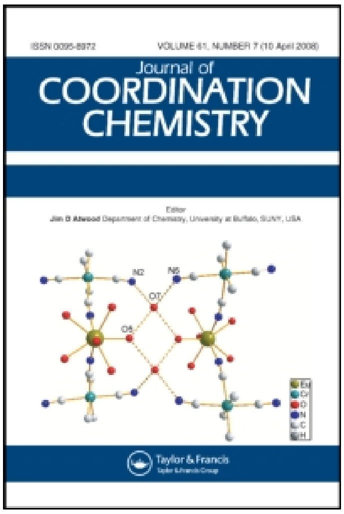

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SHORT COMMUNICATION

The Long-range ^1H-^{14}N Spin Coupling in Transition Metal Complexes of Alkyl Isocyanides[1]

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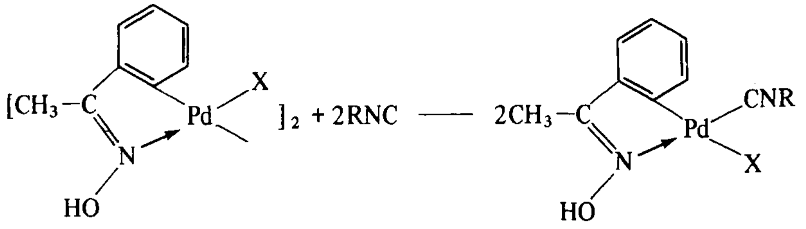
Long-range ^1H–^{14}N spin coupling constants have been observed in the proton nmr spectra of several isocyanides,[2] and a coordinated compound, $(CH_3)_3B \longleftarrow CNC(CH_3)_3$.[3] On the other hand, such spin coupling constants, hitherto, have not been observed in the various transition metal complexes of isocyanides.[4] A possible explanation for this is that formation of a complex generally introduces an electric field gradient about the ^{14}N nucleus and consequently the spin-spin coupling disappears.

In this communication we report the first observation of long-range ^1H–^{14}N spin coupling constants in transition metal complexes of isocyanides.

The proton nmr spectrum of *1*[5], formed by the reaction of acetophenone oxime complex[6] of palladium with isopropyl isocyanide (equation 1), showed a doublet of triplets for the isopropyl methyl groups and a septet of triplets for the methine group (Figure 1).

The $(CH_3)_3C$ resonance of *2a*[5] showed a well-defined triplet separated by 2.1 Hz, whereas that of *2b*[5] or *2c*[5] showed an unresolved apparent triplet and a relatively broad singlet, respectively (Figure 2). Variable temperature experiments were carried out on *2b* and *2c*[7]. The broad line for the t-butyl group sharpened to a triplet with splitting of 2.0 Hz at 39° for *2b* and at 118° for *2c*, suggesting that the line broadening is due to quadrupole relaxation. ^1H–^{14}N decoupling of *2* produced a sharp singlet.

The $(CH_3)_3C$ resonances of the complexes (*3*, *4*, and *5*)[8] were relatively broad singlets. Upon heating the samples, a well-defined triplet (J_{NH} = 2.0 Hz) was observed at 45° for *3a*, at 75° for *3b*, and 120° for *3c*. The broad line of *4* remained unchanged even at 130°. Variable temperature experiments of *5* were unsuccessful due to decomposition of the complex. The ^1H–^{14}N decoupling of these complexes sharpened each broad line.



(1)

1 R = $(CH_3)_2CH$; X = Cl
2a R = $(CH_3)_3C$; X = Cl
b R = $(CH_3)_3C$; X = Br
c R = $(CH_3)_3C$; X = I

^1H–^{14}N decoupling of *1* converted the signals due to the isopropyl methyl and methine groups to a doublet and a septet, respectively. We believe this is the first case of a resolvable ^1H–^{14}N interaction in the transition metal complexes of isocyanides.

In theory a 1:1:1 triplet would be expected for ^1H–^{14}N coupling but in the actual spectra the central signal of the triplets appeared more intense. This is due to partial collapse of the coupling by quadrupole relaxation. A similar behavior has been

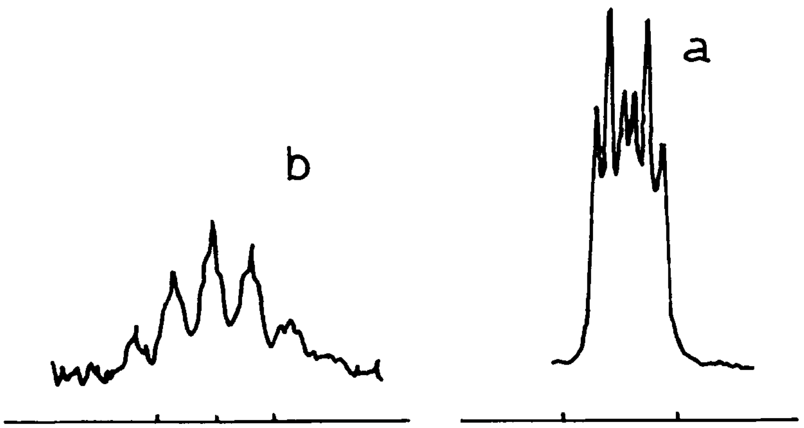


FIGURE 1 The nmr spectra of the compound *1*. (a) The methyl resonance of $(CH_3)_2CHNC$, (b) the methine resonance of $(CH_3)_2CHNC$.

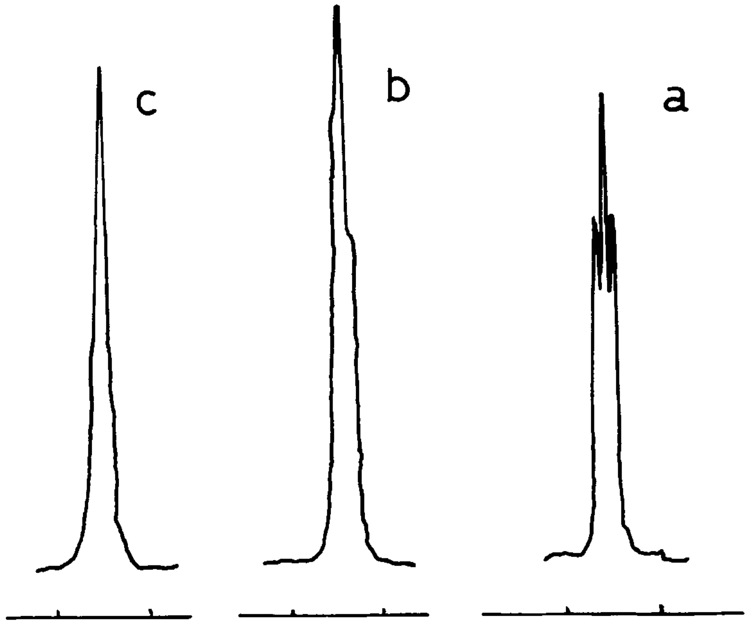
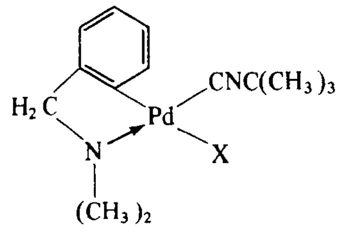
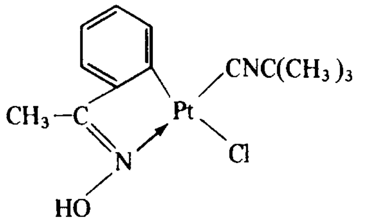


FIGURE 2 The methyl resonance of $(CH_3)_3CNC$ in the compound *2*. (a) *2a*, (b) *2b*, and (c) *2c*.

noted in ^{13}C–^{14}N coupling of several isocyanide complexes, e.g. $Cr(CO)_5(CNC_6H_{11})$.[9]



3a X = Cl. *3b* X = Br. *3c* X = I.



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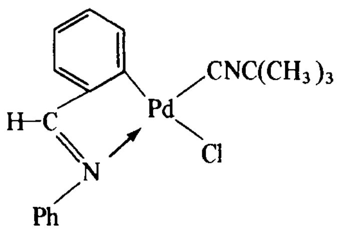

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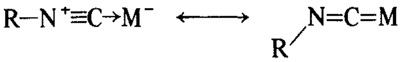
TABLE I
The nmr and ir spectra of the coordinated isocyanide and transition temperature of singlet to triplet

Compd	nmr in $CDCl_3$				ir in $CHCl_3$ ^{g} cm^{-1}	
		Hz				
	ppm	J_{NH}	Width^a	Approx. transition temp., °C	ν_{NC}	Δ
1	1.57^b	2.1			2218	77
	4.21^c	1.0				
2a	1.61^d	2.1			2216	82
b	1.64^e	2.0^h	4.2	39	2212	78
c	1.64^f	2.0^h	3.0	118	2208	74
3a	1.62^e	2.0^h	4.2	45	2211	77
b	1.61^f	2.0^h	3.0	75	2209	75
c	1.60^f	2.0^h	2.4	120	2206	72
4	1.65^f	2.0^h	2.4	>130	2206	72
5	1.65^e		4.2	–	2214	80

[a] half height value.
[b] doublet of triplets. $J_{HH} = 6.0$ Hz.
[c] septet of triplets. $J_{HH} = 6.0$ Hz.
[d] triplet.
[e] broad triplet.
[f] broad singlet.
[g] free $(CH_3)_3CNC$ and $(CH_3)_2CHNC$ exhibit ν_{NC} at 2134 and 2141 cm^{-1} (in $CHCl_3$), respectively. The deviation from these data is less than 0.5 cm^{-1}.
h, J_{NH} in the transition temperature.

In the complexes (*2* and *3*) the approximate transition temperature of a singlet to a triplet due to a t-butyl group increased with decrease of the room temperature line width and with decrease of the electronegativity of the halogen. The transition temperature increased with decrease of the value $\Delta = [\nu_{NC}(\text{coordinated}) - \nu_{NC}(\text{uncoordinated})]$. The electronic structure of an isocyanide can be considered as a hybrid of the two forms A and B;[4]



$$R{-}N^+{\equiv}C{\rightarrow}M^- \longleftrightarrow \underset{R}{\diagup}N{=}C{=}M$$

A positive Δ is attributed to predominant contribution of the polar structure (A). It is concluded that the conditions which lead to an increase in Δ are favourable for observation of ^1H–^{14}N coupling in these complexes of the isocyanides. This is probably not a general result. Further studies are now in progress.

ACKNOWLEDGEMENT

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structure. The studies on these complexes will be reported in the near future.

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