Synthesis and Solid-State Characterization of Platinum Complexes with Hexadentate Amino- and Iminophosphine Ligands

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Hexadentate ligands were synthesized from the cis,cis-1,3,5-triaminocyclohexane and coordinated to Pt(0) and Pt(II) precursors. Since the resulting complexes are negligibly soluble, solid-state NMR spectroscopy was applied to analyse the bonding modes of the hexadentate ligands.
Abstract

Hexadentate ligands \(cis,cis-C_6H_9(N=CHC_6H_4(PPh_2))_3\) (1) and \(cis,cis-C_6H_9(NHCH_2C_6H_4(PPh_2))_3\) (2) were synthesized starting from the \(cis,cis-1,3,5\)-triaminocyclohexane, and characterized using NMR spectroscopy and single-crystal X-ray diffraction. These ligands can bind both Pt(0) and Pt(II) metal centers using either or both of the soft phosphine moieties and the hard amine/imine moieties. In many cases the resulting complexes are negligibly soluble; hence, \(^{31}\)P and \(^{195}\)Pt solid-state NMR (SSNMR) spectroscopy was applied to analyse the bonding modes of the hexadentate ligands. The \(^{195}\)Pt SSNMR spectroscopy of these complexes is particularly challenging, since \(^1\)H-\(^{195}\)Pt cross polarization is extremely inefficient, the \(^{195}\)Pt longitudinal relaxation times are extremely long and the \(^{195}\)Pt powder patterns are expected to be quite broad due to platinum chemical shift anisotropy. It is demonstrated that the ultra-wideline \(^{195}\)Pt SSNMR spectra can be efficiently acquired with a combination of frequency-stepped piecewise acquisitions and cross-polarization/Carr-Purcell Meiboom-Gill (CP/CPMG) NMR experiments. The \(^{195}\)Pt and \(^{31}\)P SSNMR data are correlated to important structural features in both Pt(0) and Pt(II) species.

Keywords

multidentate ligands, Pt(0), Pt(II), solid-state NMR; \(^{195}\)Pt NMR; \(^{31}\)P NMR; platinum chemical shift tensors; CPMG pulse sequence
Introduction

The design and synthesis of multidentate ligands, which complex to a variety of metals via two or more atoms, continues to be an important research area in coordination chemistry. The success of multidentate ligands such as EDTA, corroles and porphyrins in stabilizing metal centers in various oxidation states have spurred this continued interest. More recently, a number of studies have demonstrated the use of transition metal complexes containing phosphorus- or nitrogen-based multidentate ligands as catalysts for various transformations such as olefin and ketone hydrogenation,\(^1\) allylic alkylation,\(^2\) Suzuki cross-coupling reactions and hydroboration,\(^3\) and olefin oligomerization.\(^4\) In homogeneous catalysis, where controlled variability of the metal oxidation state at the different steps of a catalytic cycle is crucial, the adaptability observed in hemilabile ligands proves to be a major asset in preventing the degradation of the catalyst and enhancing reactivity.\(^5\)

One of our groups has initiated a research program aimed at synthesizing heterobimetallic species having both Lewis acids and late transition metals in the same framework.\(^6\) In order to include two transition metals having distinct reactivity on the same ligand, it is necessary to have at least two sites with distinct chemical affinities. One of the best strategies relies on the affinity of soft ligands, such as phosphines, to bind low-oxidation state metals, and the affinity of hard ligands, such as amines and imines, to bind high-oxidation state metals.\(^7\) The \textit{cis,cis}-triaminocyclohexane framework is known to bind selectively and strongly with early metals when all of the amino functionalities are in the axial position.\(^8\) Hence, it is logical to postulate that the addition of soft donors (such as phosphines) to the three amino moieties will also favor late metal coordination.
Some heterobimetallic species form as precipitates during synthesis. Though crystalline in nature, their insolubility prohibits the growth of single crystals of the size and quality necessary for single-crystal X-ray diffraction experiments. Since the species discussed herein feature both phosphorus-containing ligands and platinum atoms, $^{31}$P and $^{195}$Pt solid-state NMR (SSNMR) experiments should prove useful for their structural characterization. While $^{31}$P SSNMR experiments conducted under conditions of magic-angle spinning (MAS) and cross polarization (CP) are routine, the $^{195}$Pt SSNMR experiments on such systems are more challenging, since the platinum chemical shift anisotropies (CSA) are expected to be very large, resulting in extremely broad patterns with correspondingly low signal to noise (S/N) ratios. However, there are a number of techniques that can be applied which are suitable for the enhancement of S/N and the acquisition of high quality $^{195}$Pt NMR spectra. In particular, the combination of frequency-stepped piecewise acquisition of extremely broad spectra, and S/N enhancement via CP and repeated echo acquisition via quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) type pulse sequences, have proven very successful for the acquisition of ultra-wideline (UW) SSNMR spectra of both spin-1/2 and quadrupolar nuclei.

Herein, in the first of a series of articles that will be devoted to the stabilization of heterobimetallic species with the cis,cis-triaminocyclohexane framework, we report the synthesis of two new hexadentate trisaminotrisphosphino ligands and their coordination behavior in the presence of Pt(0) and Pt(II) precursor complexes. The structures of these complexes are characterized with a combination of solution and solid-state NMR experiments, FTIR spectroscopy and X-ray diffraction techniques.
Results and discussion

Ligand synthesis. The condensation of three equivalents of 2-diphenylphosphanylbenzaldehyde with cis,cis-1,3,5-triaminocyclohexane affords the Schiff base cis,cis-C₆H₉(N=CHC₆H₄(PPh₂))₃ (1, 67% yield), which is then reduced using a slight excess of LiAlH₄ to afford the hexadentate ligand cis,cis-C₆H₉(NHCH₂C₆H₄(PPh₂))₃ (2, 74%, yield) as a colorless powder, as depicted in Scheme 1.

Insert Scheme 1

The $^{31}P\{^1H\}$ NMR spectrum of 1 in benzene-$d_6$ exhibits a single resonance for the three equivalent phosphines at -12.6 ppm, close to -13.0 ppm observed for a similar tripodal ligand N(CH₂CH₂N=CH(α-C₆H₄)PPh₂)₃.$^{13}$ The single resonance indicates that the phosphorus sites are chemically equivalent, and implies that the cyclohexane moiety likely has C₃ symmetry which makes all moieties equivalent. The $^1H$ NMR spectrum of 1 is consistent with this hypothesis: the hydrogen atoms on the cyclohexane ring are observed at three different resonances at 2.98, 1.97 and 1.41 ppm. The $^3J_{H-H}$ coupling constants of 11.7 Hz and 3.6 Hz for the hydrogens geminal to the imine moiety at 2.98 ppm are typical of axial protons,$^{14}$ confirming that bulky iminophosphane groups are in equatorial positions. Furthermore, the doublet at 9.04 ppm ($^4J_{H-P} = 4.9$ Hz) is typical of an imine moiety close to phosphorus atom.$^{13}$

Upon reduction with LiAlH₄, the imine resonance in the $^1H$ NMR spectrum disappears and a new resonance is observed at 4.11 ppm ($^3J_{H-H} = 7.07$ Hz, $^4J_{H-P} = 1.53$
Hz). The chemical shifts of the protons on the cyclohexyl ring are similar to those of 1, except for the axial proton on the carbon bound to the amine (δ = 2.11 ppm). The amine resonance, which is the only signal not correlated to a carbon in the $^1$H-$^{13}$C HMOC NMR spectrum, is found at an unusually low chemical shift (0.78 ppm). The small difference in the $^{31}$P{$^1$H} NMR chemical shift between 1 and 2 (-12.6 versus -15.0 ppm) indicates minor chemical modifications at the phosphorus atoms.

Crystals of 1 and 2 suitable for X-ray analyses were grown by slow diffusion of pentane in a THF solution, and their ORTEP representations are illustrated in Figures 1 and 2, respectively. Both compounds crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$. In both solid state structures, the functional groups are in equatorial positions. A notable feature in the solid state packing of 1 and 2 is the different conformations of the N-substituents, contrary to what is observed in solution. In both compounds, one of the lone pair of electrons of the phosphine moieties is rotated in the opposite direction relative to the other two. The ORTEP diagrams illustrate the sheer bulk of the iminophosphanes and the possible difficulties of designing a synthesis that would result in the orientation of all three functional groups in axial positions. As expected, the average C-N distances (1.259(6) Å) in 1 are narrower than the average distances in 2 (1.462(9) Å), and are characteristic of this family of compounds.\textsuperscript{15}

\textbf{Insert Figures 1 and 2 (ORTEP)}

\textbf{Coordination Chemistry with Platinum(0).} The addition of a colourless solution of tris(bicyclo[2.2.1]heptene)platinum(0) (Pt(nbr)$_3$) to a solution containing an
equimolar amount of compound 1 in toluene gave an orange solid after removal of the volatile materials. A series of new signals and the absence of the characteristic peak of 1 at -12.1 ppm in the $^{31}$P{$^1$H} NMR spectrum indicate that all the phosphorous moieties of 1 are involved in a coordination to platinum. Three pairs of doublets of equal integrated intensities are observed at 50.7 and 28.6 ppm ($^2$J$_{P-P} = 7.5$ Hz; $^1$J$_{P-Pt} = 2076$ Hz and $^1$J$_{P-Pt} = 1818$ Hz, respectively, 3a), 47.5 and 27.1 ppm ($^2$J$_{P-P} = 7.5$ Hz; $^1$J$_{P-Pt} = 1988$ Hz and $^1$J$_{P-Pt} = 1940$ Hz, respectively, 3b), and 46.1 and 26.5 ppm ($^2$J$_{P-P} = 4.1$ Hz; $^1$J$_{P-Pt} = 1940$ Hz and $^1$J$_{P-Pt} = 1940$ Hz, respectively, 3c), as well as a singlet at 29.0 ppm corresponding to the major product (4).

The $^1$H NMR spectrum gives further information on the nature of 3. Three doublets of doublets of equal integrated intensity are present in the hydride region at -1.2, -1.5, and -2.2 ppm ($^2$J$_{H-Pcis} = 26.4$ Hz and $^2$J$_{H-Ptrans} = 172$ Hz for 3a, $^2$J$_{H-Pcis} = 25.0$ Hz and $^2$J$_{H-Ptrans} = 178$ Hz for 3b, and $^2$J$_{H-Pcis} = 23.0$ Hz and $^2$J$_{H-Ptrans} = 178$ Hz for 3c). It is possible to assign each coupling constant by selective $^1$H{$^{31}$P} NMR spectroscopy of individual resonances: $^{31}$P signals at higher field correspond to the phosphine cis to the hydride, while the resonances at the lower field correspond to the trans phosphine. Also, three different imine signals are observed at 10.0, 9.6, and 9.5 ppm. Although it was not possible to purify the reaction mixture or obtain a single crystal for structural analysis, comparison with the work of Kurosawa et al. on the addition of related iminophosphines to Pt(nbr)$_3$ allow a clear assignment of all species.16 3a-3c are assigned as the compounds resulting from C-H oxidative addition of the C-H imine bond. The assignment of the resonances for the cyclohexane ring could not be made due to the great complexity of the $^1$H NMR spectrum; however, it is speculated that three different
isomers are present in solution, which may be due to $\text{C}_6\text{H}_9(\kappa^2-\text{C},\text{P-}
\text{N}\equiv\text{C}(\text{C}_6\text{H}_4)(\text{PPh}_2)\text{Pt(H)}(\text{P-N}))_{3-\text{x}}(\text{N}\equiv\text{CHC}_6\text{H}_4(\text{PPh}_2))_{\text{x}}$ $(\text{x} = 0 \text{ to } 2)$ where one to three metals are coordinated to the hexadentate ligand for various conformers present in solution (Scheme 2). Kurosawa et al. assigned the signal at 29.8 ppm to a species identified as $(\text{N-P})_2\text{Pt(nbd)}$ ($^1J_{\text{P-Pt}} = 3537$ Hz). While 4 has a chemical shift very close to this, no $^1J_{\text{P-Pt}}$ coupling constant was observed.

Insert Scheme 2

One equivalent of Pt(nbr)$_3$ was stirred with one equivalent of 2 in toluene. A yellow precipitate insoluble in the usual solvents appeared after a few minutes (5), differing from the analogous reaction with 1 (Scheme 3). When the same reaction was done on a smaller scale in an NMR tube, free norbornene was observed by $^1\text{H}$ NMR spectroscopy as the only soluble species. In order to get more information on this precipitate, SSNMR and FTIR spectroscopy were applied (vide infra).

Insert Scheme 3

Solid-State NMR and IR Spectroscopy of the Pt(0) complexes. The solid-state $^{31}\text{P}[^1\text{H}]$ MAS NMR spectrum of 5 (Figure 3(a)) shows only one signal at $\delta_{\text{iso}} = 37.0(2.1)$ ppm ($\delta_{\text{iso}} = -16.7$ ppm for the uncoordinated ligand, 2). $^{31}\text{P}^{-195}\text{Pt}$ $J$-coupling is observed via the $^{195}\text{Pt}$ satellites ($^1J_{\text{P-Pt}} = 4460(350)$ Hz), and is similar to that of a comparable compound, tris(triphenylphosphine)platinum(0) ($\delta(^{31}\text{P}) = 49.9$ ppm, $^1J_{\text{P-Pt}} = 4550$ Hz,
Initial $^{195}\text{Pt}\{^{1}\text{H}\}$ solution NMR experiments were unsuccessful in detecting any resonances for 5; hence, solid-state $^{195}\text{Pt}$ NMR experiments were conducted. Both $^{195}\text{Pt}$ MAS Bloch decay (single pulse) and $^{1}\text{H}-^{195}\text{Pt}$ CP/MAS NMR experiments were attempted on these samples without any success. Absence of signal in the $^{195}\text{Pt}$ MAS NMR experiments using long recycle delays (i.e., inter-scan delays of greater than 6 minutes) indicate that the $^{195}\text{Pt}$ $T_1$ constants must be extremely long, whereas the failure of the $^{1}\text{H}-^{195}\text{Pt}$ CP/MAS NMR experiments, even at very low spinning speeds, suggest that $^{1}\text{H}$ and $^{195}\text{Pt}$ nuclei are not proximate, and that the small $^{1}\text{H}-^{195}\text{Pt}$ dipole-dipole couplings are averaged, resulting in poor CP efficiency.

Insert Figure 3 (solid-state NMR of 5)

Therefore, a different strategy was applied to acquire these spectra. Static (i.e., stationary sample) $^{1}\text{H}-^{195}\text{Pt}$ CP NMR experiments were conducted, in order to exploit signal enhancement from CP and short proton $T_1$'s. However, since these $^{195}\text{Pt}$ static NMR powder patterns are expected to be broad and have very low signal to noise (S/N), the spectra were acquired using (i) frequency-stepped piecewise acquisition and (ii) Carr-Purcell Meiboom-Gill (CPMG) echo trains. Piecewise acquisition is necessary since the entire $^{195}\text{Pt}$ NMR powder pattern cannot be uniformly excited with standard coils and amplifier powers; hence, the transmitter frequency is stepped in uniform increments across the entire pattern, and individual sub-spectra are collected and then co-added to produce the final pattern. Acquisition of CPMG echo trains, the lengths of which are limited by the $^{195}\text{Pt}$ transverse relaxation time constants, $T_2$, further enhance the S/N.
The piecewise $^1$H-$^{195}$Pt CP/CPMG NMR spectrum of 5 does not reveal a clearly resolved, classical platinum CSA pattern (Figure 3(b)); rather, the pattern is suggestive of a distribution of Pt sites, making it difficult to accurately simulate the spectrum and extract the chemical shift (CS) tensor parameters (see Table 1 for parameter definitions). The spikelets comprising this spectrum are the result of the direct Fourier transformation of the CPMG echo train. The pattern covers a breadth of ca. 1350 ppm, and is clearly not representative of an axially symmetric CS tensor (i.e., the skew, $\kappa$, does not equal +1 or -1, since there is no localization of intensity at either the low or high frequency ends of the powder pattern). The centre of gravity of the pattern is ca. -4755(120) ppm, and is comparable to that of the tris(triphenylphosphine)platinum(0) compound ($\delta_{\text{iso}} = -4600$ ppm, in C$_7$D$_8$ at -80°C).$^{17}$ The relatively small pattern breadth and clearly non-axial CS tensor are consistent with a distorted, non-planar Pt environment.

**Insert Tables 1 to 3**

Comparison of the IR spectrum of 5 with free ligand 2 shows that the N-H amine bands are similar (3298 cm$^{-1}$ for 2 and 3302 cm$^{-1}$ for 5). This, and the lack of Pt-N vibrations$^{18}$ usually observed between 275 cm$^{-1}$ and 535 cm$^{-1}$ (Figure 4) imply the absence of interactions between the amine and the platinum, as expected for a platinum(0) compounds which prefer binding to soft ligands such as phosphines.

**Insert Figure 4 (stack plot of IR in N-Pt region)**
The insolubility of the yellow precipitate (opposite to that observed for 4) and the spectroscopic evidence above make us postulate that 5 possesses a polymeric structure (Scheme 3). Changing the rate or sequence of addition, or the number of equivalents of Pt(nbr)$_3$, does not change the nature of the resulting product. The use of a starting material with stronger ligands, such as Pt(PPh$_3$)$_4$, did not yield any new product, and the starting materials were recovered. This suggests that the lack of solubility of 5 and the fast ligand substitution reaction inhibit eventual reactions with the amine moieties and subsequent oxidation of the amine into the imine (vide infra).

**Coordination chemistry of platinum(II) salts.** One equivalent of the platinum precursor, (cod)PtI$_2$, was added to either 1 or 2; yellow precipitates were isolated. Quite surprisingly, the resulting compounds have $^1$H NMR spectra with very broad signals between 0.8 – 2.2 ppm, 3.4 – 4.5 ppm, and 6.5 – 8.0 ppm. $^{13}$C{$^1$H} NMR experiments failed to yield any observable signals. The broad $^1$H resonances are suggestive of some sort of dynamic process; therefore, $^1$H NMR spectra were acquired at -60 °C. The $^1$H peaks sharpen, but are still broad, preventing the observation of any fine structure (see supporting information, Figure S1). Smaller scale syntheses in NMR tubes yielded free cod as the only product detectable in solution, and no insoluble species were observed.

Interestingly, despite the lack of success with $^1$H NMR and $^{13}$C{$^1$H} NMR experiments, relatively clean $^{31}$P{$^1$H} spectra were observed, revealing several broad resonances. For example, when 2 was added to (cod)PtI$_2$, signals were observed at -14.47, -15.40 ppm, and 4.22 ppm. The former two resonances are assigned as free pendant phosphines since their chemical shifts are closely related to free ligand 2. The latter is attributed to the presence of a square-planar intermediate, [PtI$_2$(NHR$_2$)(PAr$_3$)].$^{19}$
It is therefore assumed that several fluxional processes are taking place when only one equivalent of (cod)PtI$_2$ is added to the hexadentate ligand, such as a change of conformation in the cyclohexane ring, the presence of slow rotation around the C-N bond of the aminocyclohexane, and/or ligand exchange within a same hexadentate framework or with another hexadentate ligand.$^{20}$

In order to limit the number of fluxional processes, the addition of three equivalents of platinum precursors was attempted. Compound 1 was treated with three equivalents of (cod)PtI$_2$ to afford 6 (Scheme 4) as an orange powder; however, solubility issues once again limited the application of solution NMR experiments, and solid-state NMR spectroscopy was applied to characterize this complex (vide infra). It was possible, however, to isolate few crystals for single-crystal X-ray diffraction experiments from a diffusion of ethanol into both very dilute and saturated solutions of 6 in DMSO. The platinum is in a square-planar environment (Figure 5) and it is bound to 1 using a κ$^2$-N,P interaction in a cis fashion, with the iodides located at the two remaining sites. As observed for 1, all three functional groups are in an axial position of the cyclohexyl ring, with all the iodides pointing upwards. However, the quasi-square-planar geometry of two of the three platinum environments is distorted with the angles of trans-substituents being significantly less than 180° (P(1)-Pt(1)-I(1) and N(1)-Pt(1)-I(2) of 166.60(4)° and 165.43(11)°, respectively, and P(3)-Pt(3)-I(5) and N(3)-Pt(3)-I(6a) of 174.97(5)° and 162.23(12)°, respectively). The average Pt-N and Pt-P bond lengths of 2.058(4) and 2.2182(16) Å, respectively, are in the range expected for iminophosphine platinum (II) complexes. A similar reaction of 2 with three equivalents of (cod)PtI$_2$ yielded a similarly insoluble product, 7 (Scheme 5), that is also discussed below.
Solid State NMR and IR Spectroscopy of the Pt(II) complexes. For a solid sample of 6, a single resonance was observed using both $^1$H-$^{31}$P CP/MAS and $^1$H-$^{195}$Pt CP/CPMG NMR spectroscopy (Figure 6), indicating that all coordination sites have similar bonding modes, and that the $^{31}$P nuclei are chemically equivalent. The single $^{31}$P resonance appears at 10.0(1.3) ppm ($^1J_{P\text{-}Pt} = 3425(700)$ Hz), and compares very well to a previously reported complex, [PtI$_2$(2-(diphenylphosphinobenzylidene-α-methylbenzylamine)], which has a chemical shift of 9.4 ppm and $^1J_{P\text{-}Pt} = 3425$ Hz from solution $^{31}$P{${^1}$H} NMR spectra.\textsuperscript{21}

Insert Figure 6 (Solid state NMR of 6)

The $^{195}$Pt CP/CPMG NMR spectrum reveals a sharp, well-defined pattern with $\delta_{\text{iso}}$ = -4400 (75) ppm, $\Omega = 3600$ (125) ppm and $\kappa = -0.82$ (4). These parameters were obtained by first comparing a simple CSA pattern to the outer manifold of the CPMG spikelet pattern, and then refining them via simulations of the spikelet pattern using the SIMPSON simulation package.\textsuperscript{22} These parameters describe a platinum CS tensor with the following principal components: $\delta_{11} = -2006(3)$ ppm, $\delta_{22} = -5738(3)$ ppm and $\delta_{33} = -5756(3)$ ppm. The least shielded (highest frequency) component of the CS tensor, $\delta_{11}$, is
the distinct component, and due to the molecular symmetry, is likely oriented in a
direction perpendicular to a square planar Pt environment. The intermediate and most
shielded components, δ_{22} and δ_{33}, are similar in magnitude, and accordingly, are likely
oriented in the square plane in similar electronic environments. This result is consistent
with those for square planar Pt(II) complexes of analogous systems, including
Pt^{II}[N(iPr_2PSe)_2]_2^{23} and one of the starting reagents for this reaction, (cod)PtI_2. For
comparison, a simple $^{195}$Pt{$^1$H} MAS NMR spectrum was acquired for (cod)PtI_2 (Figure
7(a)), from which Herzfeld-Berger analysis$^{24}$ was used to extract the following CS tensor
parameters: δ_{iso} = -4281 (5.4) ppm, Ω = 3472 (4.4) ppm and κ = -0.85 (4). Coordination
of platinum by the imine moieties was confirmed by FTIR spectroscopy, which reveals
Pt-N stretching bands at 525 cm$^{-1}$ and 539 cm$^{-1}$, thereby confirming that the three
platinum atoms coordinate to each one N-P moieties of the hexadentate ligand (Figure 4).

**Insert Figure 7 (Solid state NMR of codPtX2)**

The $^1$H-$^{31}$P CP/MAS NMR spectrum of 7 (Figure 8(a)) reveals a single, broad
resonance centered at 6.0 (4.6) ppm; however, no $^{195}$Pt satellites are clearly discernable
underneath the broad lineshape. There are several chemically distinct $^{31}$P sites which
give rise to a distribution of resonances and serve to obscure the satellite peaks arising
from $^{31}$P-$^{195}$Pt $J$-coupling. However, the $^{31}$P chemical shift is in the typical range for
(NHR_2)(PPh_3)PtCl complexes, which normally occur at ca. 4 ppm.$^{19}$

**Insert Figure 8 (Solid state NMR of 7)**
The $^1\text{H}-^{195}\text{Pt}$ CP/CPMG NMR spectrum of 7 (Figure 8(b)) is somewhat more complex than that of 6. There are overlapping signals corresponding to two different Pt environments, one having $\delta_{\text{iso}} = -4550(100)$ ppm, $\Omega = 3400(175)$ ppm and $\kappa = -0.88(7)$, and the other having $\delta_{\text{iso}} = -4300(60)$ ppm, $\Omega = 4550(150)$ ppm and $\kappa = -0.75(5)$. Due to the poor S/N and low spectral resolution, the errors associated with these values are high, and it is difficult to quantify the net contribution from each type of $^{195}\text{Pt}$ site (the simulated powder patterns are presented in a 1:1 integrated intensity ratio in Figure 8(b) for comparison). The first set of parameters indicate a Pt site similar to that observed for 6; however, the second set of parameters, though possessing similar values of $\delta_{\text{iso}}$ and $\kappa$, has a significantly larger span, similar to those of the (cod)PtCl$_2$ species (also acquired with MAS, Figure 7(b)), with $\delta_{\text{iso}} = -3361(10)$ ppm, $\Omega = 6200(150)$ ppm and $\kappa = -0.86(5)$, and the completely planar Pt(II)[S$_2$C$_2$(CF$_3$)$_2$]$_2$ species$^{25}$ (though it should be noted that the latter species has a positive skew). Again, the distinct span and negative skew for each pattern indicate that there are clearly two chemically distinct Pt environments which are both square planar in nature. FTIR spectroscopy again confirms the coordination of platinum by the amine moieties, with Pt-N stretching bands were observed at 516 cm$^{-1}$ and 527 cm$^{-1}$, along with typical N-H vibration modes.

**Reactivity and structural characterization of one equivalent of (cod)PtCl$_2$ with 2.** When one equivalent of (cod)PtCl$_2$ is in solution for an extended period of time (more than one week) in the presence of 2, an insoluble material was isolated. The $^1\text{H}$ NMR spectrum of the solution shows only free cod and 1 as the soluble species, thereby demonstrating that the ligand is being oxidized by the platinum complex. The $^1\text{H}-^{31}\text{P}$
CP/MAS NMR spectrum of 8 reveals a resonance at 3.1(4.2) ppm (Figure 9(a)). There is a small peak to high frequency, which if treated as a $^{195}$Pt satellite, reveals a $^1J_{P\text{-}Pt}$ of 3310(700) Hz, similar to compound 7. However, the low frequency satellite, if it does exist, is obscured by the presence of a broad resonance at ca. -17.1(3.9) ppm, which may correspond to uncoordinated phosphine moieties. Another resonance at 32.3(3.4) ppm is similar to the phosphorus chemical shift of 5 in C$_6$D$_6$. The $^1$H-$^{195}$Pt CP/CPMG spectrum (Figure 9(b)) has similar parameters to those observed for 6 and 7 ($\delta_{iso} = -4400(50)$ ppm, $\Omega = 3950(75)$ ppm; $\kappa = -0.80(7)$), again indicating the presence of a square-planar species. However, the agreement between the simulation and the experimental data is not perfect, especially in the region of the low-frequency (rightmost) discontinuity. It is possible that there is an underlying pattern of low integrated intensity, perhaps corresponding to the presence of a Pt(0) species; however, we cannot confirm this with MAS NMR experiments for the reasons discussed above.

Conclusions

Two new hexadentate iminophosphine and aminophosphine ligands have been synthesized. A preliminary investigation of their coordination chemistry with platinum(0) and platinum(II) shows interesting reactivity and suggests great promise for future directions in synthesis. Both reactions of 1 and 2 with Pt(nbr)$_3$ yield compounds where the ligand interacts with the phosphine of the hexadentate ligands. In the case of the iminophosphine, the C-H activation of the amino proton was also observed. For the Pt(II) salts, the affinity of the higher oxidation state metal and N,P-coordinated ligands were observed by both $^{31}$P and $^{195}$Pt solid-state NMR.
SSNMR experiments have proven very useful in the characterization of these insoluble compounds. The $^{195}\text{Pt}$ SSNMR spectra, while challenging to acquire, revealed useful information about the nature of the Pt sites. The $^{195}\text{Pt}$ SSNMR spectra of the Pt(0) species, 5, reveal some degree of disorder at the Pt centres, as well as a moderate span and non-axial skew which are consistent with non-square planar Pt sites. On the other hand, the Pt(II) species are crystalline, and have extremely broad, well-defined CSA patterns which indicate platinum CS tensors similar to those of other square planar Pt(II) complexes which have been thoroughly characterized by single-crystal XRD and $^{195}\text{Pt}$ SSNMR spectroscopy. Finally, the $^{31}\text{P}$ SSNMR spectra are extremely useful for both establishing connectivity/coordination between Pt and P-containing ligands, and identifying P-containing starting reagents and by-products of these reactions.

The results presented herein clearly show that both Pt(0) and Pt(II) complexes can be stabilized by the hexadentate ligand, opening the way for interesting applications in stabilizing reactive intermediates in catalysis, and that investigations of the solid-state structures using both XRD and SSNMR are important for future rational design of these systems. The hemilabile hexadentate framework of 1 and 2 offers several sites that can stabilize various oxidation states of platinum, and should demonstrate adaptability during catalytic processes. Indeed, whereas in most systems the reduction of platinum would lead to the loss of the metal as platinum black, here, the presence of multiple bonding sites allows for the platinum to be stabilized. It is possible that an analogous palladium system could prove very useful in catalysis by stabilizing the reduced Pd oxidation states and increasing the life span of the catalyst. Further studies on the reactivity and structure of such platinum and palladium complexes are currently underway.
Experimental Section

Cis,cis-1,3,5-triaminocyclohexane·3HBr,\textsuperscript{26} 2-diphenylphosphanylbenzaldehyde,\textsuperscript{27} tris(bicyclo[2.2.1]heptene)platinum(0),\textsuperscript{28} and dichloro(1,5-cyclooctadiene)platinum(II)\textsuperscript{29} were prepared according to literature procedures. Diiodo(1,5-cyclooctadiene)platinum(II) was purchased from Strem chemicals and used as received. Dry and deoxygenated solvents were used. HPLC grade toluene was passed through a resin column and collected under nitrogen. \textsuperscript{1}H (400.0 MHz), \textsuperscript{31}P{\textsuperscript{1}H} (161.9 MHz) and \textsuperscript{13}C{\textsuperscript{1}H} (100.568 MHz) solution NMR spectra were recorded on a Varian Inova NMR AS400 spectrometer or on a Bruker NMR AC-300 spectrometer (\textsuperscript{1}H (300.0 MHz), \textsuperscript{31}P{\textsuperscript{1}H} (121.42 MHz) and \textsuperscript{13}C{\textsuperscript{1}H} (75.42 MHz).

VT-NMR experiments: \textsuperscript{1}H (400MHz) and \textsuperscript{31}P{\textsuperscript{1}H}(161.904 MHz) NMR spectra were acquired in CDCl\textsubscript{3} at +22°C, 0°C, -20°C, -40°C and -55°C. The probes were tuned at each temperature. The temperatures were measured using a thermocouple inside the probe which was calibrated with methanol prior to use.

Solid-State NMR. Solid-state NMR spectra were collected using a Varian Infinity Plus NMR spectrometer with an Oxford 9.4 T (\textsuperscript{1}H = 400 MHz) wide-bore magnet with <\textsubscript{o}(\textsuperscript{195}Pt) = 87.34 MHz and <\textsubscript{o}(\textsuperscript{31}P) = 161.81 MHz. The experiments were performed using 4.0 mm HXY, 4.0 mm HX, and 2.5 mm HX MAS probes along with zirconia rotors. Air sensitive samples were packed under a dry nitrogen atmosphere and sealed with air-tight Teflon caps in 4.0 mm o.d. rotors. \textsuperscript{195}Pt chemical shifts were referenced with respect to a 1.0 M solution of Na\textsubscript{2}PtCl\textsubscript{6} (\textit{*iso} = 0.0 ppm) and \textsuperscript{31}P chemical shifts were referenced with respect to an 85 % solution of H\textsubscript{3}PO\textsubscript{4} (\textit{*iso} = 0.0 ppm).
Static $^{195}$Pt NMR experiments were conducted using the cross-polarization Carr-Purcell-Meiboom-Gill (CP/CPMG) pulse sequence.\textsuperscript{11} Individual sub-spectra were collected by stepping the frequency of the transmitter across the full breadth of the powder pattern in increments ranging from 15 to 30 kHz.\textsuperscript{10} The number of Meiboom-Gill (MG) loops was set to either 40 or 81, depending on the $T_2$ of the sample. A $^1$H B/2 pulse width of 1.98 or 2.04 $\mu$s was utilized, along with a contact time of 3 or 4 ms, recycle delay of 3 s, spectral width of 500 kHz, and spikelet separation of 5 or 10 kHz. Each powder pattern required the acquisition of 8 to 16 sub-spectra which were subsequently co added to form the overall spectrum. A $^1$H cross-polarizing power of 161 or 75 kHz and decoupling power of 75 kHz were used. $^{195}$Pt MAS experiments were conducted using a standard Bloch decay pulse sequence with decoupling applied. A B/2 pulse width of 0.83 $\mu$s, spectral width of 1100 kHz, and pulse delay of 30 s were used to acquire the powder pattern.

$^1$H-$^{31}$P CP/MAS NMR experiments were performed utilizing the variable-amplitude cross polarization (VACP) pulse sequence,\textsuperscript{30} along with two-pulse phase modulation (TPPM) decoupling.\textsuperscript{31} A $^1$H B/2 pulse width of 3.38 $\mu$s was employed along with contact times of 2 and 3 ms, recycle delays of 3 s, and a spectral width of 100 kHz. A $^1$H cross-polarizing power of 56 kHz and decoupling powers ranging from 56 to 115 kHz were used. Spinning speeds of 10 and 12 kHz were employed. The solid state $^{31}$P MAS NMR experiments for sample 5 were performed on a Bruker Advance spectrometer with SGU, 161.9 MHz ($^{31}$P), with a MAS 4mm diameter probe and a zirconia rotor. The experiments were performed utilizing the single sequence, along with two-pulse phase modulation (TPPM) decoupling. A $^{31}$P $\pi/2$ pulse width of 3.75 $\mu$s was employed along
with recycle delays of 4 s, and a spectral width of 64 kHz. A spinning speed of 6.7 kHz was employed. Simulations of solid-state NMR spectra were performed using the WSOLIDS\textsuperscript{32} and SIMPSON\textsuperscript{32} software packages.

**Vibrational spectroscopy.** Spectra were recorded on a Magna IR 850 Nicolet FTIR spectrometer with a DTGS detector and a Golden Gate sampler.

**Crystallographic Structural Determinations.** Crystallographic data are reported in Table 4. Single crystals were coated with Paratone-N oil, mounted using a glass fibre and frozen in the cold nitrogen stream of the goniometer. The data were collected on a Bruker SMART APEX II diffractometer, except for 1 that was collected on a Bruker AXS P4/SMART 1000 diffractometer. The data were reduced (SAINT)\textsuperscript{33} and corrected for absorption (SADABS).\textsuperscript{34} The structure was solved and refined using SHELXS-97 and SHELXL-97.\textsuperscript{35} In the case of 6, two highly disordered ethanol molecules are present in the cell, which was confirmed by both the volume and the electron density of the disordered molecules using the PLATON software.\textsuperscript{36} Since it was not possible to solve these molecules, they were squeezed using PLATON.\textsuperscript{36} All non-H atoms were refined anisotropically. The hydrogen atoms were placed at idealized positions. Neutral atom scattering factors were taken from the International Tables for X-Ray Crystallography.\textsuperscript{37} All calculations and drawings were performed using the SHELXTL package.\textsuperscript{38} The final models for 1 and 2 were checked either for missed symmetry or voids in the crystal structure using the PLATON software.

\textit{cis,cis-C}_{6}H_{9}(N=CHC}_{6}H_{4}(PPh_{2})_{3} \ (1): \ \textit{cis,cis}-1,3,5-triaminocyclohexane-3HBr (500 mg, 1.34 mmol) and sodium methoxide (2.18g, 40.3 mmol) were dissolved in 40 ml of THF and heated under reflux for 18 hours. The resulting slurry was filtered and THF
was removed under reduce pressure to yield 1,3,5-triaminocyclohexane as a white powder. 1,3,5-triaminocyclohexane and 2-diphenylphosphanylbenzaldehyde (1.17g, 4.0 mmol) were dissolved in 30 ml of absolute deoxygenated ethanol in presence of molecular sieves (4 Å) and heated under reflux for 24 hours, during which a yellow precipitate appeared. The reaction mixture was cooled at -20°C and 1 was isolated as a yellow powder by decanting the supernatant (855mg, 67 % yield). Crystals were grown from slow diffusion of pentane in a THF solution of 1. $^1$H NMR (C$_6$D$_6$), $\delta$ = 9.04 [d ($^4$J$_{H-H}$ = 4.9 Hz), 3H, CH=N], 8.25 [m, 3H, o-PAr], 7.37 [m, 12H, o-PPh$_2$], 7.02 [m, 27H, Ar], 2.98 [tt $^3$J$_{H-H}$ = 3.6Hz; 11.7Hz, 3H, NCH], 1.97 [dd, $^3$J$_{H-H}$ = 12.2Hz; 12.2Hz, 3H, CHHax], 1.41 [dt, $^3$J$_{H-H}$ = 3.5Hz; 12.2Hz, 3H, CHHeq]: $^{31}$P{$^1$H} (C$_6$D$_6$) $\delta$ = -12.56; $^{13}$C{$^1$H} (C$_6$D$_6$) $\delta$ = 157.35 [d, $^3$J$_{C-P}$ = 20.6Hz], 140.52 [d, $^2$J$_{C-P}$ = 17.2Hz], 137.79 [d, $^1$J$_{C-P}$ = 20.3Hz], 137.60 [d, $^1$J$_{C-P}$ = 10.6Hz], 134.39 [d, $^1$J$_{C-P}$ = 20.0Hz], 133.75 [s], 130.24 [s], 129.02 [s], 129.97 [s], 128.88 [s], 128.43 [d, 4.5 Hz], 66.53 [s], 41.36 [s]. IR-ATR (diamond cell), $\nu$/cm$^{-1}$ 1632 [C=N, str, m], 742 [P-o-Ar C-H def., s], 694 [P-Ar C-H def., s]. HRMS (APPI) calc. for C$_{63}$H$_{54}$N$_3$P$_3$ (M$^+$) = 945.3531; found 945.3529. Elemental analysis Calc. for C$_{63}$H$_{54}$N$_3$P$_3$ C 79.98 H 5.75 N 4.44; found C 79.45 H 5.72 N 4.45

**cis,cis-C$_6$H$_9$(NHCH$_2$C$_6$H$_4$(PPh$_2$))$_3$ (2):** To a solution of 1 in 50 mL of toluene (1.29g, 1.36 mmol), a suspension of LiAlH$_4$ (0.155g, 4.09 mmol) in 10 ml of toluene is added. The suspension is stirred at room temperature for 48 hours. The reaction is then filtered to remove excess LiAlH$_4$ and quenched with ethanol and water. The volatiles were removed under vacuum and the remaining solid washed with 3 portions of 20 ml of diethyl ether, and dried under vacuum to yield 2 as a yellow powder (0.95g, 74 % yield). $^1$H NMR (C$_6$D$_6$), $\delta$ = 7.62 [m, o-PAr, 3H], 7.38 [m, o-PPh$_2$, 12H], 7.08 [m, Ar, 27H],
4.11 [d, \(^3J_{H-H} = 7.07\text{Hz}, CH_2, 6\text{H}]), 2.11 [m, \(^3J_{H-H} = 11.6\text{Hz}, \(^3J_{H-H} = 4.2\text{Hz}, NCH, 3\text{H}]),
1.77 [dt, \(^2J_{H-H} = 11.6, \(^3J_{H-H} = 3.3\text{Hz}, CH\text{Heq}, 3\text{H}), 0.78 [dd, \(^3J_{H-H} = 6.9\text{Hz}, \(^3J_{H-H} = 11.6\text{Hz}, NH, 3\text{H})]. 0.62 [q, \(^2J_{H-H} = 11.6\text{Hz}, \(^3J_{H-H} = 11.6\text{Hz}, CH\text{ax}, 3\text{H}); \(^3^1\text{P}[^1\text{H}] (C_6D_6) \delta = -15.01 \text{ppm}; \(^1^3\text{C}[^1\text{H}](C_6D_6) \delta = 146.25 [d, (\(^1J_{C-P} = 23.8\text{Hz})], 137.88 [d, (\(^3J_{C-P} = 11.3\text{Hz})], 136.09 [d, (\(^2J_{C-P} = 14.4 \text{Hz})], 134.32 [d, (\(^2J_{C-P} = 19.8\text{Hz})], 134.01 [s], 128.72 [d, (\(^2J_{C-P} = 6.8 \text{Hz})], 128.72 [s], 128.56 [s], 128.18 [s], 127.36 [s], 53.66 [s], 50.02 [d, \(^3J_{C-P} = 21.8\text{Hz}], 40.71 [s] \text{ppm. IR-ATR (diamond cell), } \nu/\text{cm}^{-1} 3298 [\text{N-H str.}, w], 740 [\text{N-H wag., C-P str.}, s] 694 [\text{P-Ar C-H def.}, s] \text{ HRMS (APPI) calc. for } C_{63}H_{54}N_3P_3 (M^+) = 951.4000; \text{found 951.3988. Elemental analysis Calc. for } C_{63}H_{60}N_3P_3 C 79.47 \text{ H 6.35 N 4.41; found C 78.76 H 6.36 N 4.39}}

cis,cis-C_6H_9(N=CHC_6H_4(PPh_2))_3 + \text{Pt(nbr)}_3 (3a-c and 4): In a Schlenk tube under nitrogen, tris(bicyclo[2.2.1]heptene)platinum(0) (86 mg, 0.18 mmol) was dissolved in 5 ml toluene immediately followed by 1 (170 mg, 0.18 mmol). The yellow solution was stirred for 12 hours and the volatiles removed under vacuum. The product was dissolved in minimum toluene and pentane was added. A precipitated appeared at -35°C and was filtered. The product was washed with 5 portions of hexane (3mL) to afford an orange powder (100 mg, 50% yield). \(^1\text{H NMR (C_6D_6, 22°C), } \delta = 10.0 [s], 9.6 [s], 9.5 [s], 9.46 [s, 1H], 8.46 [m, 3H], 7.77 [m, 15H], 6.84 [m, 26H], -1.2 [dd, \(^2J_{H-Pcis} = 26.4 \text{Hz, } \(^2J_{H-Ptrans} = 172 \text{Hz}], -1.5 \text{[} \(^2J_{H-Pcis} = 25.0 \text{Hz, } \(^2J_{H-Ptrans} = 178 \text{Hz]}), -2.2 \text{[} \(^2J_{H-Pcis} = 23.0 \text{Hz, } \(^2J_{H-Ptrans} = 178 \text{Hz]}); \(^3^1\text{P}[^1\text{H}] \delta = 50.7 [dd, \(^2J_{P-P} = 7.5 \text{Hz, } \(^1J_{P-P} = 2076 \text{Hz}], 28.6 [dd, \(^1J_{P-P} = 7.5 \text{Hz, } \(^1J_{P-P} = 1818 \text{Hz}], 47.5 [dd, \(^2J_{P-P} = 4.11\text{Hz, } \(^1J_{P-P} = 1988 \text{Hz}], 27.1 [dd, \(^2J_{P-P} = 4.11\text{Hz, } \(^1J_{P-P} = 1940 \text{Hz}], 26.5 \text{ppm }[\(^2J_{P-P} = 4.11\text{Hz, } \(^1J_{P-P} = 1940 \text{Hz]}], 46.1 [s, \(^1J_{P-P} = 1940\text{Hz}], 29.0 [s] \text{ppm. } \(^3^1\text{P CP/MAS } \delta_{iso} = 46.313, 25.522, 2.460 \text{ppm. } ^{195}\text{Pt CP/CPMG}
$\delta_{\text{iso}} = -4755(50) \text{ ppm}$, $\Omega = 1350(60)$, $\kappa = -0.33(6)$. IR-ATR (diamond cell), $\nu/\text{cm}^{-1}$ 1632 [C=N, str, m], 743 [P-o-Ar C-H def., s], 692 [P-Ar C-H def., s].

**cis,cis-C$_6$H$_9$(NHCH$_2$C$_6$H$_4$(PPh$_2$))$_3$ + Pt(nbr)$_3$ (5):** In a Schlenk tube under nitrogen, 2 (150 mg, 0.16 mmol) is dissolved in 3 ml of toluene. Tris(bicyclo[2.2.1]heptene)-platinum(0) (76.4 mg, 0.16 mmol) in 0.5 ml toluene is then added to the stirred solution of 2. The color of the reaction changes from clear to yellow instantly and after a few minutes the product starts to precipitate. The reaction is stirred for 12 hours after which the suspension is filtered and dried under vacuum. The yellow powder is washed with 3 portions of pentane (1 mL). (162 mg, 78 %) NMR $^{31}$P{$^1$H} (MAS 121.42 MHz) $\delta = 37$ (2.1) ppm [t, $^1J_{P,Pt} = 4460$ (350) Hz]. $^{195}$Pt CP/CPMG $\delta_{\text{iso}} = -4755(120)$ ppm. IR-ATR (diamond cell), $\nu/\text{cm}^{-1}$ 3302 [N-H str., w], 741-729 [N-H wag., C-P str., m] 691 [P-Ar C-H def., s]. Anal. Calcd: for C$_{63}$H$_{60}$N$_3$P$_3$Pt; C 65.96 H 5.27 N 3.66 found: C 65.39 H 5.39 N 3.35

**cis,cis-C$_6$H$_9$(NHCH$_2$C$_6$H$_4$(PPh$_2$))$_3$ + 3 (cod)PtI$_2$ (6):** 82 mg (0.09 mmol) of 1 was dissolved in 4 ml toluene and 3 equiv. of Diiodo(1,5-cyclooctadiene)platinum(II) (145 mg, 0.26 mmol) were added. The reaction was refluxed for 48 hours during which a precipitate was formed. The precipitate was filtered, washed with 3 portions of pentane (3 mL) and dried under vacuum to afford 137 mg (69% yield). Crystals were grown by a slow diffusion of ethanol in a DMSO solution of 6. $^{31}$P CP/MAS $\delta_{\text{iso}} = 10.0$ (1.3) [$^1J_{P,Pt} = 3425(700)$ Hz] ppm. $^{195}$Pt CP/CPMG $\delta_{\text{iso}} = -4400$ (75) ppm, $\Omega = 3600(125)$, $\kappa = -0.82(4)$. IR-ATR (diamond cell), $\nu/\text{cm}^{-1}$ 1621[C=N, str, m], 746 [P-o-Ar C-H def., s], 690 [P-Ar C-H def., s], 525, 527 [Pt-N, str, s]. Elemental analysis Calc: for C$_{63}$H$_{54}$N$_3$P$_3$Pt$_3$I$_6$ C 33.00 H 2.37 N 1.83; found C 28.55 H 2.16 N 1.58.
cis,cis-C₆H₉(NHCH₂C₆H₄(PPh₂))₃ + 3 (cod)PtI₂ (7): 2 (150 mg, 0.158 mmol) was dissolved in 4 ml toluene. Diiodo(1,5-cyclooctadiene)platinum(II) (264mg, 0.474 mmol) was added and the solution refluxed for 18h. A precipitate was formed and filtered to afford an orange powder which was washed with 3X 5ml of hexane and dried under vacuum (174 mg, 60% yield). ¹H NMR (CDCl₃, 400MHz, 22°C), δ = 7.47 [m, br] ppm. ³¹P CP/MAS δiso = 6.0 (4.6) ppm. ¹⁹⁵Pt CP/CPMG δiso = -4550(100) ppm, Ω = 3400(175), κ = -0.88(7); δiso = -4300(60) ppm, Ω = 4550(150), κ = -0.75(5). IR-ATR (Golden gate), ν/cm⁻¹ 3145 [N-H str., w], 746 [N-H wag., C-P str., s] 690 [P-Ar C-H def., s], 516, 527 [Pt-N, str., s]. Elemental analysis Calc: for C₆₅H₆₀N₃P₃Pt C 32.92 H 2.63 N 1.83; found C 36.50 H 3.00 N 2.01

cis,cis-C₆H₉(NHCH₂C₆H₄(PPh₂))₃ + codPtCl₂ (8): 2 (156 mg, 0.16 mmol) was dissolved in 4 ml toluene. Dichloro(1,5-cyclooctadiene)platinum(II) (55 mg, 0.15 mmol) was added and the solution stirred at room temperature for 12 hours. A precipitate is formed which is filtered, then washed with 3 x 3 ml of pentane and dried under vacuum (100 mg, 51 % yield). ¹H NMR (CDCl₃, 400MHz, 22°C), δ = 7.79-6.67 [m, aromatic]; ³¹P{¹H} (CDCl₃, 161.904 MHz, 22°C) δ = 35.67 [s], 7.40 [s], 7.31 [s], -13.03 [s] ppm. RMN-VT ¹H (CDCl₃, 400MHz, -55°C), δ = 8.05-6.32 [m, aromatic], 5.93 [m, CH₂], 5.76 [m, CH₂], 5.61 [s, CH₂] ppm. ³¹P{¹H} (CDCl₃, 161,904 MHz, -55°C) δ = 39.70 [br], 36.29 [s], 33.68 [s], 18.13 [br], 8.39-7.54 [m], -5.5 [s], -13.08 [s] ppm. ³¹P CP/MAS δiso = 32.3 (3.4), 3.1 (4.2) [¹Jp-Pt/2 = 1655 (350) Hz], -17.1 (3.9) ppm. ¹⁹⁵Pt CP/CPMG δiso = -4400 (50) ppm, Ω = 3950(75), κ = -0.80(7). IR-ATR (Golden gate), ν/cm⁻¹ 3380 [N-H str., w], 747-723 [N-H wag., C-P str. m] 692 [P-Ar C-H def., m], 543, 519 [Pt-N, str., s].
Acknowledgments

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Supporting Information Available: Crystallographic data have been deposited with CCDC (CCDC No. 718421 for 1, CCDC No. 718422 for 2, and CCDC No. 718423 for 6). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk, or via the internet at www.ccdc.cam.ac.uk.
References


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### Tables

**Table 1.** $^{195}$Pt static CP/CPMG NMR experimental parameters.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Site</th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
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<td>5</td>
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<td>-4755 (120)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>6</td>
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<td>3600 (125)</td>
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<td>1</td>
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<td>2</td>
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<td>4550 (150)</td>
<td>-0.75 (5)</td>
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<td>8</td>
<td></td>
<td>-4400 (50)</td>
<td>3950 (75)</td>
<td>-0.80 (7)</td>
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</tbody>
</table>

$a$ Isotropic chemical shift: $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. $b$ Span: $\Omega = \delta_{11} - \delta_{33}$. $c$ Skew: $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$. $d$ Due to disorder at the Pt sites, only the centre of gravity is reported for the spectrum of this compound, as opposed to the isotropic shift. No CS tensor parameters could be extracted.

**Table 2.** $^{31}$P CP/MAS NMR experimental parameters.

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<tr>
<td>7</td>
<td>6 (4.6)</td>
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<td>8</td>
<td>32.3 (3.4), 3.1 (4.2), -17.1</td>
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**Table 3.** $^{195}$Pt MAS NMR experimental parameters.

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<td>-3361 (10)</td>
<td>6200 (150)</td>
<td>-0.86 (5)</td>
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</table>

$a$ Isotropic chemical shift: $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. $b$ Span: $\Omega = \delta_{11} - \delta_{33}$. $c$ Skew: $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$. Note that the uncertainties for the analytical HBA simulation for (cod)PtI$_2$ are significantly lower than that of the approximate SIMPSON simulation.
Table 4. Crystallographic data

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<td><strong>formula</strong></td>
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<td>C_{63}H_{54}I_{6}N_{3}P_{3}Pt_{3}</td>
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<td>Triclinic</td>
<td>Monoclinic</td>
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<td>P-1</td>
<td>P2(1)/n</td>
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<td>17.9294(17)</td>
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<tr>
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<td>14.198(1)</td>
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<tr>
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<td>14.874(1)</td>
<td>28.744(3)</td>
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<td><strong>α, β, γ (deg)</strong></td>
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<td>94.163(1), 106.963(1), 109.808(1)</td>
<td>90.0, 93.231(1), 90.0</td>
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<tr>
<td><strong>V (Å³)</strong></td>
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<td>2592.1(3)</td>
<td>7789.8(13)</td>
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<td><strong>D_{calc} (g·cm⁻³)</strong></td>
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<td><strong>Temp (K)</strong></td>
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<td>12227/31797</td>
<td>18753/94515</td>
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<td><strong>R_{int}</strong></td>
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<td>0.0231</td>
<td>0.0418</td>
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<td><strong>final R indices [I &gt; 2σ(I)]</strong></td>
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<td>R₁ = 0.0445, wR₂ = 0.1308</td>
<td>R₁ = 0.0388, wR₂ = 0.0933</td>
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<td><strong>R indices (all data)</strong></td>
<td>R₁ = 0.0886, wR₂ = 0.1556</td>
<td>R₁ = 0.0584, wR₂ = 0.1308</td>
<td>R₁ = 0.0592, wR₂ = 0.0987</td>
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</table>
Schemes

Scheme 1

Scheme 2

Scheme 3
Scheme 4.

Scheme 5.
Figure Captions

Figure 1. ORTEP diagram (50% probability) of 1. Hydrogen atoms have been omitted for clarity.

Figure 2. ORTEP diagram (50% probability) of 2. Hydrogen atoms have been omitted for clarity.

Figure 3. (a) $^{31}$P MAS NMR spectrum of 5, with $^{1}J_{P-Pt}$ shown; spinning sidebands are denoted with asterisks. (b) Static $^{1}$H-$^{195}$Pt CP/CPMG NMR spectrum of 5 (bottom trace). The slightly rolling baseline in (b) is an artifact of the co-addition of the sub-spectra.

Figure 4. FTIR spectrum of the region characteristic of Pt-N vibrations of 1 (black line), 2 (red line), 5 (green line), 6 (dark blue line), and 7 (light blue line).

Figure 5. ORTEP diagram (50% probability) of 6. Hydrogen atoms have been omitted for clarity.

Figure 6. (a) $^{31}$P CP/MAS NMR spectrum of 6, with $^{1}J_{P-Pt}$ shown; spinning sidebands are denoted with asterisks. (b) Static $^{195}$Pt CP/CPMG NMR spectrum of 6 (bottom trace), numerical simulation of the CPMG pattern using SIMPSON (middle trace), and analytical simulation of the corresponding static pattern using WSOLIDS (top trace).

Figure 7. (a) $^{195}$Pt MAS ($\nu_{rot} = 15.5$ kHz) NMR spectrum of (cod)PtI$_2$ (bottom trace) and simulation (top trace, using experimental parameters extracted via Herzfeld-Berger analysis). (b) $^{195}$Pt MAS ($\nu_{rot} = 15.5$ kHz) NMR spectrum of (cod)PtCl$_2$ (bottom trace) and numerical simulation (top trace, using SIMPSON). In each case, the isotropic peak is denoted with an asterisk.
Figure 8. (a) $^{31}$P CP/MAS NMR spectrum of 7; spinning sidebands are denoted with asterisks. (b) Static $^1$H-$^{195}$Pt CP/CPMG NMR spectrum of 7 (bottom trace), numerical SIMPSON simulation (middle trace), and analytical WSOLIDS simulation (top trace).

Figure 9. (a) $^{31}$P CP/MAS NMR spectrum of 8; spinning sidebands are denoted with asterisks. (b) Static $^1$H-$^{195}$Pt CP/CPMG NMR spectrum of 8 (bottom trace), numerical SIMPSON simulation (middle trace), and analytical WSOLIDS simulation (top trace).
Figures

Figure 1.
Figure 2.
Figure 3.
Figure 4.
Figure 5.
Figure 6.
Figure 7.
Figure 8.
Figure 9.