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The ^{15}N NMR spectra of some dihydrobis(triphenylphosphine)rhodium(III) complexes of aromatic N-donor carboxylates

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Abstract

^{15}N (natural abundance) NMR spectral data are reported for a series of complexes $[RhH_2(PPh_3)_2(NArCO_2)]$ ($NArCO_2$ = pyridine-2-carboxylate, 6-methylpyridine-2-carboxylate, pyrazine-2-carboxylate, quinoline-2-carboxylate, isoquinoline-1-carboxylate, and quinoxaline-2-carboxylate), and were obtained by the INEPT method with polarisation transfer from the hydride lying *trans* to nitrogen. The ^{15}N signal moves upfield by 35–50 ppm up on coordination of nitrogen to the metal, $^2J(^{15}N-^1H_{trans})$ has a value of ca. 25 Hz, and $^1J(^{103}Rh-^{15}N)$ lies in the range 9.1–10.1 Hz.

Introduction

The sensitivity of the ^{15}N nucleus to its chemical environment makes ^{15}N NMR spectroscopy a potentially valuable technique in the study of metal complexes of nitrogen-donor ligands. However its usefulness is limited by the low natural abundance (0.37%) of ^{15}N, which necessitates high sample concentrations (since in most cases ^{15}N enrichment is not feasible), and consequently by the availability, solubility and stability in solution of the compound of interest. By means of polarisation transfer methods (e.g. INEPT [1]) signal intensities can be enhanced by a factor $\gamma H/\gamma N = 10$, reducing the time required for data collection by a factor of 100 and making possible use of samples of concentration ≥ 0.05 *M* (in a field of 4.7 T and a tube of 10 mm diameter). The applicability of these methods is restricted to compounds in which the nitrogen is spin-coupled to at least one hydrogen with a coupling constant of sufficient magnitude to permit the successful operation of the polarisation transfer pulse sequence.

In many cases the N-donor ligand either contains no hydrogen or shows too small a $^{15}N-^1H$ coupling or too complex a coupling pattern to be of practical value. Here a $^{15}N-^1H$ coupling to a hydrogen independent of the ligand is a potential

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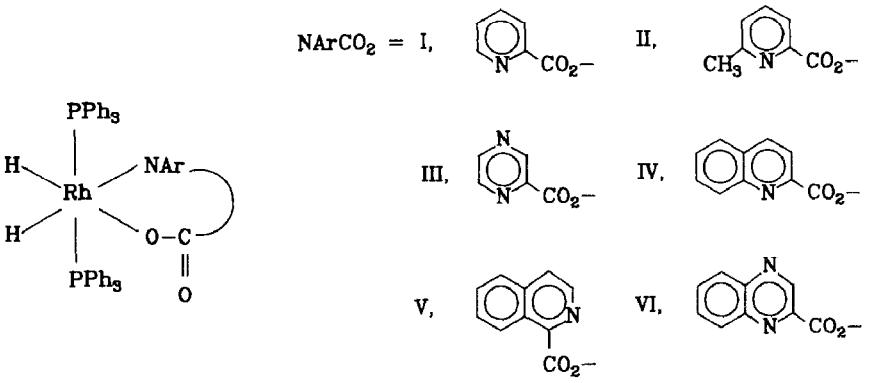

Fig. 1. Structure of the complexes $[RhH_2(PPh_3)_2(NArCO_2)]$.

answer; such coupling is found in metal hydride complexes in which the hydride lies *trans* to the N-donor ligand. Measurement of $^2J(^{15}N-^1H_{trans})$ requires a complex with a second $^{15}N-^1H$ coupling of known magnitude through which to transfer polarisation, and a fairly high solubility in a suitable solvent. The complex $[RhH_2(PPh_3)_2$(pyridine-2-carboxylate)] (I) (Fig. 1) [2] fulfils these conditions.

Experimental

The complexes $[RhH_2(PPh_3)_3(NArCO_2)]$ (I–VI) were prepared in high yield (70–90%) by reaction of $[RhH(PPh_3)_4]$ with the free carboxylic acid $NArCO_2H$ [2]. They are quite soluble (0.05 to 0.7 *M*) in chloroform (in which they decompose slowly) and methylene chloride (in which they are fairly stable).

Spectra were recorded on a Bruker AC200 FT spectrometer operating at 20.29 MHz, probehead diameter 10 mm. Solutions in CH_2Cl_2/CD_2Cl_2 (~ 6/1) were prepared under nitrogen, with the nitromethane reference contained in a capillary (internal diameter ~ 2 mm) aligned along the axis of rotation.

A spectral width of 7000 Hz and an acquisition time of 1.16 s were used; after zero-filling this gave a digital resolution of 0.2 Hz/Pt. The relaxation delay was 4 s. INEPT delay times were based on $^{15}N-^1H$ coupling constants of 2 Hz (for quinoline-2-carboxylic acid), 11 Hz [for the remaining carboxylic acids and for measurement of $^2J(^{15}N-^1H_{trans})$] and 25 Hz [for the $^{15}N\{^1H\}$ spectra of the complexes]. All spectra were obtained with refocussing of magnetisation.

Results and discussion

In an experiment involving complex I, polarisation was transferred from the 6-hydrogen [$^2J(^{15}N-^1H) = 11.4$ Hz] and a spectrum was obtained with decoupling of the aromatic protons only, with coupling to the hydrides still effective. After correction for a phase distortion a value of $^2J(^{15}N-^1H_{trans}) = 25$ (± 3) Hz was determined. Thereafter this $^{15}N-^1H$ coupling was made use of in polarisation transfer, and $^{15}N\{^1H\}$ spectra were recorded in which the coordinated nitrogen resonated as a doublet of triplets (Fig. 2). Spectral data for complexes I–VI are shown in Table 1, and for the free carboxylic acids in Table 2.

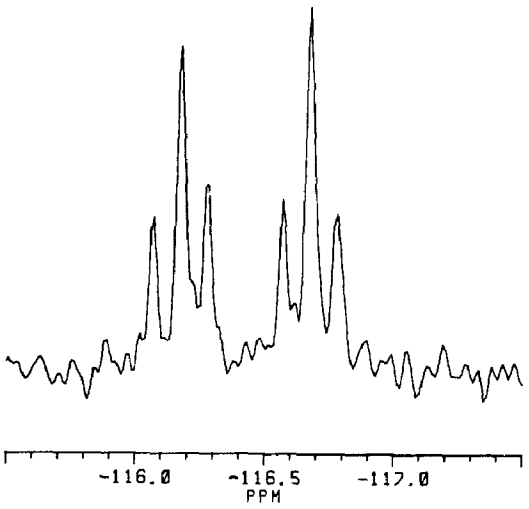

Fig. 2. The $^{15}N\{^1H\}$ spectrum of complex V; 0.3 *M* solution in CH_2Cl_2/CD_2Cl_2, 64000 scans, $\delta(^{15}N)$ relative to neat CH_3NO_2 (ext. standard). $^1J(^{103}Rh-^{15}N)$ 10.1, $^2J(^{31}P-^{15}N)$ 2.1 Hz.

The ^{15}N resonances move upfield by 35–50 ppm upon coordination of nitrogen to the metal. The measurements are for samples in two different solvents (DMSO and CH_2Cl_2), but since the ^{15}N chemical shifts of pyridine in the same two solvents have been reported to differ by only 2.2 ppm [6] this change can be attributed almost entirely to coordination to the metal. Comparison of the chemical shifts of N(4) in free and complexed pyrazine-2-carboxylic acid reveals a relatively small difference of 4.2 ppm, suggesting that N(4) is not greatly influenced by coordination of N(1) to the metal and that electron density back-donated from filled metal orbitals is localised largely on N(1).

The values of $^1J(^{103}Rh-^{15}N)$ for complexes I–VI cover a narrow range of 9.1–10.1 Hz, indicating that there is little variation in the character of the metal–nitrogen bond and a relatively insignificant influence of the ring substituents. However the presence of a metal-bound carboxyl group *ortho* to the pyridine

Table 1

^{15}N spectral data for the complexes $[RhH_2(PPh_3)_2(NArCO_2)]$ [a]

Complex	$\delta(N(1))$ [b]	$\delta(N(2))$	$\delta(N(4))$	$^1J(^{103}Rh-^{15}N)$ [c]	$^2J(^{31}P-^{15}N)$	$^2J(^{15}N-^1H\,trans)$	$^2J(^{15}N-^1H\,cis)$
I	−115.3			9.7	1.9	25 ± 3	≤ 3
II	−111.8			9.7	1–2.5		
III	−93.7		−49.6	9.6	1–2		
IV	−114.1			9.2	1–2		
V		−116.4		10.1	2.1		
VI	−93.8		−51.0	9.1	1.6		

[a] Solvent CH_2Cl_2/CD_2Cl_2. Concentrations: I, 0.7 *M*; II, 0.05 *M*; III, 0.3 *M*; IV, 0.1 *M*; V, 0.3 *M*; VI, 0.2 *M*. Temperature 22°C. 60000–80000 transients recorded from each. [b] Chemical shifts are in ppm relative to neat CH_3NO_2 (external standard), negative values to high field, and are uncorrected for bulk susceptibility effects. The corrected values (ref. [3]) lie 1.4 ppm to low field of the values tabulated. [c] Coupling constants (absolute magnitude) are in Hz.

Table 2

^{15}N spectral data for the carboxylic acids $NArCO_2H$ [a]

$NArCO_2H$	$\delta(N(1))$ [b]	$\delta(N(2))$	$\delta(N(4))$	$^2J(^{15}N(1)-^1H(6))$ [c]	$^2J(^{15}N(2)-^1H(3))$	$^2J(^{15}N(4)-^1H(3),^1H(5))$
Pyridine-2-carboxylic acid [d]	−66.7			11.4		
6-Methylpyridine-2-carboxylic acid	−69.1					
Pyrazine-2-carboxylic acid [e]	−47.4		−45.4	10.9		10.5
Quinoline-2-carboxylic acid	−66.9					
Isoquinoline-1-carboxylic acid		−79.0			11.2	

[a] Solvent DMSO/DMSO-d_6, concentrations 1.0–1.5 *M*, temperature 22 °C, 5000–10000 transients recorded from each. [b] Chemical shifts are in ppm from neat CH_3NO_2 (external standard), negative values to high field, and are uncorrected for bulk susceptibility effects. The corrected values (ref. [3]) lie 1.0 ppm to low field of the values tabulated. [c] Coupling constants (absolute magnitude) are in Hz. Values of $^3J(^{15}N-^1H)$ are ≤ 2 Hz. [d] See also ref. [4]. [e] See also ref. [5].

nitrogen (complex I) appears to reduce the magnitude of $^1J(^{103}Rh-^{15}N)$ by a factor of almost two relative to the value reported for a complex of unsubstituted pyridine [*trans*-$Rh(py)_4Cl_2$]Cl (17.1 Hz) [7], indicating a substantially reduced *s* character of the metal–nitrogen bond in the former case. Other complexes for which $^1J(^{103}Rh-^{15}N)$ has been reported are [*trans*-$RhCl(CO)(NO)(PPr^i_3)_2$](ClO_4) (4.5 Hz) [8], [*trans*-$Rh(en)_2Cl_2$]Cl (13.4 Hz) [7], [$RhCl(PPr^i_3)_2$(*p*-MeC_6H_4NSO)] (15.5 Hz) [9], [Rh(*o*-phen)$_3$]Cl_3 (18.4 Hz) [7], and [*trans*-$RhCl(N_2)(PCy_3)_2$] (30 Hz) [10].

The nitrogen–phosphorus coupling constant of 1–2.5 Hz (Table 1) is typical of $^2J(^{31}P-^{15}N_{cis})$ [10–12].

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