently dried under high vacuum (10^{-5} mbar) for 5 h to remove residual solvent. The resulting white solid was then transferred to a tubular quartz reactor and treated under high vacuum (10^{-5} mbar) at high temperature (r.t. to 300 °C (5 °C/min) for 1 h, 400 °C (5 °C/min) for 1 h, 500 °C (5 °C/min) for 1 h, 600 °C (5 °C/min) for 8 h). Part of the resulting grey solid (0.480 g, 0.144 mmol –OH assumed) was suspended in benzene (10 ml), and a colourless solution of **3** (0.104 g, 0.125 mmol) in benzene (10 ml) added to it slowly while stirring (100 rpm). The resulting suspension was stirred for 12 h at room temperature. The supernatant was removed, and the material washed with benzene (10 ml) three times to wash off unreacted complex. The material was then washed with pentane and subsequently dried under high vacuum (10^{-5} mbar) for 3 h to remove residual solvent. **3_Ga/SiO$_2$** was obtained as a white solid.

[(COD)PtMe]/SiO$_{2-700}$ (4/SiO$_2$): A colourless solution of **4** (0.087 g, 0.15 mmol) in benzene (10 mL) was added slowly to a suspension of SiO$_{2–700}$ (0.500 g, 0.15 mmol −OH) in benzene (10 mL) while stirring (100 rpm). The resulting suspension was stirred for 12 h at room temperature. The supernatant was removed, and the material washed with benzene (10 mL) three times to wash off unreacted complex. The material was then washed with pentane and dried under high vacuum (10^{-5} mbar) for 4 h to remove residual solvent. **4/SiO$_2$** was obtained as a white solid. Elemental analysis: Pt, 4.96 wt. %.

[(DMPE)PtMe]/SiO$_{2\text{-}700}$ (5/SiO$_2$): A suspension of off-white/brown **5** (0.035 g, 0.093 mmol) in benzene (10 mL) was added slowly to a suspension of SiO$_{2-700}$ (0.311 g, 0.093 mmol −OH) in benzene (10 mL) while stirring (100 rpm). The resulting suspension was stirred for 12 h at room temperature with gradual disappearance of **5** in the suspension. The supernatant was removed, and the material washed with benzene (10 mL) three times to wash off unreacted complex. The material was then washed with pentane and dried under high vacuum (10^{-5} mbar) for 2 h to remove residual solvent. **5/SiO$_2$** was obtained as a white solid. Elemental analysis: 4.39 wt.% Pt; 1.35 wt.% P.

Molecular DFT Calculations. Atomic coordinates were optimized with DFT using Gaussian09.[101] Geometry optimizations were performed using the B3LYP functional[107] in combination with Pople's 6-31G(d) basis sets for H, C, Si atoms and 6-31+G(d) for negatively charged atoms (P, O).[108] The Los Alamos LANL2TZ basis set was used for Pt atoms in conjunction with the associated pseudopotential.[109] NMR calculations were performed using ADF 2016 with the PBE0 functional and Slater-type basis sets of quadruple-ζ quality (QZ4P) for Pt and triple-ζ quality (TZP) for other atoms.[102] Relativistic effects were treated by the 2-component zeroth order regular approximation (ZORA).[95-96, 110] The calculated ^{195}Pt chemical shifts were referenced to (COD)PtCl$_2$, with an experimental isotropic chemical shift of −3360 ppm, and a calculated isotropic shielding of 5483 ppm. Calculated shielding tensors are plotted as 3D representations of $\sum_{ij} r_i\, s_{ij} r_j$, polar functions with scaling factors adjusted towards the best readability.[111]

While the chemical shift (δ) is always reported with respect to a reference compound, DFT calculations output the magnetic shielding with respect to the bare nucleus (σ); the equation below is used to convert calculated shielding values to chemical shift values, which are ordered so that $\delta_{11} > \delta_{22} > \delta_{33}$.

$$\begin{pmatrix} \delta_{11} & 0 & 0 \\ 0 & \delta_{22} & 0 \\ 0 & 0 & \delta_{33} \end{pmatrix} = \sigma_{\text{iso}}^{\text{ref}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} - \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix} \quad (1)$$

Plane-wave DFT Calculations. The hydrogen atom positions of $Pt(acac)_2$ in the previously reported crystal structure[91] were optimized using plane-wave density functional theory (DFT). The CASTEP[112] program was used with the PBE-GGA functional[113] and the TS dispersion correction scheme.[114] A *k*-point spacing of 0.07 $Å^{-1}$ was used for the Monkhorst-Pack grid.

Solid-State NMR Experiments. All experiments were performed at 9.4 T using a Bruker Avance III HD console. ^{1}H, ^{31}P and ^{195}Pt chemical shifts were indirectly referenced to tetramethylsilane using the ^{1}H shift of adamantane at 1.82 ppm. Analytical simulations were performed with the TopSpin solid lineshape analysis module (sola) or ssNake *v*1.1.[115]

Fast MAS $^{1}H\{^{195}Pt\}$ *NMR Experiments.* A Bruker 1.3 mm HX probe and the MAS frequency was 50 kHz unless mentioned otherwise. Cisplatin and L-histidine·HCl·H_2O were purchased and used as received from Alfa Aesar and Fluka, respectively; rotors of these samples were packed under ambient conditions. All other rotors were packed in an argon glovebox and rotors were spun with nitrogen gas. $^{1}H\{^{195}Pt\}$ TONE D-HMQC-4 and PE RESPDOR experiments were performed using $SR4_1^2$ dipolar recoupling[85] that was applied at the 2nd order R^3 condition.[116] ^{1}H 90° and 180° pulse durations of 2.5 and 5 μs, respectively were used. The ^{195}Pt sideband-selective pulses were optimized by determining the rf fields that maximized D-HMQC signal intensities using different pulse lengths (Table S1), with longer duration pulses providing more selectivity (Figure S3-S4). The $^{1}H\{^{71}Ga\}$ PE RESPDOR experiment used 30 μs ^{71}Ga saturation pulses with a 330 kHz rf field. In $^{1}H\{^{195}Pt\}$ TONE D-HMQC-4 experiments, SHAPs used tanh/tan shapes with a 20 μs duration, *ca.* 275 kHz rf field and 5 MHz sweep width. Lee-Goldburg spinlock pulses of ca. 1 ms total duration were applied at a rf field of 150 kHz at the appropriate transmitter offset frequency.[86, 117] For sideband-selective $^{1}H\{^{195}Pt\}$ TONE D-HMQC-4 experiments the ^{195}Pt offset for the SHAP inversion pulses was held constant, approximately in the center of NMR powder pattern, while the offset of the sideband-selective pulses was varied. For both TONE D-HMQC-4 and PE RESPDOR sideband-selective experiments the probe was not retuned for each offset. Retuning the probe was found to have a minimal effect on sideband intensities (Figure S5).

Total $SR4_1^2$ dipolar recoupling durations of 1.92 ms (**1**, TONE D-HMQC-4), 2.88 ms (**1**, PE RESPDOR), 3.2 ms (**2**, TONE D-HMQC-4 and PE RESPDOR), 1.76 ms (**3/SiO$_2$**, TONE D-HMQC-4), 2.08 ms (**3/SiO$_2$**, PE RESPDOR), 2.56 ms (**4/SiO$_2$**, TONE D-HMQC-4) and 2.4 ms (**3_Zn/SiO$_2$** and **3_Ga/SiO$_2$**, PE RESPDOR) were used in the various sideband-selective experiments. For the molecular compounds and silica-supported compounds 60 μs, 9 kHz rf field and 40 μs, 16 kHz rf field sideband-selective saturation pulses were employed, respectively. For **4/SiO$_2$** 40 μs sideband-selective pulses with a 12 kHz rf field were used. In case of **1**, although the maximum dephasing observed with PE RESPDOR was only ca. 9% with a total recoupling duration of 2.88 ms, the tolerance to MAS instability is higher at shorter recoupling durations (only 0.7% variation of the RESPDOR S_0 signal intensity was observed, which is the primary source of error in the measurements, Figure S7A). A longer recoupling duration provides more dephasing (Figure S7D) but results in a 'noisier' ^{195}Pt sideband manifold (Figure S11). Therefore, recoupling durations shorter than that providing maximal dephasing may be preferred for the variable offset PE RESPDOR experiments.

The experimental ^{195}Pt sideband-selective patterns are best reproduced by numerical simulations, as performed here using SIMPSON (*vide infra*). Alternatively, an approximate estimate of the CSA values can be obtained using Herzfeld-Berger analysis (HBA).[118-119] For example, with cisplatin, the isotropic shift was fixed to −1834 ppm while Ω and κ were fitted using the HBA program. The estimated CSA parameters for cisplatin were $\Omega = 9776$ ppm and $\kappa = -0.65$ with TONE D-HMQC-4, and $\Omega = 9584$ ppm and $\kappa = -0.64$ with PE RESPDOR (Figure S32). The HBA program used for fitting assumes ideal sideband intensities during fitting; however, the intensities of the ^{195}Pt pattern from the sideband-selective experiments deviate from the ideal pattern and can only be reproduced using numerical simulations. Therefore, HBA should be performed only to estimate the ^{195}Pt CSA.

^{31}P{^{195}Pt} NMR Experiments. All ^{1}H-^{31}P{^{195}Pt} experiments were performed using a Bruker 2.5 mm HXY probe. The pulse sequences used for the acquisition of ^{1}H-^{31}P{^{195}Pt} CP *J*-HMQC and sideband-selective *J*-resolved spectra are shown in Figure S27. Pulse durations of 2.5 μs ($\pi/2$, ^{1}H), 4.75 μs (π, ^{31}P) and 2-2.5 μs ($\pi/2$, ^{195}Pt) were used. The constant-time 2D ^{1}H-^{31}P{^{195}Pt} CP *J*-HMQC spectrum of **5** was acquired with 12.5 kHz MAS, 8 scans, 1.5 s recycle delay ($1.3\times T_1$), indirect spectral width of 500 kHz, 822 complex t_1-increments and a total *J*-evolution time ($2\times m\times\tau_r$) of 1.28 ms (Figure 6C). The ^{1}H→^{31}P CP duration was set to 2.5 ms and optimal ^{1}H and ^{31}P spinlock rf powers of 75 kHz and 83 kHz, respectively, were used; the ^{1}H rf power was ramped from 85-100%. For all experiments with **5/SiO$_2$**, a ^{1}H→^{31}P CP duration of 5 ms and optimal ^{1}H and ^{31}P spinlock rf powers of 105 kHz and 83 kHz, respectively, were used; the ^{1}H rf power was ramped from 90-100%. The sideband-selective ^{1}H-^{31}P{^{195}Pt} CP *J*-resolved

spectra of **5/SiO₂** was acquired with 25 kHz MAS, 1800 scans and 1.5 s recycle delay per point; the total *J*-evolution time ($2\times m\times\tau_r$) was set to 560 μs, and a 40 μs ^{195}Pt saturation pulse at 22 kHz rf was applied. The offset was incremented in steps of the MAS frequency and 21 sub-spectra were obtained. The total duration of each echo in the CPMG train was set to 800 μs and 55 spin echoes were acquired. 100 kHz SPINAL-64 decoupling was applied during *J*-evolution periods and signal acquisition.[120]

SIMPSON simulations. All ^{1}H{^{195}Pt} SIMPSON simulations were performed with a 50 kHz MAS frequency and a ^{1}H Larmor frequency of 400.498 MHz. The ^{1}H-^{195}Pt dipolar coupling was set to –3500 Hz and an optimal recoupling duration of 2.88 ms was used. For the simulations shown in Figure 2, the rep168 crystal file and 24 gamma angles were used for powder averaging. For all other simulations in the main text, the rep320 crystal file and 13 gamma angles were used. 60 μs selective excitation pulses with an optimized 9 kHz rf field were used in the simulations for all molecular compounds, whereas shorter 40 μs duration pulses at 16 kHz rf were used for the surface compounds. The optimal rf fields for the sideband-selective excitation pulses in D-HMQC agree well between simulations and experiments (Table S1). In all cases, the offset frequency of a sideband was determined by first varying the offset in small steps of 1-2 kHz, followed by stepping the transmitter offset in steps equal to the MAS frequency. Note that the TONE D-HMQC-2 sequence was used for SIMPSON simulations throughout this work, while TONE D-HMQC-4 was used for experiments. TONE D-HMQC-2 was used for simulations because TONE D-HMQC-4 relies on experimental rf inhomogeneity, which is absent in the simulations, to dephase uncorrelated signals.[86] The sideband-selective ^{31}P{^{195}Pt} *J*-resolved experiments with **5/SiO₂** were simulated using a ^{31}P-^{195}Pt J-coupling of 1825 Hz, a *J*-evolution time of 560 μs, and a 25 kHz MAS frequency as in the experiments.

Plots showing the root mean square deviation (RMSD) between experimental and simulated patterns are provided in the SI for all samples. Briefly, the sideband NMR spectra were fit with the following procedure: (i) visual inspection of the sideband manifold provides a preliminary estimate of the principal components of the CSA tensor, (ii) the skew of the CS tensor was fixed while the span was varied and (iii) finally, the span with the lowest RMSD was fixed and the skew was varied to determine the best fit.

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Supporting Information

Additional experimental and simulated NMR spectra, and experimental details can be found in the supporting information. Pulse sequences, SIMPSON simulation input files, and raw NMR data for main text Figures are available for download at https://doi.org/10.5281/zenodo.6639016.

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