

# New Pt···H—N Bonds Characterized by $^{15}\text{N}$ -Filtered and 2D NOESY $^1\text{H}$ NMR Spectroscopy

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New Pt···H—N bonding modes in two cycloplatinated complexes,  $[\text{Pt}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2-C,N})(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{H-2-C,H})\text{Br}]$  (1) and  $[\text{Pt}(1\text{-C}_{10}\text{H}_6\text{NMe}_2\text{-8-C,N})(1\text{-C}_{10}\text{H}_6\text{NMe}_2\text{H-8-C,H})\text{Br}]$  (2), were characterized by  $^{15}\text{N}$ -filtered and 2D NOESY  $^1\text{H}$  measurements. Both 1 and 2 show markedly different interactions of an  $\text{RNMe}_2\text{H}^+$  group with a platinum centre; the  $^1J(^{15}\text{N},^1\text{H})$  values of 69 and 59 Hz for 1 and 2, respectively, are considerably less than those of the related free and protonated organic amine systems. The corresponding  $^1J(^{195}\text{Pt},^1\text{H})$  values are 72 and 180 Hz, respectively. An approach both to understanding and recognizing these Pt···H—N interactions is presented.

KEY WORDS NOESY  $^{15}\text{N}$ -filtered, Pt-amine complexes Cyclometallation Pt···H—N interactions

## INTRODUCTION

There is continuing interest<sup>1</sup> in the coordination of  $\text{H}_2$ ,  $\text{HSiR}_3$  and  $\text{HCR}_3$  molecules to transition metals through use of the sigma electrons of the appropriate H—X bond (X = H, Si, C, etc.). With many of these molecules it is possible to convert this bonding interaction into new M—H and M—X bonds via a formal oxidative addition. For the specific case of the C—H bond as donor to the metal it is now recognized that the interaction can vary from substantial (agostic)<sup>2</sup> to very weak (ca. 2–5% of a normal metal–hydride interaction).<sup>3</sup> The M···H—C interaction does not seem to be restricted to any particular metals and has been encountered in complexes with a variety of monodentate and chelating ligands.<sup>4</sup> Crabtree *et al.*<sup>5a</sup> offered a scheme, based on the ideas of Bürgi and Dunitz,<sup>5b</sup> to show the developing interaction of a C—H bond with a transition metal.

In contrast to the many examples of M···H—C interactions, there are only three examples<sup>6–8</sup> of related N—H interactions with a transition metal, and all of these are concerned with complexes of platinum. A direct approach to the investigation of these new Pt···H—N interactions using the  $^1J(\text{Pt},\text{H})$  and  $^1J(\text{N},\text{H})$  spin–spin coupling constants should be informative and allow us to clarify their relationship to M···H—C systems. Indeed, we can consider the magnitude of the one-bond  $^{15}\text{N}$ – $^1\text{H}$  spin–spin coupling constant in a

fashion analogous to that employed for  $^1J(^{13}\text{C},^1\text{H})$  values.<sup>2</sup> With the exception of our complex  $[\text{Pt}(1\text{-C}_{10}\text{H}_6\text{NMe}_2\text{-8-C,N})(1\text{-C}_{10}\text{H}_6\text{NMe}_2\text{H-8-C,H})\text{Br}]$  (2), which is the initiator of this work,<sup>8</sup> no  $^1J(\text{N},\text{H})$  coupling constant data were available for those compounds containing Pt···H—N interactions.

In a preceding paper<sup>9</sup> we suggested that nuclear Overhauser effects (NOEs), combined with suitable reporter ligands,<sup>10</sup> are useful in locating pendant C—H bonds in complexes of Pd(II) and Pt(II). The concept is a simple one, based on triangulation with protons that are in ligands both *cis* and *trans* to the ligand bearing the C—H bond of interest. In a straightforward extension, NOE criteria should also be able to give us some idea of how an N—H bond is positioned with respect to a metal centre.

We show here that both  $^1J$  and NOE data may have some general validity for evaluating Pt···H—N interactions.

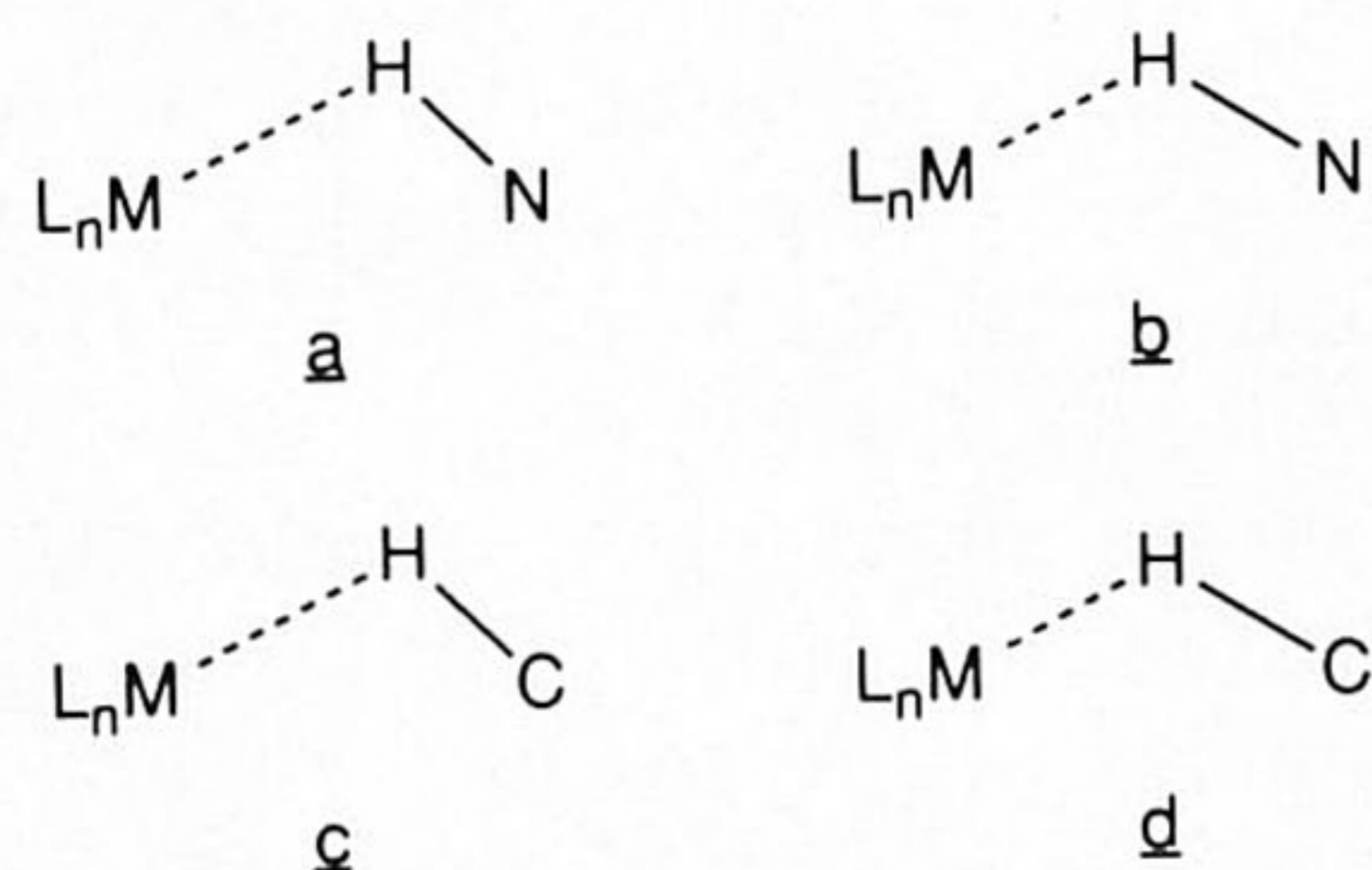
## RESULTS AND DISCUSSION

### Coupling constants

For the new complexes  $[\text{Pt}(\text{C-N-C,N})(\text{C-NH-C,H})\text{Br}]$  [ $\text{C-N} = \text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2}$  (1) and  $1\text{-C}_{10}\text{H}_6\text{NMe}_2\text{-8}$  (2)], one expects the  $^1J(^{15}\text{N},^1\text{H})$  value to resemble that for an ammonium salt if the interaction is primarily Pt···H—N (type *a* in Scheme 1), but to be significantly lower as one moves towards an increased  $\text{L}_n\text{M}\cdots\text{H}$  interaction (type *b* in Scheme 1). The two complexes 1

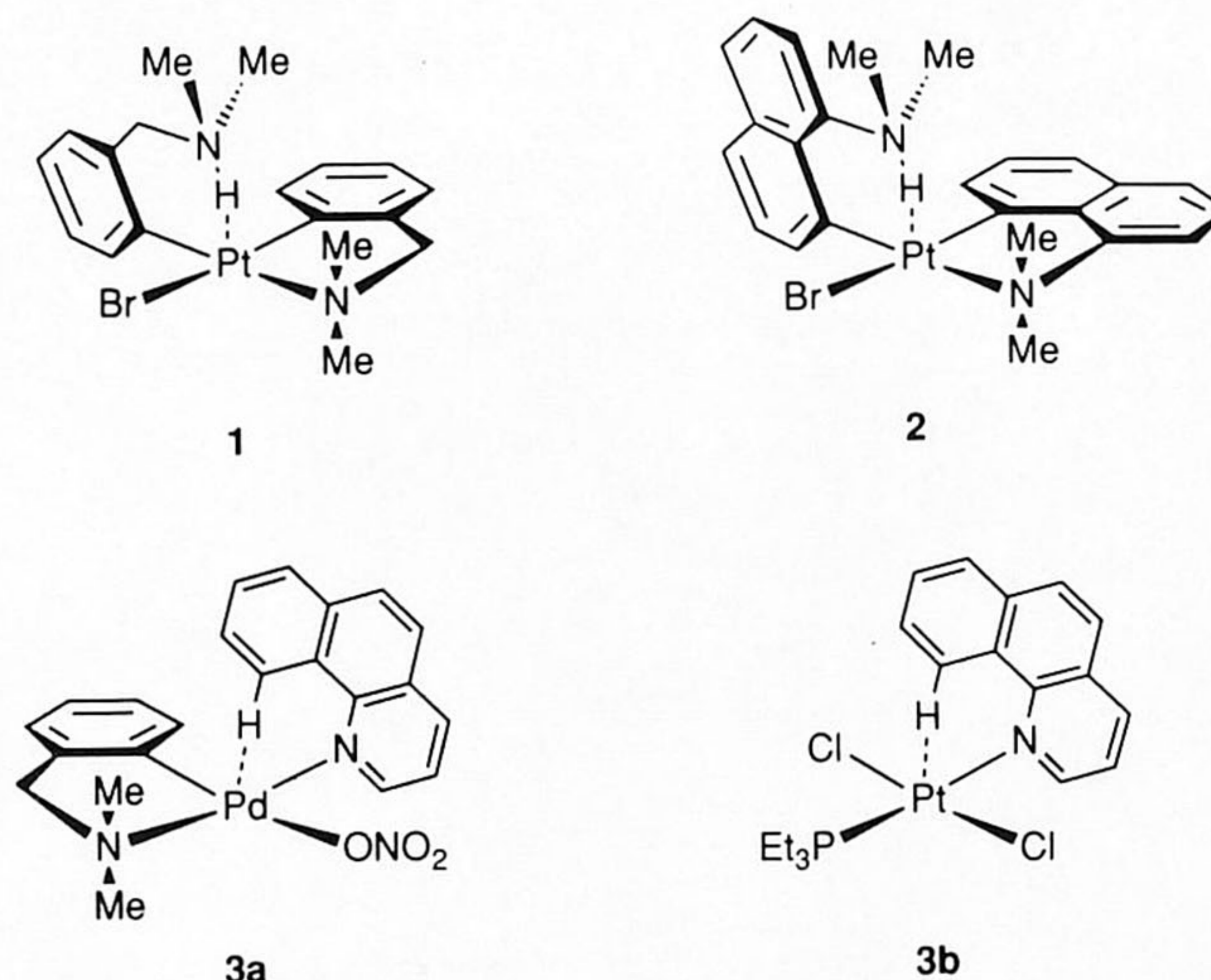
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Scheme 1. CH and NH interactions with a metal centre.

and **2** (see Scheme 2) are related in that they both contain two potential *C,N*-chelate ligands. In each complex one of these two ligands is, indeed, cyclometallated with both C and N acting as ligating atoms. The second ligand has only the carbon coordinated with the H atom of the  $\text{RNMe}_2\text{H}^+$  group in a situation for potential interaction with the metal centre. Previous <sup>1</sup>H NMR spectra have revealed that the two carbon ligands are mutually *cis* positioned.<sup>8</sup> The <sup>1</sup>H spectra for these compounds show a broad, very low-field signal for the NH at 11.34 and 15.78 ppm for **1** and **2**, respectively (Table 1). These low-field shifts are typical for protons positioned in a pseudo-fifth position above the coordination plane of a square-planar metal complex.<sup>11</sup> However, we have shown<sup>12</sup> that a significant part of this deshielding may be due to anisotropic effects associated with the metal and, consequently, these chemical shifts are not in themselves an unambiguous indicator of the bonding situation.

Scheme 2. Complexes with  $\text{M}\cdots\text{H}-\text{N}$  and  $\text{M}\cdots\text{H}-\text{C}$  interactions.

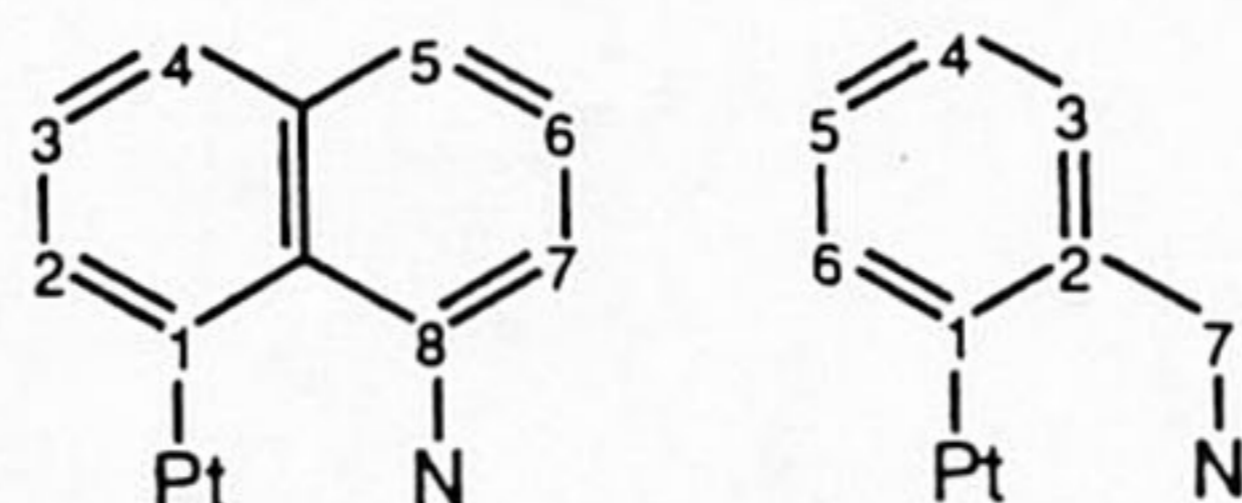
<sup>15</sup>N-filtered <sup>1</sup>H NMR measurements on these two complexes afford  $^1J(^{15}\text{N},^1\text{H})$  values of *ca.* 69 and 59 Hz, for **1** and **2**, respectively, and the spectrum of **1** is shown in Fig. 1. The one-bond <sup>15</sup>N to proton spin-spin coupling constant in *N*-methylaniline,  $\text{C}_6\text{H}_5\text{N}(\text{H})\text{Me}$ , has been reported<sup>13</sup> to be 78 Hz at 34 °C and 89 Hz at -80 °C in acetone-*d*<sub>6</sub>. For aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ , the value is 82.1 Hz in acetone<sup>13</sup> and for the anilinium ion<sup>13</sup> it is 76.0 Hz. Taking a value of *ca.* 75–80 Hz as a fair average for  $^1J(^{15}\text{N},^1\text{H})$  in both free and protonated

Table 1. <sup>1</sup>H NMR data<sup>a</sup> for complexes **1** and **2**

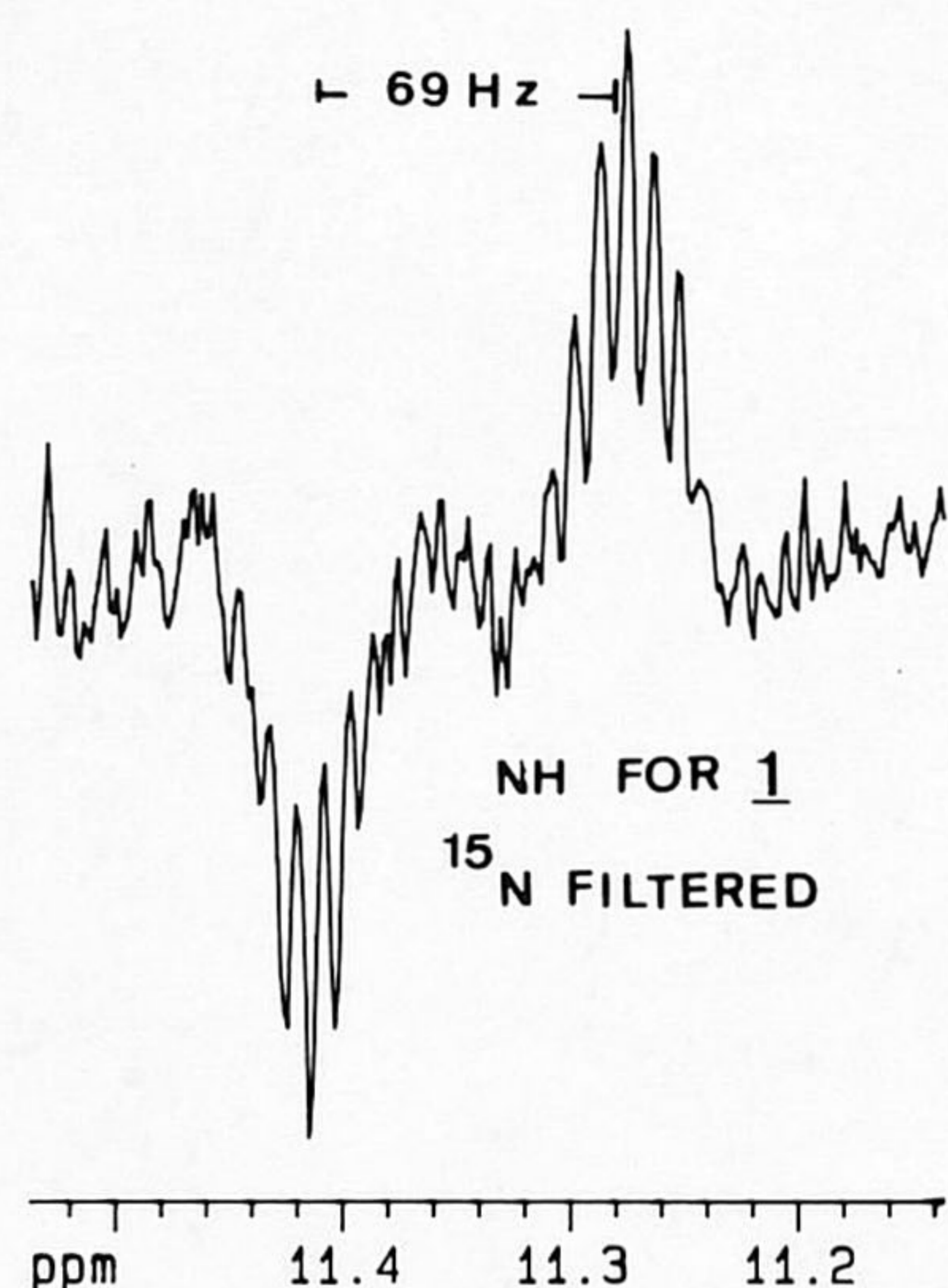
H	<b>1</b> δ(H)	<i>J</i> (Pt,H)	<b>2</b> δ(H)	<i>J</i> (Pt,H)	Others
H-2			8.28	72	
H-3	6.86		7.35		
H-4	7.00		7.62		
H-5	6.98		7.98		
H-6	7.82	67	7.45		
H-7			7.42		
H-7 <sup>b</sup>	4.09				$^3J(\text{H}-7,\text{NH}) = 4.2$ , $^2J(\text{H}-7,\text{H}-7) = 11.8$
H-7	4.03				$^3J(\text{H}-7,\text{NH}) = 6.5$
Me <sup>b</sup>	2.65		3.32		
Me	2.72		2.62		
NH	11.34	72	15.78	180	$^1J(^{15}\text{N},^1\text{H}) = 69 \text{ Hz (1), } 59 \text{ Hz (2)}$
H-2'			6.24	79	
H-3'	6.97		6.88		
H-4'	6.90		7.45		
H-5'	6.67		7.62		
H-6'	6.36	78	7.4		
H-7'			7.54		
H-7'	3.88				$^2J(\text{H}-7',\text{H}-7') = 13.8$
H-7' <sup>b</sup>	3.77				
Me'	2.93		3.55		
	2.92		3.55		

<sup>a</sup> Data were recorded at room temperature in  $\text{CDCl}_3$  (**1**) and  $\text{CD}_2\text{Cl}_2$  (**2**) solutions. Chemical shifts are in ppm relative to TMS and coupling constants are in Hz. The primed numbering corresponds to the cyclometallated ligand.

<sup>b</sup> Pointing towards the aromatic system of the second C-N ligand.







**Figure 1.**  $^{15}\text{N}$ -filtered proton spectrum of **1** showing the NH proton absorption and its corresponding 69 Hz coupling constant to nitrogen (AMX 500,  $\text{CDCl}_3$ ).

aryl amine systems, then in **1** and **2** this coupling has been reduced by *ca.* 10 and 20%, respectively. In the  $^1\text{H}$  NMR spectra of **1** and **2** the NH proton signal possesses  $^{195}\text{Pt}$  satellites, whose separations are 72 and 180 Hz, respectively. Taken together with the  $^1J(^{15}\text{N}, ^1\text{H})$  results, these data now allow a preliminary suggestion as to the relative nature of the bonding in the two complexes. For this purpose it is useful to remember that for terminal hydrides  $^1J(^{195}\text{Pt}, ^1\text{H})$  is *ca.* 600–1500 Hz, whereas the same coupling in a bridging hydride is *ca.* 200–600 Hz. For complex **1**, in which the NH proton has the smaller interaction with platinum and only a minor 10% reduction in the  $^1J(^{15}\text{N}, ^1\text{H})$  value, the interaction suggested is closer to  $\text{Pt}\cdots\text{H}-\text{N}$ , i.e. a type *a* molecule, in which the H–N bond is still relatively strong. For complex **2**, in which there is a significant reduction in the  $^1J(^{15}\text{N}, ^1\text{H})$  value and a larger  $^1J(^{195}\text{Pt}, ^1\text{H})$  value, we are approaching a bridging type bonding mode  $\text{Pt}\cdots\text{H}\cdots\text{N}$ , i.e. a type *b* molecule. The  $\text{Pt}\cdots\text{H}-\text{N}$  moiety in **2** in the solid state has a geometry close to linear and it might best be described as a three-centre, four-electron interaction, i.e.  $\text{Pt}^-\cdots\text{H}-\text{N}^+$ , as was recently proposed for the intermolecular, solid-state,  $\text{Pt}\cdots\text{H}-\text{N}$  interaction in  $[\text{NPr}^n_4]_2[\text{PtCl}_4] \cdot \text{cis-}[\text{PtCl}_2(\text{NH}_2\text{Me})_2]$ .<sup>7</sup> However, one has to bear in mind that both **1** and **2** are zwitterionic complexes and, therefore, there might be significant electrostatic contributions to the bonding in a  $\text{Pt}^-\cdots\text{H}-\text{N}^+$  moiety; for this reason, further theoretical,<sup>14</sup> structural and synthetic studies on **1** and **2** and related complexes are in progress.<sup>15</sup> Complexes **1** and **2** are, to our knowledge, the first chemical examples (either C–H or N–H) in which a continuum of interaction can be demonstrated and, from the spectroscopic side, these represent the first examples of the use of a nitrogen NMR parameter to define  $\text{M}\cdots\text{H}-\text{N}$  bonding.

## NOEs

Our previous consideration<sup>9,12</sup> of related complexes (Scheme 2, complexes **3a** and **3b**) with pendant but

movable C–H bonds involved the use of several NOEs, one from an *N*- $\text{CH}_3$  group and one from a proton *ortho* to the metallated carbon. For an  $\text{M}\cdots\text{H}-\text{C}$  bonding situation (type *c* and *d*), the CH proton can come within the *ca.* 3 Å range necessary to develop an NOE with these spins. Crude calculations for **1** and **2** show that if the N–H bond is tight (*ca.* 0.8 Å) and the N  $\text{sp}^3$  hybridized, then the distance to any aromatic proton will be greater than 3 Å. However, if there is a significant  $\text{Pt}\cdots\text{H}-\text{N}$  bonding for **1** and **2**, the metal-bonded  $\text{NMe}_2$  function of the cyclometallated ligand will readily act as a reporter, as one of the Me groups should lie about 3 Å from the N–H bond. Sections of the 2D NOESY spectra for **1** and **2** are shown in Fig. 2. Both show medium-intensity cross-peaks stemming from a selective NOE from an *N*- $\text{CH}_3$  to the NH. Volume integration of the relevant signals reveals no significant difference in this NOE for the two complexes. Although these data support an NH hovering over the metal, they are not sufficiently quantitative to allow further detailed interpretation. In passing, we note that an interligand  $\text{H}^2', \text{CH}_3$  NOE in **2** allows us to assign the markedly different  $\text{CH}_3$  resonances of the  $\text{HNMe}_2$  moiety. The peak at 3.33 ppm is due to the methyl above and directed towards the Pt–Br bond and that at 2.62 ppm to the methyl above the aromatic ring of the C,N-bonded ligand; this is confirmation of a tentative assignment based on anisotropic effects. In contrast to the work cited above<sup>9</sup> we did not find in either **1** or **2** any significant NOEs between the NH and the proton situated *ortho* to the Pt–C bond (or any other aromatic proton). This lack of an NOE is good evidence that there is little freedom of movement for the NH function in either molecule, and is in keeping with the observed Pt,H spin–spin coupling constants. A pseudo-square pyramidal arrangement for **1** and **2** with the proton of the H–N bond positioned in the apical position is, from a steric point of view, a very favourable arrangement since the aryl ligands are then mutually perpendicular.

In conclusion, we suggest two new NMR probes for detecting the, as yet, rarely reported type of  $\text{M}\cdots\text{H}-\text{N}$  bonding. One method involves heavy-atom to proton spin–spin coupling constants and the second, which is less definitive, is based on nuclear Overhauser effects. Additional work to refine the methods is in progress.

## EXPERIMENTAL

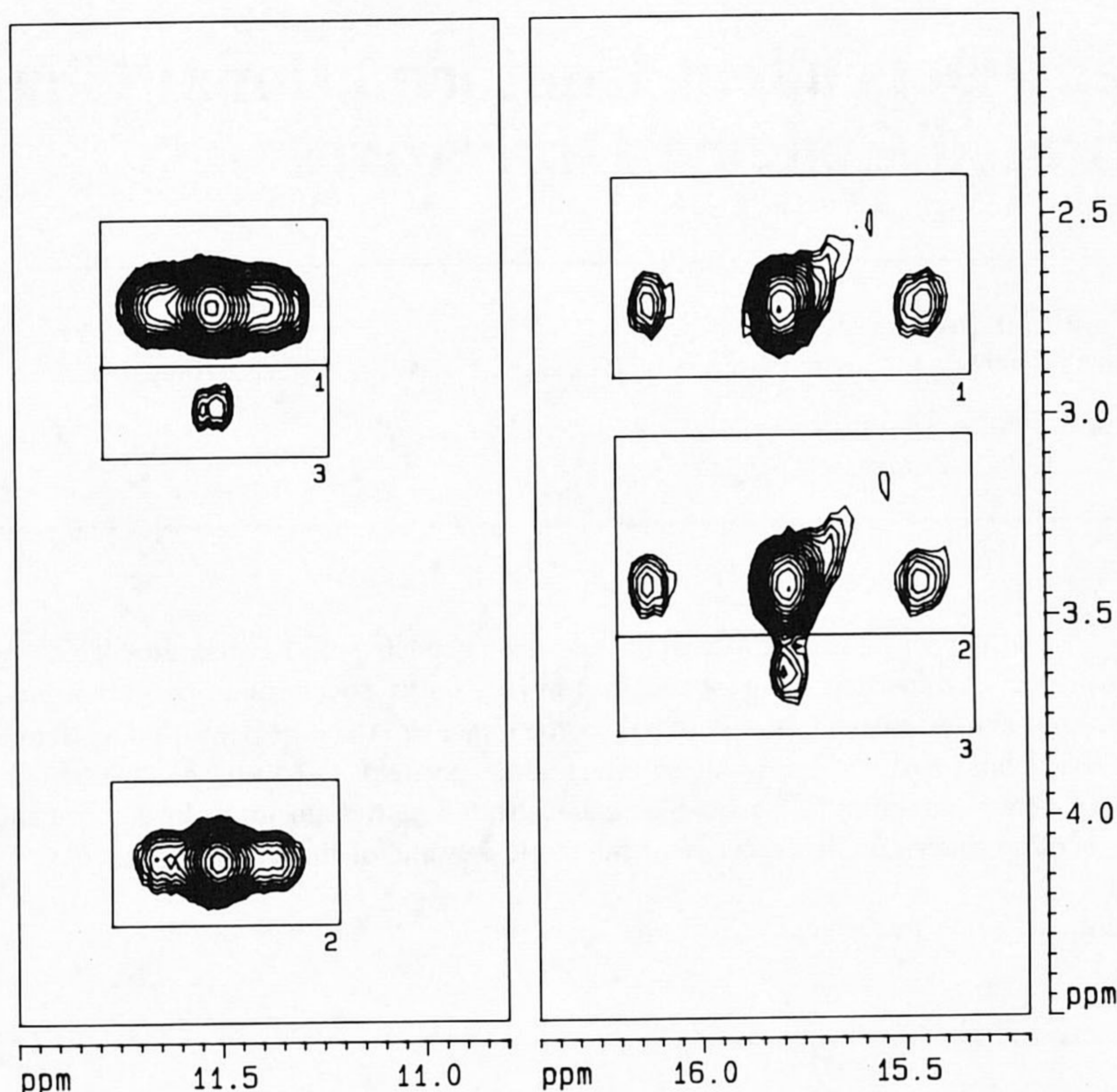
### Materials

Compounds **1** and **2** were obtained as described previously.<sup>8</sup>

### NOESY

The phase-sensitive (TPPI method)  $^1\text{H}$  NOESY experiments were recorded at 250.13 MHz on a Bruker AC 250 spectrometer operating in the Fourier transform mode using a mixing time of 900 ms. The time domain





**Figure 2.** Sections of the <sup>1</sup>H NOESY spectra for **1** (left) and **2** (right) showing the cross-peaks arising from the interactions between the NH with its <sup>195</sup>Pt satellites and its proximate protons. The less intense signals in box 3 arise from the inter-ligand NOEs (AC 250).

data (512 × 2048 points in  $t_1$  and  $t_2$ , respectively), acquired with 32 scans (4 dummy) per increment, were transferred to a Model X32 workstation and processed with zero filling and cosine square apodization in both dimensions prior to double Fourier transformation.

### <sup>15</sup>N-filtered <sup>1</sup>H

Nitrogen-filtered <sup>1</sup>H spectra were recorded at 500.13 MHz on a Bruker AMX 500 spectrometer employing

the sequence  $90(^1\text{H})-\Delta-90(^{15}\text{N})_x-90(^{15}\text{N})_{+x/-x}-\text{Acq}(+/-)$ , where  $\Delta$  was chosen as 7.2 ms. A total of 4096 transients were stored to a single FID.

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