

STRUCTURES OF RHODIUM COMPLEXES CONTAINING SUBSTITUTED HYDRAZINES FROM MULTINUCLEAR NMR STUDIES*

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Abstract—Natural abundance ^{15}N NMR measurements, using the INEPT pulse sequence, have been used in conjunction with ^{31}P NMR studies to elucidate the structures of several rhodium complexes containing monomethyl- and 1,1-dimethyl hydrazine.

There has been much previous work on transition metal complexes containing hydrazine, substituted hydrazine and hydrazido ligands as a result of their importance as intermediates in the conversion of dinitrogen to ammonia and amines.^{1–3} In the case of alkyl substituted hydrazines, it is known that they are less basic than hydrazine.^{4,5} For unsymmetrically methyl-substituted hydrazines ($\text{NH}_2\text{NH}_x\text{Me}_{2-x}$, $x = 0, 1$), the inequivalent nitrogens† obviously have different basicities, and IR studies suggest that protonation always occurs at the methyl-substituted nitrogen atom.⁶ However, in transition metal complexes steric effects appear to be more important than electronic effects, since X-ray studies show that it is the unsubstituted nitrogen, N_α , which coordinates to the metal in $[\text{RuH}(\text{COD})(\text{NH}_2\text{NMe}_2)_3]\text{PF}_6$ ($\text{COD} = 1,5\text{-cyclo-octadiene}$)⁷ and *trans*- $[\text{Rh}(\text{CO})(\text{NH}_2\text{NH}_x\text{Me}_{2-x})(\text{PPh}_3)_2]\text{ClO}_4$ ($x = 0, 1$).⁸ Nevertheless, the substituted nitrogen can coordinate to a metal, as found for the complex $[(\text{COD})\text{ClRu}\{\mu: \eta^2\text{-(NH}_2\text{NMe}_2)\}(\mu\text{-Cl})(\mu\text{-H})\text{RuH}(\text{COD})]\text{BPh}_4$,⁹ where the hydrazine acts as a bridging ligand, with the two nitrogen atoms being coordinated to different ruthenium atoms.

^{15}N NMR measurements could be of great value in elucidating the structures of complexes con-

taining coordinated nitrogen, but due to the low natural abundance, low sensitivity and negative gyromagnetic ratio of the ^{15}N nucleus, most of the previous work has been done on complexes where the nitrogen atoms have been isotopically enriched.^{10–12} However, in a previous publication,¹³ we showed how the geometry of $[\text{RhH}_2(\text{bipy})(\text{PPh}_3)_2]\text{Cl}$ could be elucidated from ^{15}N NMR measurements at the natural abundance level using the INEPT pulse sequence described by Morris and Freeman.¹⁴

We now report how related ^{15}N NMR measurements on rhodium complexes containing unsymmetrically substituted methyl hydrazines can readily identify which of the two inequivalent nitrogens is coordinated to rhodium through the observation of $^1J(\text{Rh-N})$ and $^1J(\text{N-H})$ and, in order to identify the effect of coordination, we also report direct ^{15}N NMR measurements on the free ligands. These NMR measurements on metal complexes are particularly useful when crystals suitable for X-ray analysis cannot be obtained.

EXPERIMENTAL

General and instrumental

Neat liquids (with CD_2Cl_2 external lock) were used to obtain ^1H and direct ^{15}N NMR spectra of the ligands, whereas ^{15}N and ^{31}P NMR spectra of the complexes were obtained on solutions (0.16 M) in $\text{CH}_2\text{Cl}_2\text{-CD}_2\text{Cl}_2$ in 10 mm NMR tubes (or in a 1 : 1 mixture of CH_3OH and CD_2Cl_2) on a Bruker AMX 400 spectrometer operating at 400.13, 40.56 and 161.98 MHz, respectively. The ^{15}N NMR spec-

* This paper is dedicated to Prof. E. W. Abel on his retirement and in recognition of his outstanding contributions to organometallic and inorganic chemistry.

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‡ Throughout this paper N_α is the NH_2 group and N_β is the methyl-substituted nitrogen atom.

tra were referenced to nitromethane (the relationship to other ^{15}N NMR reference standards has been reviewed by Mason,¹⁵ the ^1H NMR spectra were referenced to TMS and the ^{31}P NMR spectra were referenced to 85% H_3PO_4 in D_2O).

$[\text{RhCl}(\text{PPh}_3)_3]$ and $[\text{RhCl}(\text{PPh}_3)_2]_2$ were prepared by standard methods.¹⁶ Monomethylhydrazine and 1,1-dimethylhydrazine were used as supplied by Aldrich. Solvents were dried using standard drying agents. All the complexes were prepared, in NMR tubes *in situ* under nitrogen using standard Schlenk techniques, as follows.

Preparation of $[\text{Rh}(\text{PPh}_3)_3(\text{NH}_2\text{NHMe})]\text{Cl}$ (**1**)

Addition of NH_2NHMe (36 μl) to a solution of $[\text{RhCl}(\text{PPh}_3)_3]$ (0.3 g) and PPh_3 (0.5 g) in a mixture of CD_2Cl_2 and MeOH (1 : 1) gave an orange solution of **1**.

Preparation of $[\text{RhCl}(\text{PPh}_3)_2(\text{NH}_2\text{NHMe})]$ (**2**) and $[\text{RhCl}(\text{PPh}_3)_2(\text{NH}_2\text{NMe}_2)]$ (**3**)

Addition of the respective hydrazines to $[\text{RhCl}(\text{PPh}_3)_2]_2$ in the molar ratio 2 : 1 (1 : 1 based on Rh) in CH_2Cl_2 – CD_2Cl_2 gave solutions of **2** and **3**.

Preparation of $[\text{Rh}(\text{PPh}_3)_2(\text{NH}_2\text{NHMe})_2]\text{Cl}$ (**4**) and $[\text{Rh}(\text{PPh}_3)_2(\text{NH}_2\text{NMe}_2)_2]\text{Cl}$ (**5**)

Addition of the respective hydrazines to $[\text{RhCl}(\text{PPh}_3)_2]_2$ in the molar ratio 4 : 1 (2 : 1 based on Rh) in CD_2Cl_2 and MeOH (1 : 1) gave solutions of **4** and **5**.

RESULTS AND DISCUSSION

The direct proton-coupled ^{15}N NMR spectra of NH_2NMe_2 , at room temperature and at 213 K, are shown in Fig. 1. The room temperature ^{15}N NMR spectra of NH_2NMe_2 consists of a sharp resonance at -324 ppm and a broad resonance at -283 ppm, which at low temperature is resolved into a triplet, $\delta(^{15}\text{N}) = -283$ ppm, $^1J(^{15}\text{N}-^1\text{H}) = 65$ Hz. this indicates that the room temperature resonance at -283 ppm corresponds to the $-\text{NH}_2$ nitrogen (N_α), while that at -324 ppm corresponds to the $-\text{NMe}_2$ nitrogen (N_β). In the case of NH_2NHMe (Fig. 2), there are two resonances at -329.5 and -306.8 ppm and the resonance at $\delta(^{15}\text{N}) = -306.8$ ppm is resolved at low temperature into a quartet with a much smaller coupling constant of 2.6 Hz, which can be attributed to $^2J(^{15}\text{N}-^1\text{H})$. This assignment of the low-field ^{15}N resonance to the $-\text{NHMe}$

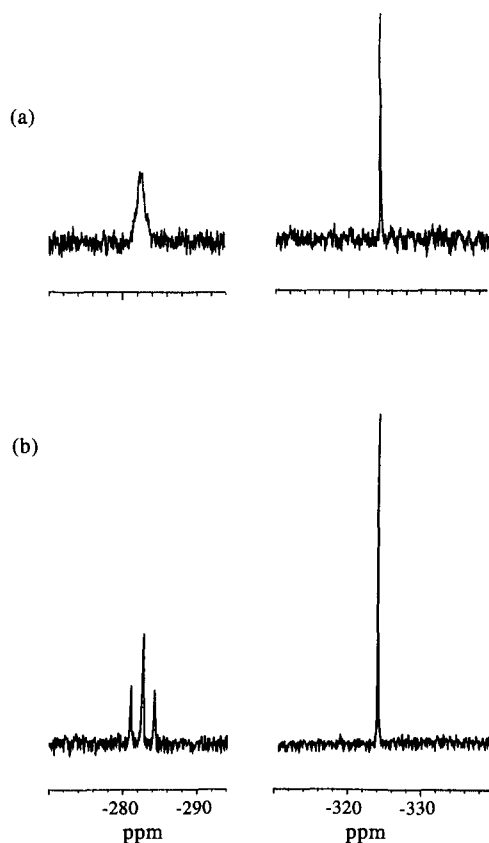


Fig. 1. The direct proton-coupled ^{15}N NMR spectra of NH_2NMe_2 at room temperature (a) and 213 K (b).

group, N_β , is supported by the following observations:

1. The ^{15}N NMR spectrum of NH_2NHMe , even at low temperatures, shows no evidence for $^1J(^{15}\text{N}-^1\text{H})$ on either of the ^{15}N resonances.
2. The ^1H NMR spectrum of NH_2NHMe both at room and low temperatures consists of two equally intense resonances, one due to the rapidly exchanging N–H protons and the other due to the methyl protons.

The ^{15}N NMR data for these compounds have been reported previously, but the resonances were not assigned to specific nitrogen atoms.¹⁷

The spectroscopic data for $\text{NH}_2\text{NH}_x\text{Me}_{2-x}$ ($x = 0, 1$) are summarized in Table 1.

In order to structurally characterize the complexes **1**–**5** described in the Experimental section, we have used a combination of ^{31}P and ^{15}N NMR measurements.

Thus, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** consists of a doublet of triplets and a doublet of doublets in the intensity ratio 1 : 2, consistent with the presence of a T-shaped $\text{Rh}(\text{PPh}_3)_3$ group. The proton-decoupled ^{15}N NMR spectrum obtained using the

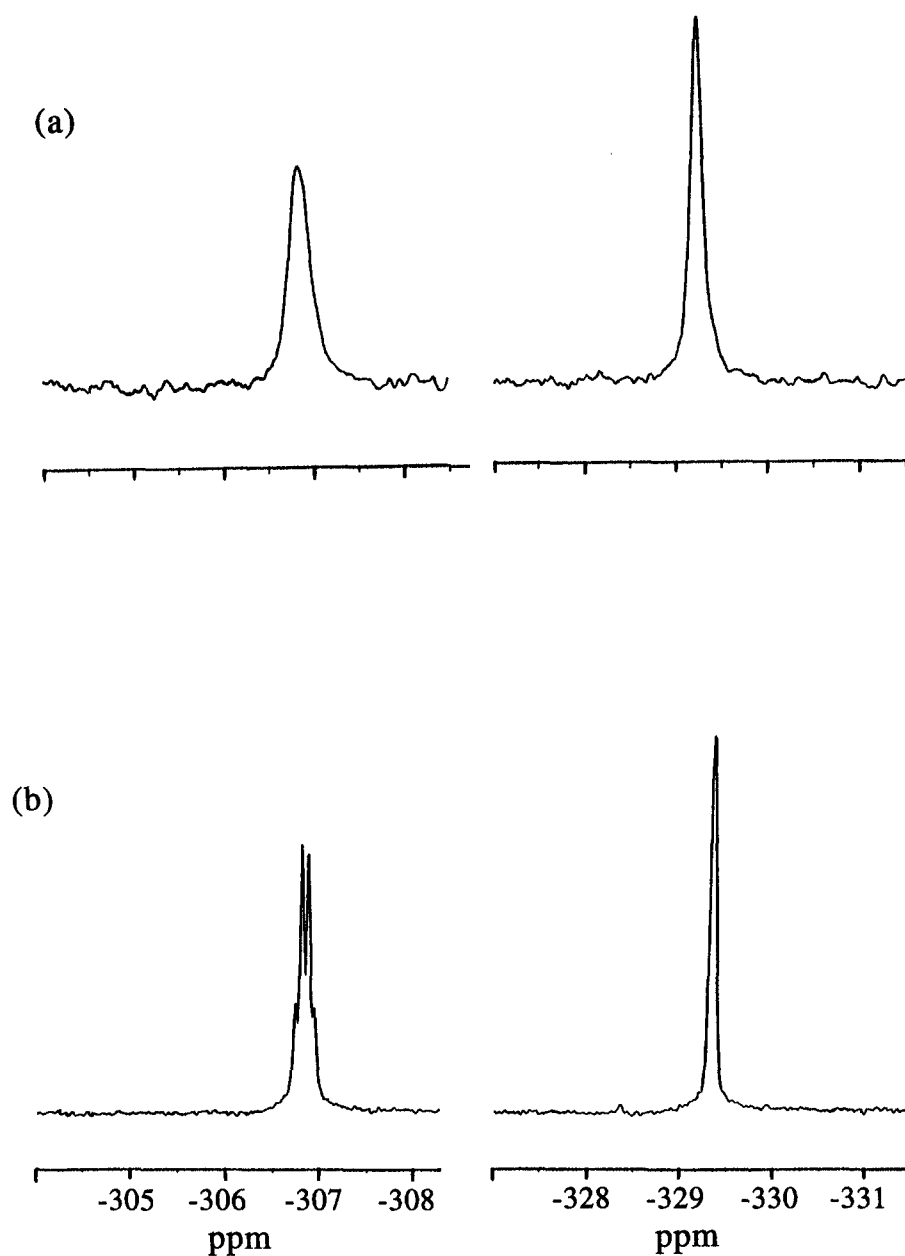


Fig. 2. The direct proton-coupled ^{15}N NMR spectra of NM_2NHMe at room temperature (a) and 243 K (b).

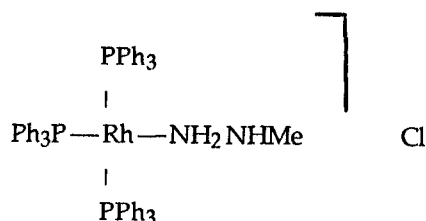
Table 1. ^{15}N NMR data for NH_2NHMe and NH_2NMe_2

Compound	$\delta(\text{N}_\alpha)$ (ppm)	$\delta(\text{N}_\beta)$ (ppm)	$^1J(\text{N}_\alpha\text{--H})$ (Hz)	$^2J(\text{N}_\beta\text{--CH})$ (Hz)
NH_2NHMe^a	−329.5	−306.8		2.6
$\text{NH}_2\text{NMe}_2^b$	−283.0	−324.3	65	

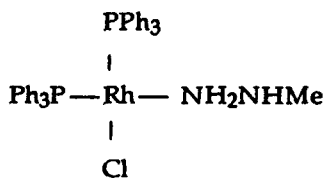
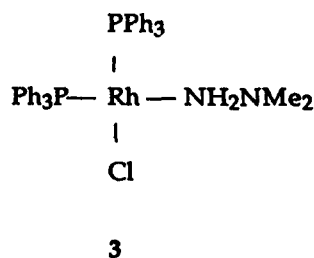
^a At 243 K.

^b At 213 K.

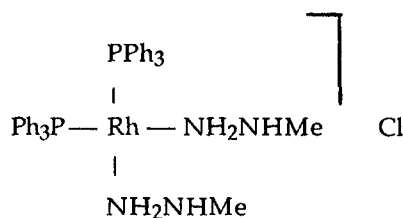
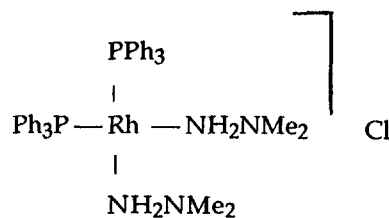
INEPT pulse sequence is shown in Fig. 3. It can be seen that one of the resonances is due to a nitrogen atom (N_α) coupled to rhodium and to one *trans*-phosphine ligand, while there is no coupling to the other nitrogen resonance (N_β). [$^2J(^{15}\text{N}-^{31}\text{P})$ to *cis*-phosphines is not observed at the resolution obtained in these spectra.] The proton-coupled ^{15}N NMR spectrum of **1** is shown in Fig. 4. The characteristic anti-phase spectrum shows that N_α is coupled to two hydrogen atoms, while N_β is coupled to one, since the spacing between the anti-phase doublets for N_α is almost twice that for N_β . This clearly indicates that the $-\text{NH}_2$ nitrogen, N_α , is coordinated to rhodium and, in conjunction with the ^{31}P NMR data, allows us to unambiguously structurally characterize **1** as shown below:

**1**

Similarly, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2** and **3** consist of two sets of doublets of doublets, indicating the presence of two inequivalent phosphine groups per rhodium. The ^{15}N NMR spectrum of **2** is similar to that for **1**, indicating a similar mode of coordination of NH_2NHMe . However, for **3** the resonance of the $-\text{NMe}_2$ nitrogen cannot be observed in the ^{15}N NMR spectrum using the INEPT method, as the values for $^1J(^{15}\text{N}-^1\text{H})$ were used for the transfer of polarization. The ^{15}N NMR spectrum of **3** thus consists of only the resonance due to the $-\text{NH}_2$ group which is coupled to rhodium and a *trans*-phosphine ligand. Thus, **2** and **3** can be formulated as below:

**2****3**

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **4** and **5** consist of a single doublet, indicating equivalent phosphines. The ^{15}N NMR spectra are similar to **2** and **3**, and we can formulate these compounds as:

**4****5**

All the spectroscopic data for the complexes **1–5** are summarized in Tables 2 and 3.

It is thus clear that ^{15}N NMR in conjunction with ^{31}P NMR spectroscopy is a powerful tool for elucidating the structures of nitrogen-containing rhodium/phosphine complexes.

The ^{15}N NMR spectra, which can be acquired at the natural abundance level, are of significant importance, since such measurements provide an unambiguous distinction between hydrazine and hydrazido ligands, which is usually impossible to obtain from X-ray crystallography even when suitable crystals can be obtained.

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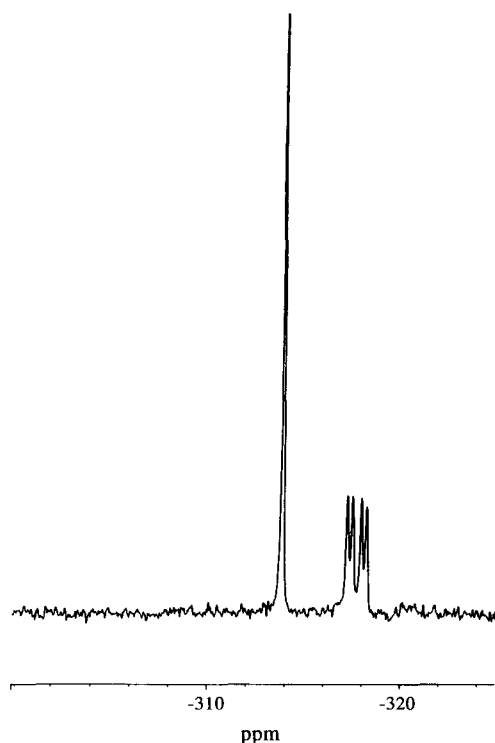


Fig. 3. The proton-decoupled ^{15}N NMR spectrum of $[\text{Rh}(\text{PPh}_3)_3(\text{NH}_2\text{NHMe})]\text{Cl}$ (**1**) obtained using the INEPT pulse sequence at 243 K.

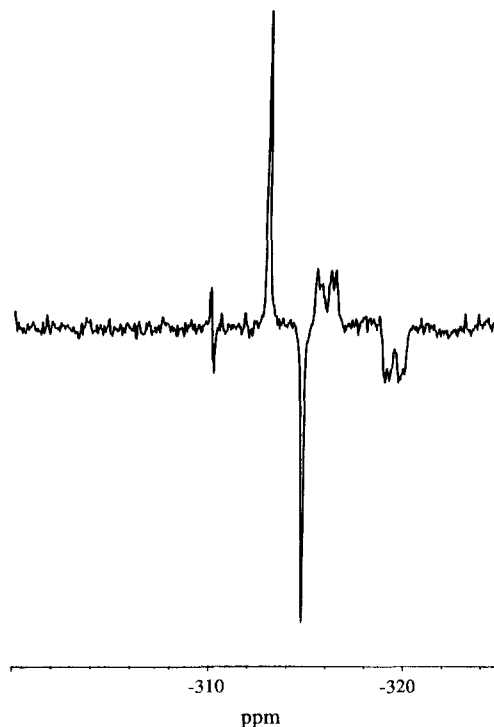


Fig. 4. The proton-coupled ^{15}N NMR spectrum of $[\text{Rh}(\text{PPh}_3)_3(\text{NH}_2\text{NHMe})]\text{Cl}$ (**1**) obtained using the INEPT pulse sequence at 243 K.

Table 2. $^{31}\text{P}\{^1\text{H}\}$ NMR data for rhodium complexes containing substituted hydrazines, $\text{NH}_2\text{NH}_x\text{Me}_{2-x}$ ($x = 0, 1$)^a

Complex ^b	$\delta(^{31}\text{P}_a)$ (ppm)	$\delta(^{31}\text{P}_b)$ (ppm)	$^1J(^{103}\text{Rh}-^{31}\text{P}_a)$ (Hz)	$^1J(^{103}\text{Rh}-^{31}\text{P}_b)$ (Hz)	$^2J(^{31}\text{P}_a-^{31}\text{P}_b)$ (Hz)
1	34.2	45.8	145.1	162.8	40.0
2	55.0 ^c	48.4 ^c	201.8	168.4	49.0
3	54.0 ^c	46.8 ^c	202.9	168.7	48.4
4		52.0		173.3	
5		52.0		174.0	

^a P_a is *trans* to PPh_3 or Cl . P_b is *trans* to $\text{NH}_2\text{NH}_x\text{Me}_{2-x}$ ($x = 0, 1$).

^b See text for numbering scheme.

^c These assignments can be reversed.

Table 3. ^{15}N NMR data for rhodium complexes containing substituted hydrazines, $\text{NH}_2\text{NH}_x\text{Me}_{2-x}$ ($x = 0, 1$) in $\text{CD}_2\text{Cl}_2\text{-CH}_2\text{Cl}_2$ for **2** and **3** and $\text{CD}_2\text{Cl}_2\text{-CH}_3\text{OH}$ for **1**, **4** and **5** at 243 K^a

Complex ^b	$\delta(^{15}\text{N}_a)$ (ppm)	$\delta(^{15}\text{N}_\beta)$ (ppm)	$^1J(^{103}\text{Rh}-^{15}\text{N}_a)$ (Hz)	$^2J(^{31}\text{P}_{trans}-^{15}\text{N}_a)$ (Hz)
1	-317.8	-313.8	11.2	29.5
2	-312.1	-316.6	10.6	36.8
3	-291.8	—	11.7	38.1
4	-320.1	-316.6	15.0	29.0
5	-295.0	—	10.6	28.5

^a N_a is the NH_2 group, N_β is the methyl-substituted nitrogen.

^b See text for numbering scheme.

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