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Natural Abundance Nitrogen-15 NMR Spectroscopy of Rhodium Complexes by Indirect Detection Using Phosphorus

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Nitrogen-15 NMR spectra of the complexes $[Rh(N_3)(PPh_3)_3]$, $[Rh_2(N_3)_2(PPh_3)_4]$ and $[Rh\{N(CN)_2\}(PPh_3)_3]$, each containing ^{15}N at natural abundance, were obtained by indirect detection (HMQC) using phosphorus as the observed nucleus. Data collection times varied from 4 h to 4 d depending upon the accuracy of the estimated value of $^2J(^{31}P,^{15}N)$ used to optimize the pulse sequence. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

The study by ^{15}N NMR spectroscopy of N-donor ligands in complexes of transition metals is of some current interest,[1,2] but is hindered by the low natural abundance (0.37%) of ^{15}N, which necessitates the use of isotopic enrichment and/or signal enhancement techniques such as INEPT[3] and indirect detection (HMQC).[4] The polarization transfer methods have, until very recently, made use exclusively of spin coupling to ^1H in order to provide enhancements by factors of up to $\gamma_H/\gamma_N = 10$ (INEPT) and $(\gamma_H/\gamma_N)^{5/2} = 316$ (HMQC), subject to the requirement of a suitable nearby proton. The use of ^1H for polarization transfer is convenient because of the high gyromagnetic ratio of ^1H, its relatively short relaxation time, the fairly high probability that a proton in the molecule of interest is spin coupled to nitrogen and the need for a spectrometer with only two transmitter channels. However, allowing for hardware considerations (i.e. a third channel), ^1H can be replaced by any other spin-$\frac{1}{2}$ nucleus of reasonably high γ and natural abundance. In practice, the options are restricted to ^{19}F, ^{31}P and ^{205}Tl. The use of ^{31}P for indirect detection, although less effective than ^1H by a factor of 10, offers a means of obtaining signals from ^{15}N at natural abundance[5] in compounds which have no suitable proton but in which ^{15}N is spin coupled to phosphorus. The method of indirect detection using ^{31}P has found application in studies of phosphazenes,[6] ^{57}Fe,[7,8] ^{61}Ni,[8] ^{103}Rh,[9] ^{183}W[8] and ^{187}Os.[10]

EXPERIMENTAL

Synthesis of complexes (1–3)

$[Rh(N_3)(PPh_3)_3]$ (**1**) was prepared by the method of Beck *et al.*[11] using NaN_3 in place of LiN_3, with $[Rh(Cl)(PPh_3)_3]$[12] in 9:1 $EtOH–H_2O$ at room temperature. ^{31}P NMR ($CDCl_3$, 300 K), δ 49.00 [dt, 1P, J(Rh,P) 179.6, J(P,P) 39.6 Hz], 31.58 [dd, 2P, J(Rh,P) 145.6 J(P,P) 39.6 Hz].

$[Rh_2(N_3)_2(PPh_3)_4]$ (**2**) was prepared *in situ* from **1** (once isolated its solubility is much reduced) in dichloromethane in the presence of air, which oxidizes the PPh_3 released by the dimerization, allowing concentrations of up to *ca.* 0.05 M to be attained. Higher concentrations ($\gtrsim$0.1 M) of **1** lead to extensive precipitation of **2**. ^{31}P NMR ($CDCl_3$, 300 K), δ 51.21 [d, J(Rh,P) 190.7 Hz].

To prepare $[Rh\{N(CN)_2\}(PPh_3)_3]\cdot CH_2Cl_2$ (**3**), a mixture of $[Rh(Cl)(PPh_3)_3]$ (0.150 g, 0.162 mmol), $NaN(CN)_2$ (0.016 g, 0.180 mmol) and PPh_3 (0.051 g, 0.194 mmol) in EtOH (5 ml) at 80 °C was stirred for 1 h to give an orange suspension. The solid was recrystallized from CH_2Cl_2–hexane to give orange crystals, which were washed with hexane and dried under vacuum (yield 60%). Elemental analysis: calculated, C 65.8, H 4.5, N 4.0; found, C 65.7, H 4.7, N 4.0%. ^{31}P NMR ($CDCl_3$, 300 K), δ 48.40 [dt, 1P, J(Rh,P) 176.9, J(P, P) 40.0 Hz], 32.79 [dd, 2P, J(Rh, P) 139.2, J(P, P) 40.0 Hz].

NMR measurements

Spectra were recorded on a Bruker DRX 400 spectrometer with a 5 mm triple resonance inverse probe having a dedicated ^{31}P channel using the HMQC pulse sequence of Bax *et al.*[4] $\{\pi/2(^{31}P)–1/[2J(^{31}P,^{15}N)]–\pi/2(^{15}N)–\tau–\pi(^{31}P)–\tau–\pi/2(^{15}N)–Acq(^{31}P)\}$. In order to optimize the delay times in the pulse sequence $^2J(^{31}P,^{15}N_{trans})$ and $^2J(^{31}P,^{15}N_{cis})$ were chosen to be 38.0 and 4.0 Hz, respectively, based on values measured from similar compounds with ^{15}N-enriched ligands.[2] With the exception of the spectrum in Fig. 2(c), for which ^{15}N decoupling was omitted, the $^{15}N–^{31}P$ spectra

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shown in Fig. 2(a), (b), (d), (g) and (h) were obtained with ^{1}H decoupling throughout and ^{15}N decoupling during acquisition from solutions of concentration *ca.* 0.3 M (0.15 M in the case of **2**) in dichloromethane under argon (air in the case of **2**) at 300 K and referenced to nitromethane. For each a spectral width in f_2 (^{31}P) of 8 ppm and an acquisition time of 0.396 s were used, giving a digital resolution of 1.26 Hz per point; in f_1 (^{15}N) the spectral width and time domain were 6 ppm and 128 [240 for spectrum (a) and 40 for spectrum (g), which was processed with linear prediction], respectively, giving, after zero filling, a digital resolution of 0.24 Hz per point. With a relaxation delay of 1 s and 400 scans per increment, data collection required 22 h. Spectra (d) and (h) were obtained with 1600 scans per increment. In order to avoid the possibility of a folded signal, spectra were first recorded with an increased spectral width in f_1 of up to 400 ppm.

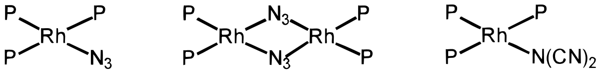
The chemical shift (0.0 ppm) of nitromethane at 300 K (CD_2Cl_2 external lock) corresponds to a frequency of 40.560 304 MHz. The protons of TMS in CD_2Cl_2 at 300 K in the same field (9.395 T) resonate at 400.130 020 MHz. The ^{31}P spectra were calibrated against 85% H_3PO_4 (external standard) at a frequency of 161.975 493 MHz.

Computer simulation

The ^{15}N–^{31}P spectra of the two possible isomeric forms of **2**, i.e. $[(Ph_3P)_2Rh\{N(N_2)\}_2Rh(PPh_3)_2]$ (**A**) and $[(Ph_3P)_2Rh(NNN)_2Rh(PPh_3)_2]$ (**B**), were simulated using the program NMRSIM.[13] Values of coupling constants used in the simulation were $^{1}J(^{103}\text{Rh},^{31}\text{P}) = 190$ Hz, $^{1}J(^{103}\text{Rh},^{15}\text{N}) = 10.5$. Hz, $^{2}J(^{31}\text{P},^{15}\text{N}_{trans}) = 38$ Hz, $^{2}J(^{31}\text{P},^{15}\text{N}_{cis} = 4$ Hz and $^{2}J(^{31}\text{P},^{31}\text{P}) = 100$ Hz. With $^{2}J(^{31}\text{P},^{31}\text{P})$ less than 100 Hz second-order distortions become evident in the f_2 (^{31}P) projection of the simulated spectra in the form of splitting of the lines of the doublet and the appearance of satellite lines at a distance of $^{2}J(^{31}\text{P},^{31}\text{P})$ from the principal lines, features which are not observed in the actual $^{31}\text{P}\{^{1}\text{H}\}$ spectrum recorded from **2**.

RESULTS AND DISCUSSION

The complexes shown in Fig. 1, all containing ^{15}N at natural abundance, were chosen for study because of their relatively high solubility and stability in dichloromethane and the absence of exchange and other processes that lead to the broadening of spectral lines. Complexes **1** and **3** have much higher solubility (in excess of 0.3 M) than **2**, but when **2** is prepared *in situ* from **1** in the presence of air (in order to oxidize PPh_3, which is released by the reaction and inhibits the conversion of **1** to **2**) concentrations of up to *ca.* 0.05 M can be attained. In solution **1** was stabilized against conversion to **2** by a twofold excess of triphenylphosphine.



1 2 3

Figure 1. Complexes used for ^{15}N NMR measurements. P = triphenylphosphine.

A signal from the α-nitrogen of complex **1** [$\delta = -320.8$ ppm, $^{1}J(^{103}\text{Rh},^{15}\text{N}) = 13.9$ Hz] is shown in the spectrum in Fig. 2(a), obtained by detection of the *trans* phosphorus (which resonates as a doublet of triplets), and in the spectrum in Fig. 2(b) obtained by detection of the two equivalent *cis* phosphorus atoms (which give a doublet of doublets). The relative positions of the cross peaks indicate that $J(^{103}\text{Rh},^{31}\text{P})$ and $J(^{103}\text{Rh},^{15}\text{N})$ have the same sign. An accurate value of $^{2}J(^{31}\text{P},^{15}\text{N}_{trans})$ of 29.4 Hz was measured from the f_2 projection of the spectrum in Fig. 2(c), recorded without ^{15}N decoupling (the purpose of which is simply to increase the signal intensity by reducing the multiplicity in the f_2 dimension). The data collection time for Fig. 2(a)–(c) was 22 h each. After optimizing the pulse sequence for the accurate value of $J(^{31}\text{P},^{15}\text{N}_{trans})$, a spectrum was obtained with a similar signal-to-noise ratio to that shown in Fig. 2(a) but with a data collection time of only 4.0 h (72 scans per increment). Efforts to obtain a signal from the β-nitrogen using delay times based on $J = 2$, 3, 4 and 5 Hz proved unsuccessful. Below 2 Hz very little magnetization remains after application of the pulse sequence.

Figure 2(d) shows a spectrum of **1**, detected using the *trans* phosphorus, with an extended period of data collection. The improved signal intensity reveals additional lines not clearly seen in Fig. 2(a) and (d). The f_1 projections of the spectra in Fig. 2(b) and (d) show ^{15}N signals in which ^{103}Rh–^{15}N and ^{31}P–^{31}P coupling are present, the latter being an unwanted outcome of the detection method serving only to reduce the signal intensity. In the spectrum in Fig. 2(b) the effects of doublet splitting by phosphorous are more severe than those of triplet splitting, shown in Fig. 2(d). The outer lines of the doublet of triplets have sufficiently low intensity that they are not readily observed in the spectra in Fig. 2(a) or (h) [obtained from complex **3** ($\delta^{15}\text{N} = -268.5$ ppm, $J(^{103}\text{Rh},^{15}\text{N}) = 19.8$ Hz) by detection of the *trans* phosphorus].

Simulated spectra of $P_2Rh\ ^{15}NRhP_2$ and $P_2Rh\ ^{15}N$ corresponding to the two possible bonding modes of the azide bridges Rh—N—Rh (**A**) and Rh—N—N—N—Rh (**B**) are shown in Fig. 2(e) and (f). The simulated spectrum of **A** [Fig. 2(e)] shows second-order effects in the f_1 (^{15}N) dimension but is almost entirely free of such effects in the f_2 dimension if the P–P coupling is taken to be ≥100 Hz. Allowing for the lower resolution of the measured spectrum of **2** [Fig. 2(g), $\delta\ ^{15}\text{N} = 347.5$ ppm, $J(^{103}\text{Rh},^{15}\text{N}) = 10.5$ Hz], the simulated spectrum [Fig. 2(e) identifies it clearly as arising from **A** and not **B**, confirming the geometry proposed by Busetto *et al.*[14] on the basis of IR data.

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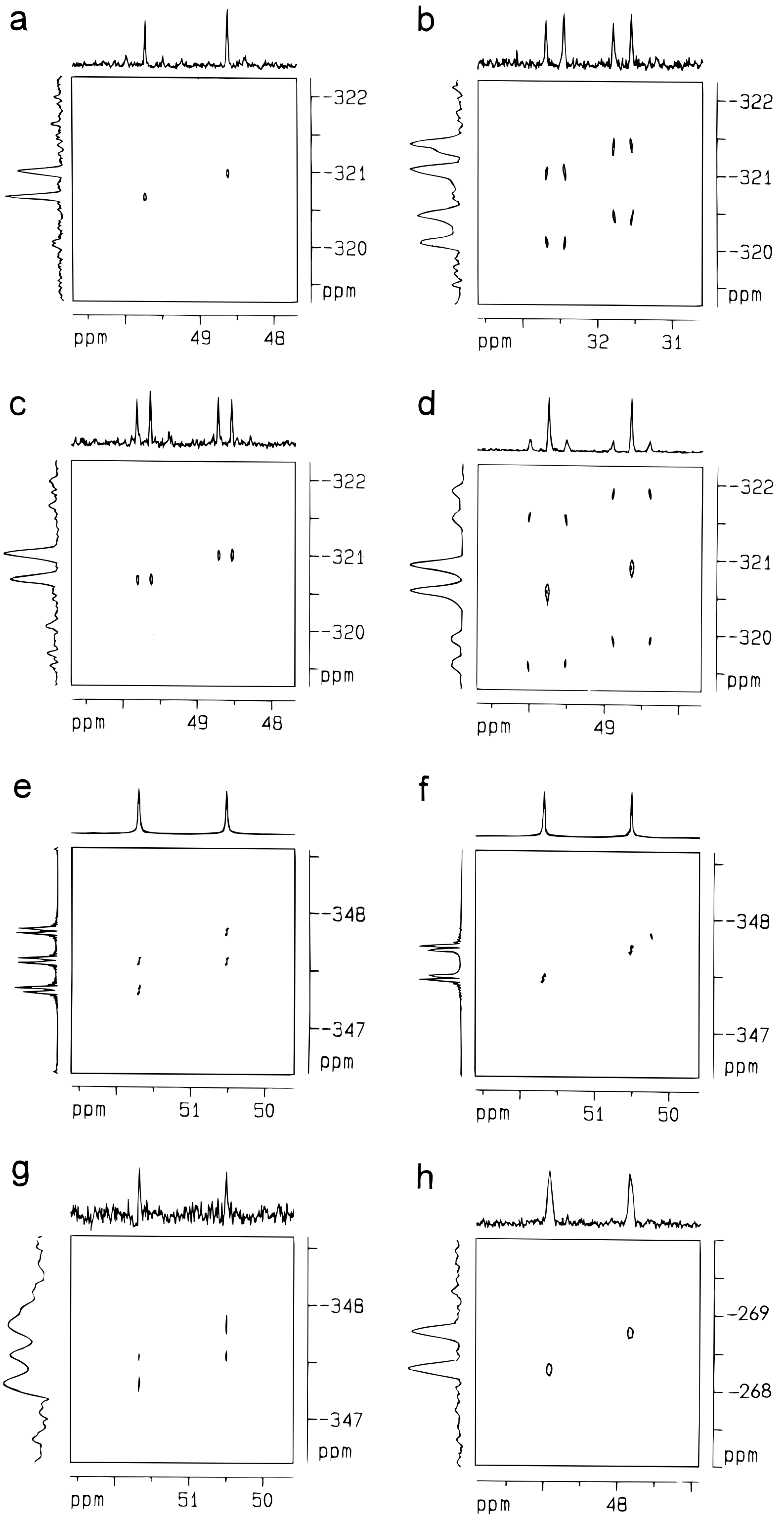

Figure 2. ^{15}N–^{31}P spectra (horizontal axis, ^{31}P; vertical axis, ^{15}N). (a)–(d) Complex **1**; detection of α-nitrogen using *trans* phosphorus (a), *cis* phosphorus, showing Rh–N and P–P coupling (b), *trans* phosphorus without decoupling, showing J(P,N) (c), with improved signal-to-noise ratio, showing P–P and Rh–N coupling (d). Simulated spectra of **2A** (bridging of N_3 by α-nitrogen only) (e) and **2B** (bridging of N_3 by α- and γ-nitrogens) (f); complex **2**, observed spectrum (g); complex **3**, dicyanamide α-nitrogen detected using *trans* phosphorus (h). Data collection times: (a)–(c) 22 h; (d) 4 d; (g) 26 h; (h) 2 d. Using the accurate value of $J(P,N_{trans})$, measured from (c) the spectrum shown in (a) was obtained with similar signal-to-noise ratio in 4 h. Solvent, dichloromethane.

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