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Monitoring *In Crystallo* Elementary Steps at Cationic, Site-Isolated, Pt-Sites using Solid-State NMR Signatures

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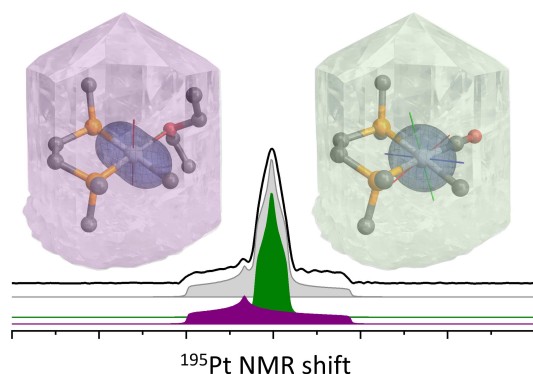
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Abstract

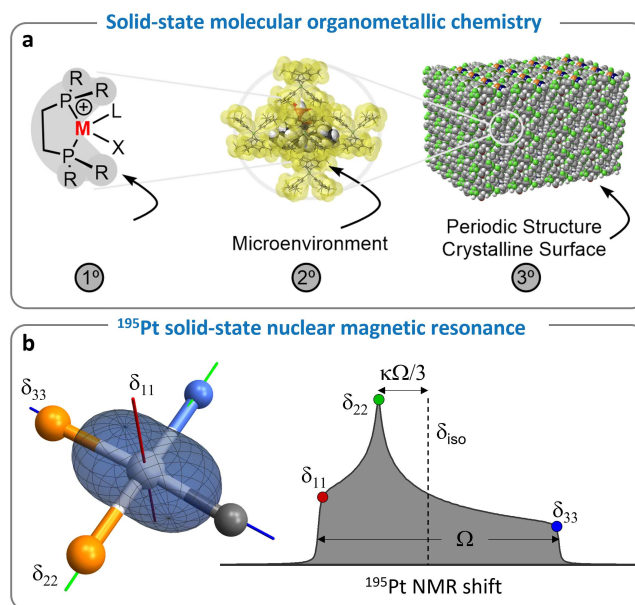
Understanding active sites and monitoring elementary steps in heterogeneous catalysis is central to establishing structure-activity relationships. In this context, solid-state molecular organometallic chemistry (SMOM) has emerged as an original approach in which reactive metal centres are site-isolated within a confined crystalline lattice. This enables *in crystallo* solid-gas transformations that are directly relevant to heterogeneous catalysis. However, experimentally-determined metal speciation of reaction products and tracking changes in the coordination environment of the metal sites upon *in crystallo* reactions can be challenging when samples are not suitable for analysis by single-crystal X-ray diffraction or three-dimensional electron diffraction. Here, we report the development of SMOM approaches to generate isolated Pt sites in well-defined environments and demonstrate how ¹⁹⁵Pt solid-state NMR spectroscopy enables reporting on the changes in the atomic-scale local structure of metal centres during *in crystallo* reactivity studies.

TOC



Introduction

Catalysis is an enabling science and technology, which has the overarching goal of developing sustainable, lower energy input, processes that are also highly selective. Whether homogeneous or heterogeneous, catalysis can be considered as a molecular phenomenon, where bonds are created and broken at the active site(s). While typically well-defined and understood at the molecular level in homogeneous processes, the complexity and dynamic behavior of heterogeneous catalysts typically prevent molecular level interrogation for these materials.^[1] While single-site and single-atom catalysts (SSCs and SACs respectively ^[2–4]) have been developed that bridge the gap between the two disciplines, their local atomic structure often remains complex due to the nature of the interaction of the metal centers with the inhomogeneous anchoring sites provided by the supporting solid carrier. An alternative approach is the use of solid-state molecular organometallic chemistry (SMOM),^[5] which has emerged as a methodology that allows for the molecular heterogeneous *in crystallo*^[6,7] reactivity and structure of organometallic complexes to be studied using solid-gas methods. In this approach, reactive metal centers are site-isolated in a confined crystalline lattice, and are surrounded by weakly coordinating anions, such as $[\text{BAr}^{\text{F}}_4]^-$ [$\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$] when the metal/ligand fragment is cationic. These anions form a stabilizing microenvironment around the active site,^[8] while the CF_3 groups also promote structural plasticity, and the ingress and egress of reactants and products through the periodic lattice.^[9] Scheme 1a diagrams this SMOM approach for cationic complexes. Examples of solid-gas single-crystal to single-crystal organometallic reactivity are known for Ti,^[10] Co,^[11,12] Rh,^[13–17] Ir,^[18–20] Pd,^[21] Cu,^[22] Ag,^[23] and Au^[24,25] complexes. In principle, these systems offer a new class of metal-based heterogeneous catalysts, with the isolated metal sites available for the catalytic process of interest. As such, they exhibit a striking resemblance to SACs/SSCs, with the advantage of being embedded in a crystalline matrix, combining the well-defined structure of molecular complexes with a solid scaffold as found in zeolites or metal-organic frameworks. While solid/gas catalysis is likely to be a surface-dominated process in non-porous molecular crystalline complexes,^[21,26–28] the structural fidelity of the bulk sample, and ability to effect selective and quantitative conversion, offers opportunities to interrogate the structure and reactivity of species that are often unstable in solution,^[17,20] or have direct relevance to surface-located active sites that are less straightforward to determine analytically.



Scheme 1. (a) The SMOM concept as applied to cationic molecular complexes *in crystallo*. **(b)** Translation of the Pt(II) local structural motif into the ^{195}Pt solid-state NMR signature.

For any heterogeneous catalyst system, gaining a detailed understanding of the local structure of metal sites remains a central challenge. For example, in SACs the absence of long-range order, low metal loadings, or the presence of site heterogeneity render many traditional characterization methods insufficient, providing very limited structural insight or indirect information. For SMOM, appropriate crystalline samples that are suitably sized, and with a discrete morphology for single-crystal X-ray diffraction (SC-XRD) may not be available, despite the material being compositionally pure. Furthermore, while the organometallic reaction products may exhibit local order, long-range crystallographic order may be impacted by the solid/gas reaction,^[29] which precludes the meaningful application of other diffraction-based techniques that could be used in micro-crystalline materials, such as powder XRD or three-dimensional electron diffraction (3DED).^[15,30–32] In these instances, experimentally-determined metal speciation is a challenge, with changes in the coordination environment and electronic structure of the metal centers upon reaction with a substrate difficult to detect and quantify.

In this context, solid-state nuclear magnetic resonance (NMR) spectroscopy offers a powerful alternative to diffraction methods, enabling access to atomic-scale structural information in complex solid-state mixtures.^[33] When combined with density functional theory (DFT) calculations, this enables the construction and validation of structural models. In particular Pt-based systems are well-suited for NMR-based studies,^[34–38] with the NMR-active spin- $1/2$ isotope ^{195}Pt possessing an NMR receptivity that is almost 20 times higher than ^{13}C . Furthermore, ^{195}Pt NMR is an exceptionally sensitive probe of the local Pt

environment, owing to its large chemical shift range.^[39–46] In solids, chemical shift anisotropies produce characteristic powder patterns, which provide a distinct fingerprint of the local coordination motifs, described by three parameters, δ_{iso} , Ω , and κ , that enables the direct interrogation of the coordination environment of Pt from these corresponding NMR signatures, Scheme 1b.

In this contribution, we report the development of SMOM approaches for the synthesis of cationic Pt-complexes, and demonstrate the use of ^{195}Pt solid-state NMR to capture the local, atomic-scale, structural changes of Pt centers upon *in crystallo* solid/gas reactions where material that is suitable for analysis by SC-XRD or 3DED is not available. Specifically, we showcase how ^{195}Pt solid-state NMR using ultra-wideline techniques^[43,47–51] under static (*vide infra*) and magic-angle-spinning (see Figure S1) conditions precisely tracks the changes in Pt-coordination environment manipulated through *in crystallo* ligand substitution and reactivity, and identifies reaction products and elementary steps in the absence of diffraction data. Ligand substitution reactions at the metal center are chosen to highlight that ^{195}Pt solid-state NMR spectroscopy provides access to the relative energy changes of frontier molecular orbitals as modulated by the ligands (e.g., σ -donor, π -acceptor, π -donor), and thus is able to monitor changes in the coordination environment around Pt. Using this methodology, we then show that a more complex manifold of reactivity can be tracked using ^{195}Pt solid-state NMR, by the selective insertion of an olefin into a metal-carbon bond, in a solid-gas process. This combined approach links molecular, heterogeneous, *in crystallo* reactivity, and structural studies using SC-XRD or 3DED, with solid-state NMR methodologies that directly report on the electronic environment at the metal center in the bulk material. It thus provides a powerful complementary analytical technique to track reactivity and monitor elementary steps in solid-state molecular materials.

Results and Discussion

Solid-state structure (3DED) of $[\text{Pt}(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)(\text{CH}_3)(\text{OEt}_2)][\text{BAr}^{\text{F}}_4]$, $1[\text{BAr}^{\text{F}}_4]$. A suitable starting point for an investigation of SMOM using Pt-complexes is one with a cationic metal/ligand fragment with a ligand that is primed for replacement by substitution, that can also be structurally characterized using diffraction methods. Kubas and co-workers' report in 2002 of $[\text{Pt}(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)(\text{CH}_3)(\text{OEt}_2)][\text{BAr}^{\text{F}}_4]$, $1[\text{BAr}^{\text{F}}_4]$,^[52] presents such a complex which has a labile diethyl ether ligand, and related Pd-complexes are well-established to be substitutionally-labile in solution.^[53,54] In their original study the SC-XRD structure of $1[\text{BAr}^{\text{F}}_4]$ was not reported, with the product of hydrolysis isolated instead, that arises from adventitious water. In our hands, a modified synthesis of $1[\text{BAr}^{\text{F}}_4]$ results in the isolation of pure crystalline material on a 600 mg scale, that is suitable for onward *in crystallo* reactivity (Supporting Materials). However – notwithstanding repeated attempts – these formed as analytically pure microcrystals (sized $\sim 50\ \mu\text{m}$) and thus were not suitable for SC-XRD using a standard laboratory-based diffractometer. Instead, 3DED was

used to determine the molecular structure. Despite a low flux being used for data collection ($0.06 - 0.07 \text{ e} \cdot \text{\AA}^{-2} \cdot \text{s}^{-1}$), the crystals were found to be radiation sensitive, and so only the initial frames of 11 independent data sets were combined to give an acceptable 93.3% completeness and $0.95 \text{ \AA}$ resolution.

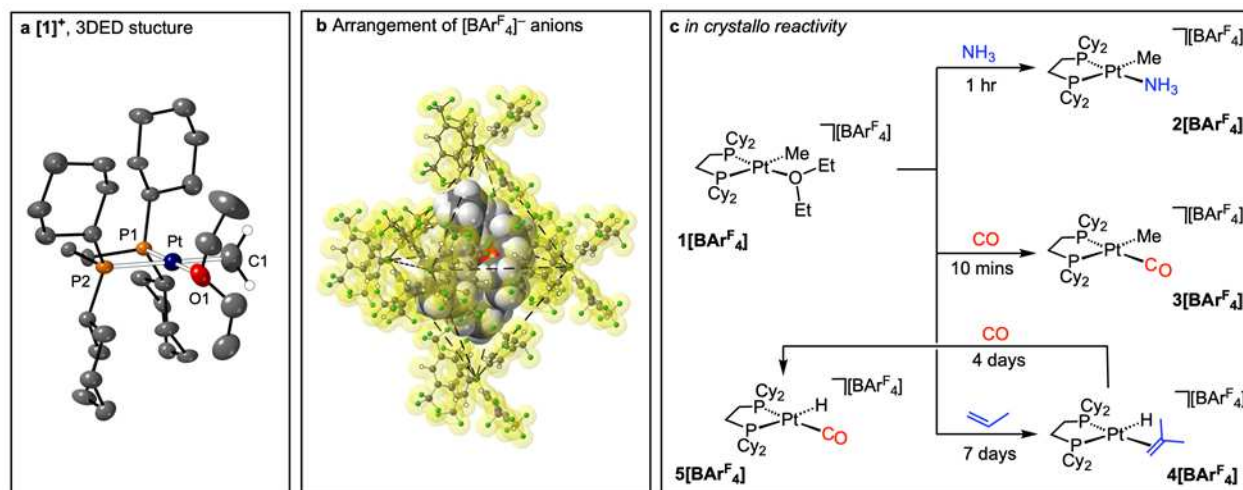


Figure 1. (a) 3DED structure of complex $1[\text{BAr}^{\text{F}}_4]$. Anions and hydrogen atoms (aside from those associated with C1) are not shown. Displacement ellipsoids displayed at the 30% probability level. Selected bond distances ($\text{\AA}$) and angles ($^\circ$): Pt–P1, 2.231(7); Pt–P2, 2.322(6); Pt–O, 2.200(17); Pt–C1, 2.082(16); P1–Pt–O1, 179.7(4); P2–Pt–C1, 175.5(5); O1–Pt–C1, 92.1(6); P2–Pt–O1, 92.3(4). (b) Arrangement of $[\text{BAr}^{\text{F}}_4]^-$ anions around a single cation in the lattice. Surfaces shown at van der Waals radii. (c) *In crystallo* reactivity of complex $1[\text{BAr}^{\text{F}}_4]$. General conditions (unoptimized): finely crushed microcrystalline complex $1[\text{BAr}^{\text{F}}_4]$, 298 K, 2 bar absolute.

Figure 1a shows the resulting molecular structure of the cation, which has a pseudo square planar Pt(II) center, flanked by the chelating phosphine, methyl (C1) and diethyl ether ligands. As expected for the different *trans* influence of methyl (good σ -donor) and diethyl ether (weaker σ - and π donor), the Pt–P distances are shorter for the phosphine *trans* to diethyl ether: Pt–P1, 2.231(7) $\text{\AA}$; Pt–P2, 2.322(6) $\text{\AA}$. Related differences have been noted in Pd-^[54] and Rh-^[27] analogs. Consideration of the packing arrangement of the $[\text{BAr}^{\text{F}}_4]^-$ anions (Figure 1b) shows that they adopt an approximate octahedral arrangement around a single Pt-centred cation, as observed for many other SMOM systems.^[17,55,56]

The ^{195}Pt solid-state NMR spectroscopic signature of $1[\text{BAr}^{\text{F}}_4]$, Figure 2b, directly reports on these atomic-level features. The sensitivity towards the Pt environment stems from the local modification of the external magnetic field by surrounding electrons, referred to as magnetic shielding, which is typically large for heavy isotopes such as ^{195}Pt . Experimentally, a larger shielding results in a more negative chemical shift. Notably, the magnetic shielding and thus the chemical shift depend on the relative orientation of the molecular structural motif to the magnetic field and is described by second-rank tensor in rigid solids, rather than a single value that describes the isotropic chemical shift in solution. This is reflected by the anisotropic broadening of the ^{195}Pt NMR signal due to microcrystalline powders, which is characterized by three

frequency positions, corresponding to the three principal-axis components of the tensor. For chemical shift tensors, the three shift positions are conventionally^[57] assigned according to $\delta_{11} > \delta_{22} > \delta_{33}$. The average value corresponds to the isotropic chemical shift δ_{iso} , while the overall width of the powder pattern is reported by the span $\Omega = \delta_{11} - \delta_{33}$. The tensor symmetry is indicated by the skew $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$, which takes values between 1 and -1 for prolate and oblate tensor shapes, respectively (see Scheme 1b). While all three parameters are sensitive towards the atomic-scale Pt environment, it is the combination of δ_{iso} , Ω , and κ , referred to as the ^{195}Pt NMR signature, which is revealing and characteristic for distinct local Pt-structure motifs.^[58–62]

In **1**[**BAr^F₄**], the Pt nucleus experiences the least shielding in the direction perpendicular to the Pt-ligand plane, a typical characteristic for Pt(II) complexes.^[60,62] This is indicated by the red vector superimposed on the computed magnetic shielding tensor of **1**[**BAr^F₄**] shown in Figure 2b, and corresponds to frequency position δ_{11} , with the highest chemical shift. Interestingly, the significantly stronger σ -donor properties of the methyl compared to diethyl ether induce a very different magnetic shielding along the P2–Pt–C1 axis, resulting in large anisotropy ($\Omega = 4700$ ppm), and a prolate tensor shape ($\kappa = 0.3$). DFT computations of the ^{195}Pt solid-state NMR signature, as performed based on the 3DED structure with optimized hydrogen positions, are in excellent agreement with the experimental data, and the ^{195}Pt chemical-shift-tensor parameters extracted from the corresponding numerical model.

With its structure and spectroscopic signature established, and synthetically useful amounts of **1**[**BAr^F₄**] available, *in crystallo* reaction chemistry was studied, focusing on replacing the diethyl ether with ligands with a different electronic signature. Figure 1c outlines these solid/gas reactivity studies, that were all performed on the 50 mg scale using finely crushed crystalline materials and 2 bar absolute of reagent gas.^[5] All of these reactions went to completion (as measured by solid-state and solution NMR spectroscopy), although the reaction times were unoptimized, and retained microcrystallinity with periodic and local order (powder XRD and solid-state NMR – see Supporting Materials). However subsequent analysis by 3DED was not successful due to a combination of radiation damage, poor data quality and the necessity of collecting small wedges of data from multiple crystals that precluded determination of the structures. Thus, ^{195}Pt solid-state NMR was used to report on the resulting metal-ligand environments.

Reaction with NH₃ and CO to form [Pt(Cy₂PCH₂CH₂PCy₂)(CH₃)(NH₃)] [BAr^F₄**] and [Pt(Cy₂PCH₂CH₂PCy₂)(CH₃)(CO)] [**BAr^F₄**].** Addition of NH₃ to microcrystalline **1**[**BAr^F₄**] resulted in the substitution of the diethyl ether ligand over a period of 1 hour (unoptimized) to give the ammonia-adduct [Pt(Cy₂PCH₂CH₂PCy₂)(CH₃)(NH₃)] [**BAr^F₄**], **2**[**BAr^F₄**], Figure 2a. This ligand exchange is quantitative, as demonstrated by ^{195}Pt solid-state NMR analysis, which clearly identifies the resulting product (Figure 2b). Liberated OEt₂ is observed in the gas-phase ^1H NMR spectrum (Figure S42).

The noticeable modification of the magnetic shielding tensor upon NH_3 substitution and the associated change in the ^{195}Pt NMR signature (Figure 2b) are consistent with the electronegativity trend across elements bound to $\text{Pt}^{[46]}$ and can be largely attributed to the associated stronger σ -donation of NH_3 compared with OEt_2 . Most significantly, the δ_{11} component shifts toward more negative values, whereas the δ_{33} component becomes more positive. Consequently, shielding along the three principal axes becomes more uniform, leading to a reduction of the anisotropy ($\Omega = 2640$ ppm), while the overall prolate tensor shape is preserved ($\kappa = 0.5$). Again, experimental and computational data are in excellent agreement.

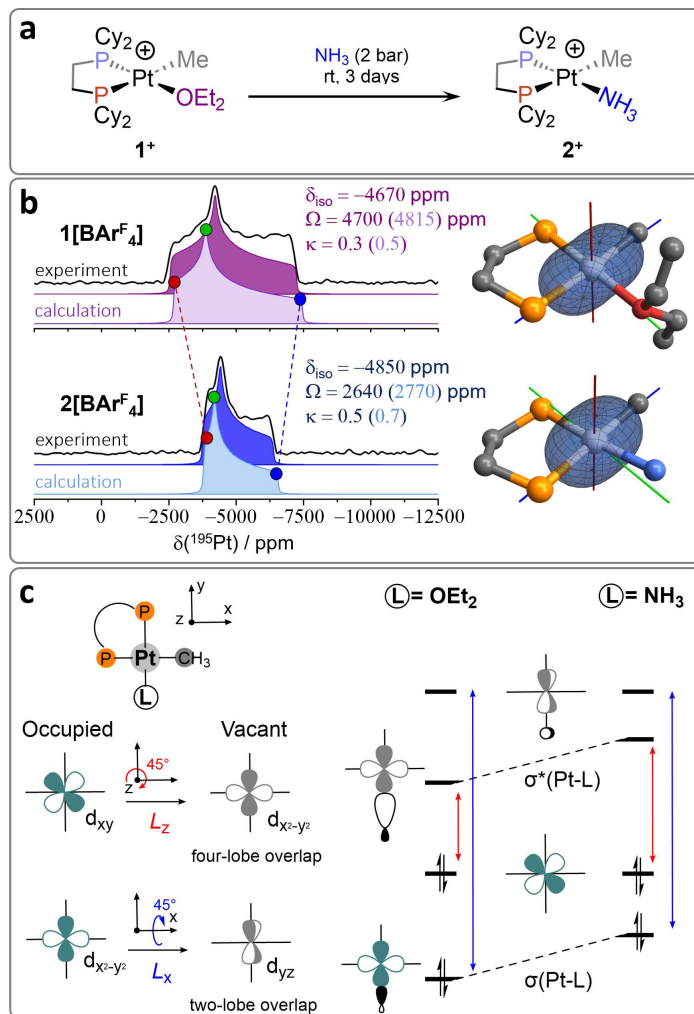


Figure 2. Tracking *in crystallo* ligand exchange and changes in frontier molecular orbitals with ^{195}Pt solid-state NMR. **(a)** NH_3 ligand substitution reaction. $[\text{BAR}^{\text{F}}_4]^-$ anions are omitted for clarity. **(b)** Below the ^{195}Pt solid-state NMR spectra of **1** $[\text{BAR}^{\text{F}}_4]$ and **2** $[\text{BAR}^{\text{F}}_4]$. The best numerical fits and DFT-calculated spectra are shown below, where δ_{11} , δ_{22} , and δ_{33} positions are marked with colored circles in red, green, and blue, respectively. The associated magnetic shielding tensors including the three principal axes that correspond to the ^{195}Pt NMR shift positions δ_{11} (red), δ_{22} (green), and δ_{33} (blue) are indicated at the right.^[63,64] The experimental (DFT-calculated) ^{195}Pt chemical-shift-tensor parameters are given explicitly. **(c)** NCS-analysis-based rationalization of the changes in the ^{195}Pt solid-state NMR signatures for the ligand substitution reaction shown in **(a)**, displaying the Pt-based coordinate frame, and below a pictorial representation of the orbital-angular-momentum-induced coupling between occupied (green) and vacant (grey) Pt-centered orbitals. On the right, the qualitative changes in the MO diagram for the ligand exchange are given. The orbital couplings determining the position δ_{11} (red) and δ_{33} (blue) are indicated by the arrows.

This example is used to demonstrate how these observations can be rationalized based on changes in the frontier molecular orbitals using natural chemical shift (NCS) analysis,^[65–67] the results of which are shown in Figure 2b. The structure of **2**[BAr^F₄] was derived from the available 3DED structure of **1**[BAr^F₄] by ligand substitution. A full geometry optimization was performed subsequently using DFT employing the PBE0 hybrid functional^[68,69] in combination with the triple- ζ def2-TZVP basis set^[70] as implemented in the Orca 6.0 package.^[71–75] Computation of the ¹⁹⁵Pt NMR properties were performed using the Amsterdam density functional (ADF) modeling suite at a comparable level of theory (PBE0/TZ2P) but with a quadrupole- ζ basis set (QZ4P) on Pt. NCS analysis using gauge-independent atomic orbital approach^[76–80] as implemented in ADF22 suggests that the position of the δ_{11} component is largely determined by the relative energies of the d_{xy} Pt lone-pair and the antibonding $d_{x^2-y^2}$ $\sigma^*(\text{Pt-L})$ ($\text{L} = \text{OEt}_2, \text{NH}_3$).^[60] These orbitals are coupled through the L_z angular momentum operator, corresponding to rotations about the z axis in a Pt-centered coordinate system. In contrast, the position of the δ_{33} component is primarily influenced by coupling between the bonding $d_{x^2-y^2}$ $\sigma(\text{Pt-L})$ ($\text{L} = \text{OEt}_2, \text{NH}_3$) and the antibonding d_{yz} , mediated through the L_x operator corresponding to rotations about the Pt x axis (P2–Pt–Me).

Notably, the Pt lone-pair and antibonding d_{yz} orbitals are comparatively insensitive to substitution of the L ligand and therefore exhibit only minor energetic changes upon replacement of OEt₂ by NH₃. In contrast, both $\sigma(\text{Pt-L})$ and $\sigma^*(\text{Pt-L})$ orbitals possess greater ligand (L) character and lie lower in energy for the more electronegative O donor. Substitution by NH₃ therefore increases these orbital energies, resulting in weaker coupling through L_z and stronger coupling through L_x . This effect is summarized in Figure 2c.

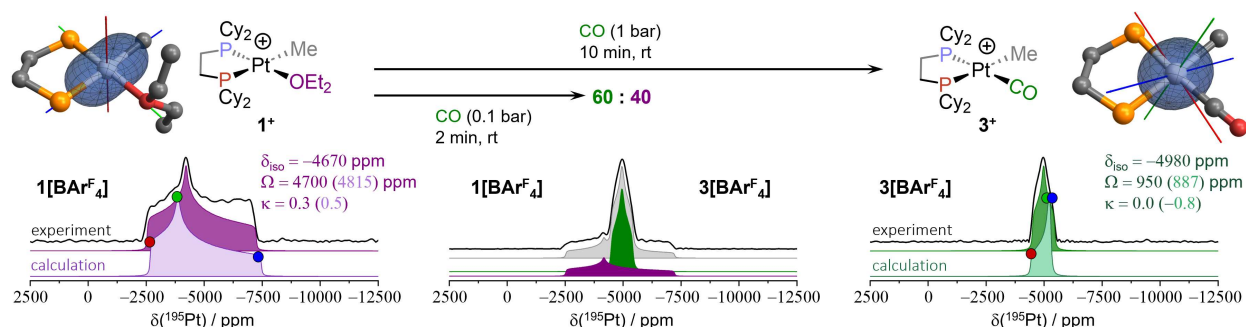


Figure 3. Partial and complete CO ligand substitution monitored by ¹⁹⁵Pt solid-state NMR. The left- and right panels show the ¹⁹⁵Pt solid-state NMR spectra of **1**[BAr^F₄] and **3**[BAr^F₄], respectively, and are composed as described in Figure 2b. The middle panel demonstrates the spectrum obtained during partial CO substitution, where overlapping but clearly distinguishable ¹⁹⁵Pt NMR signatures of **1**[BAr^F₄] and **3**[BAr^F₄] are observed.

The *in crystallo* formation of the CO-adduct, $[\text{Pt}(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)(\text{CH}_3)(\text{CO})][\text{BAr}^{\text{F}}_4]$, **3** $[\text{BAr}^{\text{F}}_4]$, from addition of CO to **1** $[\text{BAr}^{\text{F}}_4]$ is faster compared to NH_3 addition,^[81] and provided an attractive model reaction to evaluate the potential of NMR for *in crystallo* reaction monitoring. Complete conversion to **3** $[\text{BAr}^{\text{F}}_4]$ is observed after 10 min at 2 bar absolute (Figure 3), as measured by ^{31}P solution and solid-state NMR spectroscopy.

^{195}Pt solid-state NMR spectroscopy unambiguously confirms the ligand exchange and full conversion into **3** $[\text{BAr}^{\text{F}}_4]$, and there is excellent agreement between experimental and DFT-computed data, Figure 3. These calculations show that the π backbonding now present from the Pt center into the antibonding CO π^* orbital leads to substantially different magnetic shielding, reducing the anisotropy ($\Omega = 950$ ppm) and significantly modifying the tensor symmetry ($\kappa = 0$). This ^{195}Pt NMR signature of **3** $[\text{BAr}^{\text{F}}_4]$ signals a different electronic structure compared to **1** $[\text{BAr}^{\text{F}}_4]$ and **2** $[\text{BAr}^{\text{F}}_4]$, consistent with the presence of the CO ligand. However, determining the contribution of specific frontier molecular orbitals to the electronic structure is significantly more complex, and not meaningful due to several factors. These include the particularly strong influence of spin-orbit coupling arising from the coordination of CO, a very strong π -acceptor ligand, which likely opens new coupling channels (more details can be found in the Supporting Information).

Repeating the reaction under conditions of lower CO pressure (0.1 bar CO) and with shorter exposure times (2 min), demonstrates that the reaction progress can also be tracked using ^{195}Pt solid-state NMR spectroscopy, which clearly shows an ad-mixture of the two signal components due to **1** $[\text{BAr}^{\text{F}}_4]$ and **3** $[\text{BAr}^{\text{F}}_4]$. Relative integrals suggest approximately 40 % of **1** $[\text{BAr}^{\text{F}}_4]$ remaining, considering comparable relaxation properties for ^{195}Pt in **1** $[\text{BAr}^{\text{F}}_4]$ and **3** $[\text{BAr}^{\text{F}}_4]$. This is supported by similar echo-decay rates observed in the time-domain signals of the pure compounds.

Reaction with propene to selectivity form the isobutene complex $[\text{Pt}(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)(\text{H})(\eta^2\text{-H}_2\text{C}=\text{C}(\text{CH}_3)_2)][\text{BAr}^{\text{F}}_4]$, and onward reaction with CO to form $[\text{Pt}(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)(\text{H})(\text{CO})][\text{BAr}^{\text{F}}_4]$. Addition of propene to microcrystalline **1** $[\text{BAr}^{\text{F}}_4]$ resulted in the slow (7 days, unoptimized) formation of a new complex, in which the diethyl ether and methyl groups have been replaced by an isobutene ligand bound to the Pt-center, to form $[\text{Pt}(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)(\text{H})(\eta^2\text{-H}_2\text{C}=\text{C}(\text{CH}_3)_2)][\text{BAr}^{\text{F}}_4]$, **4** $[\text{BAr}^{\text{F}}_4]$. Complex **4** $[\text{BAr}^{\text{F}}_4]$ was fully characterized by solution and solid-state NMR spectroscopy (Supporting Materials), and this *in crystallo* conversion is quantitative. Notably a distinctive high field, ^1H integral, doublet of doublets is observed in the ^1H NMR spectrum (CD_2Cl_2) that indicates the presence of a new Pt–hydride: δ –3.80 [$J(\text{PH})$ 136, 11 Hz; $J(\text{PtH})$ 778 Hz] that sits *trans* to one of the phosphines (Figure S22).

The initial ^{31}P solid-state NMR data shows two sets of very similar resonances in the ratio 4:1 (Figure S27), which we assign to rotamers of the alkene ligand in the confined lattice, as solution NMR spectroscopy only show one set of environments. Recrystallization from 1,2- $\text{F}_2\text{C}_6\text{H}_4$ /hexane afforded crystalline material suitable for SC XRD, that as measured by ^{31}P solid-state NMR was compositionally pure, and had chemical shifts that were closely aligned with the minor component observed prior to recrystallization: δ 84.7 [$J(\text{PtP})$ 2944 Hz] and δ 71.0 [$J(\text{PtP})$ 1956 Hz] (Figure S24).

The resulting solid-state structure of $4[\text{BAr}^{\text{F}}_4]$ is shown in Figure 4a. The isobutene ligand is disordered equally across two positions (either *trans* to P1 and *trans* to P2). While the hydride ligand was not located, its positioning is clear, sitting opposite one of the phosphines – as signaled by the large $J(\text{PH})$ measured in the solution ^1H NMR spectrum. There is no imposed local symmetry, and so the two phosphorous environments are crystallographically distinct, as observed in the ^{31}P solid-state NMR spectrum. The methyl groups of the iso-butene ligand are directed towards the hydride, i.e. *endo*. The arrangement of $[\text{BAr}^{\text{F}}_4]^-$ anions has not changed from $1[\text{BAr}^{\text{F}}_4]$, retaining a $\sim\text{O}_h$ positioning around the cation (Supporting Materials).

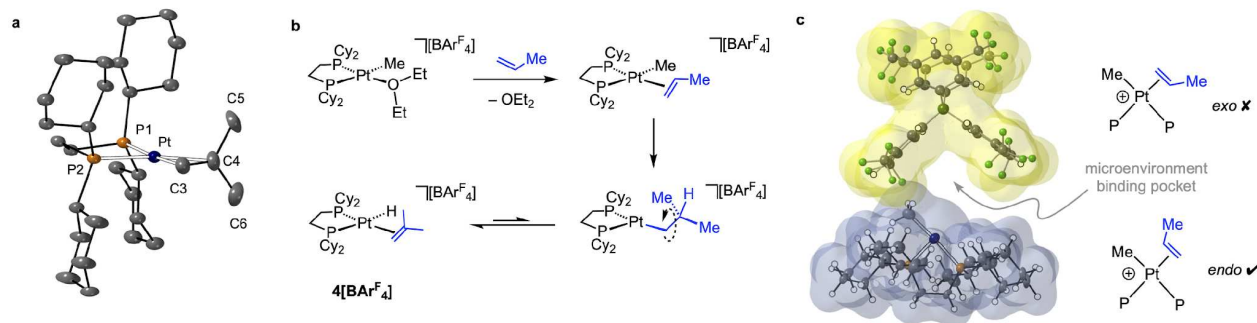


Figure 4. (a) Structure of complex $4[\text{BAr}^{\text{F}}_4]$ as determined by single crystal X-ray diffraction. Anions and hydrogen atoms are not shown. Displacement ellipsoids displayed at the 30% probability level. Selected bond distances (Å): Pt–P1, 2.2804(13); Pt–P2, 2.2707(13); Pt–C3, 2.175(11); Pt–C4, 2.279(11). (b) Suggested mechanism for the formation of $4[\text{BAr}^{\text{F}}_4]$. (c) Binding pocket for propene coordination to form exo and endo isomers, as generated by removing the Et_2O ligand from $1[\text{BAr}^{\text{F}}_4]$.

The presence of the π -accepting alkene, and the clean transformation from $1[\text{BAr}^{\text{F}}_4]$ is documented by the corresponding ^{195}Pt solid-state NMR data, Figure 5a and b. The transformation of $1[\text{BAr}^{\text{F}}_4]$ to form $4[\text{BAr}^{\text{F}}_4]$ on addition of propene has a significant impact on the magnetic shielding tensor and thus the ^{195}Pt solid-state NMR signature. The significant reduction in anisotropy ($\Omega = 1040$ ppm) and inversion of the tensor shape to oblate ($\kappa = -0.6$) compared with $1[\text{BAr}^{\text{F}}_4]$ is reflected by the experimental data and the DFT prediction.

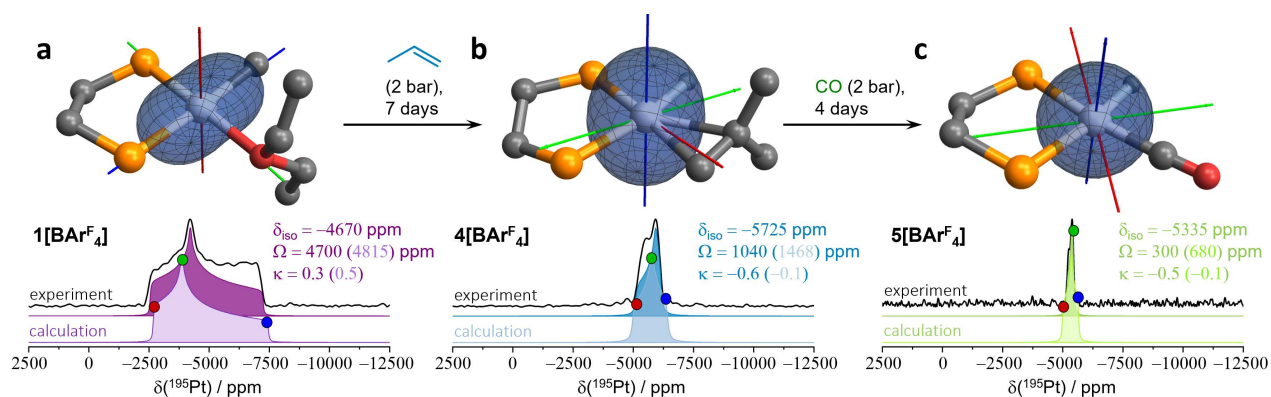


Figure 5. ^{195}Pt solid-state NMR documents the subsequent formation of **4**[BAr^F₄] and **5**[BAr^F₄]. Individual panels are composed as described in the caption of Figure 2b.

The formation of the isobutene ligand in **4**[BAr^F₄] arises from initial stereo-selective coordination of the propene in which the methyl group is orientated towards Pt–Me (*endo*) rather than away (*exo*), as no *n*-butenes are observed – that would be formed by methyl migration into the latter.^[82] This could be influenced by the microenvironment binding pocket formed from the proximal [BAr^F₄][–] anions, Figure 4c. Insertion into Pt–Me followed by β -H elimination, Figure 4b, leads to **4**[BAr^F₄]. A closely related alternative scenario is that the *exo*-propene complex can be reversibly formed, and the microenvironment controls the relative barrier to the subsequent insertion step – favoring reaction at the *endo* form. We suggest that the two isomers observed before recrystallization could potentially arise from different orientations of the *endo* propene, that leads to subtly different final orientations of the isobutene as constrained by the lattice.

Microcrystalline **4**[BAr^F₄] further reacts slowly with CO to displace the isobutene and form the corresponding carbonyl-hydride: [Pt(Cy₂PCH₂CH₂PCy₂)(H)(CO)][BAr^F₄], **5**[BAr^F₄],^[83] which was fully characterized (Supporting Materials). In the solid-state this reaction is again captured by the corresponding ^{195}Pt solid-state NMR signature, and its agreement with the DFT prediction, as shown in Figure 5c. The combination of a strong π -acceptor CO and Pt–hydride leads to a further reduction in anisotropy ($\Omega = 300$ ppm) and a retention of the oblate tensor shape ($\kappa = -0.5$).

Conclusion

In summary, we have developed SMOM approaches involving isolated Pt sites and demonstrated that ^{195}Pt solid-state NMR spectroscopy provides direct access to the local atomic-scale environment and electronic structure of metal centres during *in crystallo* solid-gas reactions. Ligand substitution and more complex insertion chemistry could be monitored directly in the solid state, enabling identification of reaction products and elementary steps even in the absence of meaningful diffraction data. The ^{195}Pt solid-state NMR signature

is particularly diagnostic of the ligand set around the metal centre, with π -accepting ligands resulting in narrow anisotropy (Ω) and oblate tensor shapes (κ) compared with σ -donors such as OEt_2 and NH_3 . This work establishes ^{195}Pt solid-state NMR spectroscopy as a powerful complementary technique to diffraction-based approaches for studying *in crystallo* reactivity in SMOM systems and highlights its broader potential for tracking elementary processes relevant to heterogeneous catalysis.

Supporting Information

The Supporting Information is available free of charge at XXX.

Full experimental details, including the synthesis and characterization of new complexes, as well as additional solid-state NMR spectra and calculations (PDF).

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