

THE  $^{14}\text{N}$  NMR STUDY OF THE N-C CHELATED  
PALLADIUM COMPLEXES OF TERT-BUTYL ISOCYANIDE

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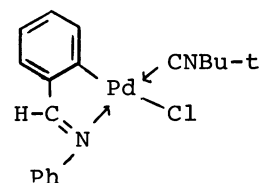
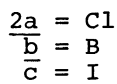
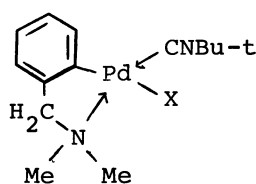
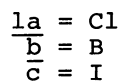
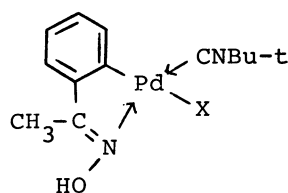
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The  $^{14}\text{N}$  nmr study of palladium complexes of oxime, N,N-dimethylbenzylamine, and Schiff's base having tert-butyl isocyanide as a ligand was examined. The  $^{14}\text{N}$  linewidths of the complexes were narrow, and increased with decrease of electronegativity of halogen. A plot of linewidths against the chemical shifts showed a linear relationship.

The non-zero electric quadrupole moment of  $^{14}\text{N}$  gives rise to broadening of  $^{14}\text{N}$  resonance signals via quadrupolar relaxation. This obscures small chemical shifts and disturbs the appearance of spin-spin coupling between  $^{14}\text{N}$  and other nuclei in the molecule. Long-range  $^1\text{H}$ - $^{14}\text{N}$  spin coupling constants have been observed in the  $^1\text{H}$  nmr spectra of tetraalkylammonium salts <sup>1</sup> and alkyl isocyanides.<sup>2</sup> Measurement of such spin coupling constants has generally been prohibited in the various transition metal complexes of isocyanide,<sup>3</sup> because of introduction of an electric field gradient about the  $^{14}\text{N}$  nucleus arising from the coordination of isocyanide to a metal. Recently, we have observed long-range  $^1\text{H}$ - $^{14}\text{N}$  spin coupling constants in palladium complexes of alkyl isocyanide.<sup>4</sup> This result suggests that the electric field gradient at the  $^{14}\text{N}$  nucleus must be very small, implying that the electron density near nitrogen is axially symmetric. Thus we can expect to see relatively narrow  $^{14}\text{N}$  nmr lines in the aforementioned complexes. There are, to our knowledge, little examples of measurement of  $^{14}\text{N}$  nmr spectra for isocyanide complexes. One example has been made by Becker et al., in which the line width was broad and was between ca 90 and 140 Hz.<sup>5</sup> We wish to report the  $^{14}\text{N}$  nmr study of palladium complexes of isocyanide, in which gives a relatively narrow line width.

The nitrogen resonance shifts for tert-butyl isocyanide ligand of the complexes (1 and 2) to higher field with increasing electronegativity of halogen are compared with the trend <sup>6</sup> that the chemical shifts of free isocyanides, RNC, decreased with increasing of electronegativity of R. The effect of paramagnetic shielding seems to be important for changes in the  $^{14}\text{N}$  chemical shifts in the transition metal complexes of isocyanide.

The chemical shift to lower field in the complexes (1a, 2a and 3) also follows the sequence of N,N-dimethylbenzylamine, Schiff's base and oxime in the bidentate ligand. If this order is related with electronegativity of nitrogen atom of the ortho-metallated ligand, its electronegativity is the similar direction to the aforementioned sequence, and then n-donor ability decreases in the aforementioned sequence. In the infrared spectra the N≡C stretching frequency supported this order: 2216  $\text{cm}^{-1}$  for 1a, 2214  $\text{cm}^{-1}$  for 3 and 2211  $\text{cm}^{-1}$  for 2a.



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The  $^{14}\text{N}$  nmr linewidth ( $\Delta N$ ) is proportional to the electric field gradient (eq) at the  $^{14}\text{N}$  nucleus and to a correlation time ( $\tau$ ). A value of the relaxation time ( $T_2$ ) may be calculated from the measured  $\Delta N$ 's:<sup>8</sup>

$$\frac{1}{T_2} = \frac{3}{8} \left( \frac{e^2 q Q}{h} \right)^2 \tau \quad (1)$$

$$\frac{1}{T_2} = \pi (\Delta N) \quad (2)$$

Table 1 shows the  $^{14}\text{N}$  chemical shift,  $\Delta N$ , and the relaxation time of tert-butyl isocyanide in the complexes.

Table 1 Chemical Shift, Linewidth and Relaxation Time of  $^{14}\text{N}$ , and Line Shape of tert-Butyl Group in the  $^1\text{H}$  NMR Spectra

$^{14}\text{N}$ nmr spectra <sup>a</sup>				$^1\text{H}$ nmr spectra <sup>b</sup>
	Chemical Shift (ppm) <sup>f</sup>	$\Delta N$ (Hz)	$T_2$ (sec)	Line Shape
<u>1a</u>	173.5	3.8	0.08	c
<u>b</u>	174.7	4.9	0.07	d
<u>c</u>	178.0	6.9	0.05	e
<u>2a</u>	170.4	5.1	0.06	d
<u>b</u>	172.4	7.5	0.04	e
<u>c</u>	176.2	12.2	0.03	e
<u>3</u>	171.6	7.2	0.04	d

a Spectra were obtained on a JEOL FX-100 spectrometer (7.14 MHz) at 26° and were measured in  $\text{CDCl}_3$ , using a 10-mm NMR tube.

b from ref. 4. c Sharp triplet. d Broad triplet. e Broad singlet

f Chemical shifts are ppm from external  $^{14}\text{NH}_4\text{NO}_3$  in  $\text{D}_2\text{O}$ . Positive values denote shifts to lower field from the  $^{14}\text{NH}_4^+$ .

The  $^{14}\text{N}$  linewidths of the complexes (1,2 and 3) were larger than that of free tert-butyl isocyanide with  $\Delta N = 1.6$  Hz, but were relatively sharp.<sup>8</sup> This indicates a very low electric field gradient at  $^{14}\text{N}$  nucleus, and has been further proved by observation<sup>4</sup> of long-range  $^1\text{H}$ - $^{14}\text{N}$  coupling constants in the  $^1\text{H}$  nmr spectra of the aforementioned complexes. The linewidths in the complexes (1, 2, and 3) increased with decrease of the electronegativity of the halogen, and did in the following order; oxime, N,N-dimethylbenzyl amine and Schiff's base in the bidentate ligands.

This behavior is related with line shape arising from long-range  $^1\text{H}$ - $^{14}\text{N}$  spin-spin coupling in the  $^1\text{H}$  nmr spectra of isocyanide complexes. Thus decrease of the linewidth causes observation of long-range coupling constant to be more easy.

A plot of linewidths against the chemical shifts is shown in Figure 1: a linear relationship was observed. It may be concluded that the linewidth is predominantly influenced by the paramagnetic term in the nuclear screening parameter for  $^{14}\text{N}$  nucleus. A decrease of the paramagnetic term would then cause the linewidth to be narrow.

The linewidths of 2a were dependent on solvent and showed a linear relationship with volume fraction of two solvents in the  $\text{DMSO-d}_6$ - $\text{CDCl}_3$  system as shown in Figure 2. This effect may result by change of the electric field gradient arising from solvation of  $\text{DMSO-d}_6$  to a palladium atom. The chemical shifts increased with increase of the volume fraction of  $\text{DMSO-d}_6$ . The temperature-variable linewidths were also examined. The raising of temperature caused the linewidth to be narrow: 2.6 Hz for 1a and 5.8 Hz for 1c at  $60^\circ$ . This change is probably related to changes in the correlation time  $\tau$ . This is compared with the fact<sup>4</sup> that the long-range  $^1\text{H}$ - $^{14}\text{N}$  coupling constants have been more clearly observed at higher temperatures in the  $^1\text{H}$  nmr spectra.

Fig. 1 Relation of chemical shifts with linewidths

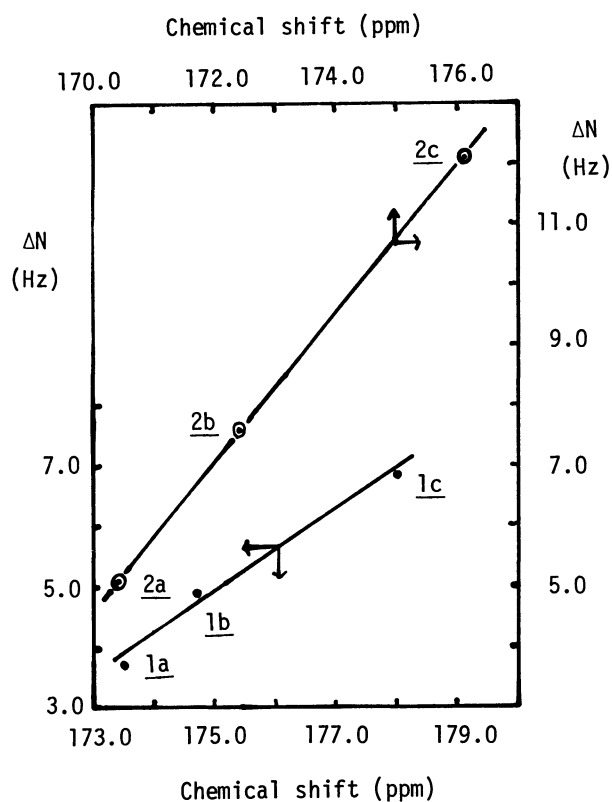
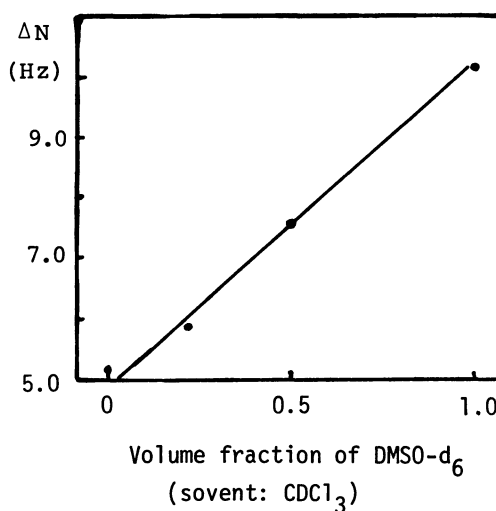


Fig. 2 Solvent effect in  $\text{CDCl}_3$  -  $\text{DMSO-d}_6$  system



The quadrupolar relaxation time calculated from  $\Delta N$  of free tert-butyl isocyanide is about 0.20 sec., being in relative agreement with  $T_2 = 0.18 \text{ sec}^9$  estimated from the  $^1\text{H}$ - $^{14}\text{N}$  coupling constant in the  $^1\text{H}$  nmr spectrum of tert-butyl isocyanide.

On the other hand, the quadrupolar relaxation times of the complexes (1, 2, and 3) fall between 0.08 and 0.03 sec. The difference of about a factor of 2-7 in  $T_2$  in going from free  $(\text{CH}_3)_3\text{CNC}$  to coordinated ones may be due to a change in the electric field gradient near the  $^{14}\text{N}$  nucleus arising from coordination of isocyanide to a metal.

#### References and Notes

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- 8) The chemical shift of free  $(\text{CH}_3)_3\text{CNC}$  in  $\text{CDCl}_3$  appeared at  $\delta$  177.5 ppm, which lies between the chemical shift of the bromide derivative and that of the iodide one in complexes (1 and 2). The similarity of the chemical shifts between free and coordinated isocyanide may cause the linewidth to be narrow.
- 9)  $T_2$  was estimated from an equation due to Pople<sup>10</sup>,  $A = 10\pi T_2 J$ , where A is a dimensionless parameter reflecting the degree of resolution of a proton multiplet (estimated roughly to be 20 for the isocyanide). J is 3.5 Hz.<sup>2a</sup>
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