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Study of Organo(2,2′-bipyridine)nickel Complexes. III. NMR Studies on the Interaction of Dialkyl(2,2′-bipyridine)nickel with Solvents and Olefins[1]

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The ^{1}H-NMR spectra of NiR_2(bpy)(bpy=2,2′-bipyridine; R=CH_3, C_2H_5, and C_3H_7) and $Ni(C_2H_5)_2$(bpy)-olefin systems (olefin=acrylonitrile and acrylaldehyde) have been studied in a temperature range from −70 °C to 80 °C. The temperature dependence of the chemical shifts of ethyl and 2,2′-bipyridine protons of $Ni(C_2H_5)_2$(bpy) in non-aromatic solvents (acetonitrile, *N*,*N*-dimethylformamide, acetone and tetrahydrofuran) is analyzed on the basis of the formation of 1: 1 solvent-solute complex. The formation constant of the 1: 1 comples, K_1, and the thermodynamic parameters $\Delta F_1°$, $\Delta H_1°$, and $\Delta S_1°$ are given. The NMR spectra of NiR_2(bpy) in aromatic solvents show the aromatic induced solvent shifts, and the chemical shifts of CH_2 and CH_3 of $Ni(C_2H_5)_2$(bpy) coincide at 76 °C in benzene to give a sharp singlet peak. The ^{13}C-NMR spectrum of $Ni(C_2H_5)_2$(bpy) in benzene shows a triplet at 10.63 ppm (CH_2, $J(^{13}C\text{–}H)=132$ Hz) and a quartet at 15.97 ppm (CH_3, $J(^{13}C\text{–}H)=128$ Hz). The formation constant of $Ni(C_2H_5)_2$(bpy)(olefin), K_2, and the thermodynamic parameters, $\Delta F_2°$, $\Delta H_2°$, and $\Delta S_2°$ have been obtained from the temperature dependence of the NMR spectra of the $Ni(C_2H_5)$(bpy)-olefin systems. The values of the chemical shift differences between CH_2 and CH_3 ($\Delta=\delta_{CH_2}-\delta_{CH_3}$) for $Ni(C_2H_5)_2$(bpy), $Ni(C_2H_5)_2$(bpy)(acrylaldehyde), and $Ni(C_2H_5)_2$(bpy)(acrylonitrile) are −0.30, 0.94 and 0.83, respectively. The increase of the values of Δ by the coordination of the electronegative olefins with nickel is regarded as indicating the increase of the electronegativity of nickel due to the back-donation from nickel to the olefin.

Variable temperature NMR study provides a powerful means for clarifying the behavior of various important compounds in solution and extensive NMR studies have been made on the behavior of non-transition metal alkyls.[2] Alkyltransition metal compounds, on the other hand, have received much less attention, and very few systematic NMR studies have been made[3] despite their significance as models for active species in various catalytic reactions such as olefin hydrogenation, isomerization, hydroformylation and polymerization.[4,5] This is mainly due to the lack of suitable diamagnetic alkyltransition metal compounds which are stable enough to allow the NMR study. Dialkyl(2,2′-bipyridine)nickel(II)[6] is suitable for detailed NMR study because of the following advantages. (1) It is thermally stable in the range from −80 to 80 °C, having sufficient solubilities in various organic solvents. (2) A series of alkyl homologs can be readily prepared which allow the study of the effect of chemical environment on each nickel alkyl. (3) It interacts with olefins to form olefin-coordinated complexes, and the effect of olefin coordination on the nature of the alkylnickel complex can be investigated. The study of the interaction of an alkyltransition metal complex with olefins is particularly important in understanding the mechanism of activation of transition metal-to-carbon bond by coordination of olefin since it constitutes a key elementary step in catalytic reactions involving olefins.[5]

Experimental

NiR_2(bpy) was prepared as reported in previous papers.[6] Deuterated solvents were used as purchased from Merck and Co., Inc. Acrylonitrile and acrylaldehyde were dehydrated and purified by distillation. The solvent, olefin, and tetramethylsilane were added to an NMR tube containing NiR_2(bpy) by a trap-to-trap distillation in a vacuum, and the NMR tube was sealed. The ^{1}H-NMR spectra were obtained with a Japan Electron Optics Laboratory PS-100 spectrometer or a Varian HR-220 spectrometer. The ^{13}C-NMR spectra were obtained with the Japan Electron Optics Laboratory PS-100 spectrometer in the pulsed Fourier transform mode at 25.15 MHz. Chemical shifts are referred to internal TMS both in ^{1}H-NMR and ^{13}C-NMR.

Results and Discussion

NMR Spectra of NiR_2(bpy) in Various Solvents. NMR Spectra of $Ni(C_2H_5)_2$(bpy) 1 at Various Temperatures: The NMR spectrum of $Ni(C_2H_5)_2$(bpy) **1** shows a triplet (at lower field) and a quartet (at higher field) of an

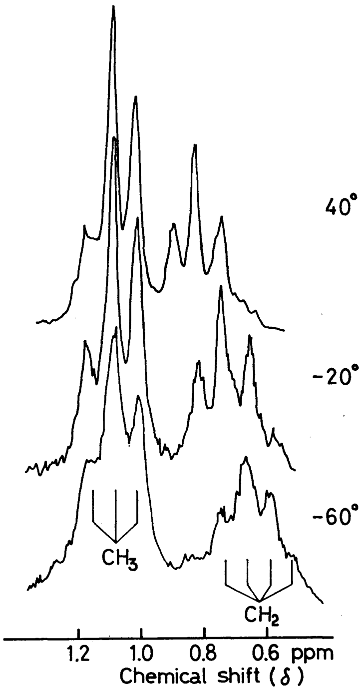


Fig. 1. 100 MHz ^{1}H-NMR spectra of C_2H_5 of $Ni(C_2H_5)_2$(bpy) in acetone-d_6 at various temperatures.

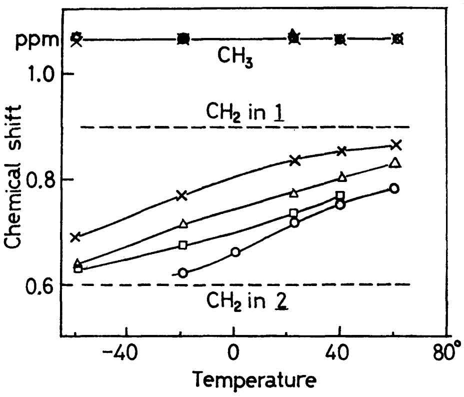


Fig. 2. Temperature dependence of the chemical shifts of CH_2 and CH_3 signals in tetrahydrofuran-d_8 (×), in acetone-d_6(△), in dimethylformamide-d_7(□), and in acetonitrile-d_3(○). Broken lines show the chemical shifts of CH_2 in **1** and **2** (see the text).

area ratio of 3: 2, which were assigned to methyl and methylene protons.[6b)]

When a non-aromatic solvent is employed, only the chemical shifts of the methylene protons of the ethyl group varies with temperature in the ethyl region, the chemical shift of methyl protons being essentially temperature independent (Fig. 1). The change of the chemical shifts of CH_3 and CH_2 signals with temperature is shown in Fig. 2.

It is seen that the chemical shift of CH_2 approaches limiting values on cooling and heating. The temperature dependence of the chemical shift of the methylene protons may be accounted for on the basis of the formation of a 1 : 1 solvent-solute complex (Eq. 1).[6c,7)]

$$\underset{\mathbf{1}}{\mathrm{Ni(C_2H_5)_2(bpy)}} + \text{solvent} \overset{K_1}{\rightleftarrows} \underset{\mathbf{2}}{\mathrm{Ni(C_2H_5)_2(bpy)(solvent)}} \qquad (1)$$

$$K_1 = \frac{[\mathbf{2}]}{[\mathbf{1}][\text{solvent}]} \qquad (2)$$

The coordination of solvent with the four coordinate nickel to form a five coordinate nickel compound **2** will cause a change of magnetic character of nickel, which affects the chemical shift of the CH_2 protons. Since the chemical shift of the CH_2 protons in three different solvents (acetonitrile, *N,N*-dimethylformamide, and acetone) approaches the same value (0.60 ppm from TMS) on cooling, we assume that the chemical shift of the CH_2 protons in the solvated species is virtually independent of the solvent coordinated. On heating, **1** becomes predominant and the chemical shift of CH_2 protons approaches 0.90 ppm.

When one assumes a rapid exchange between **1** and **2** in solutions, the ratio [**2**]/[**1**] can be calculated from the chemical shift of $CH_2(\delta)$, which is a weighted mean of the chemical shifts of CH_2 of **1** and **2**, as $(0.90-\delta)/(\delta-0.60)$.

TABLE 1. VALUES OF $[\mathrm{Ni(C_2H_5)_2(bpy)(solvent)}]/[\mathrm{Ni(C_2H_5)_2(bpy)}]$

(°C)	Acetonitrile	*N,N*-Dimethylformamide	Acetone	Tetrahydrofuran
−60				3.0
−20		3.0	1.60	0.82
0	4.0			
22	1.5	1.2	0.77	0.28
40	1.0	0.82	0.50	0.20
60	0.67			0.14

Table 1 gives the values of [**2**]/[**1**] at various temperatures.

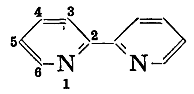
The value of [**2**]/[**1**] at certain temperatures decreases in the order acetonitrile>*N,N*-dimethylformamide> acetone>tetrahydrofuran. The order agrees with the decreasing order of coordination ability of solvent to **1** estimated with visible spectra.[6c)]

The plot of the value of [**2**]/[**1**] against $1/T$ gives a straight line. The equilibrium constant K_1 for the solvation of **1** and thermodynamic data are summarized in Table 2. The reproducibility of the curves in Fig. 2 is good.

Table 2 indicates that the enthalpy changes favor the formation of the solvent coordinated species but are compensated by the large negative entropy changes.

The signals of 2,2′-bipyridine protons of diethyl(2,2′-bipyridine)nickel appear in the range 7.5—9.0 ppm in the non-aromatic solvents. On cooling and heating diethyl(2,2′-bipyridine)nickel in the solutions, the chemical shift of each 2,2′-bipyridine proton also approaches a limiting value as in the case of the chemical shift of the methylene protons.

The chemical shifts of the 2,2′-bipyridine protons of **1** and **2**, as numbered below, were estimated from the limiting values and are listed in Table 3.



The ethyl signals of the ethyl nickel complex in aromatic solvents (benzene and toluene) show a large downfield shift presumably due to the aromatic induced solvent shift (AISS).[7,9)] In contrast to the temperature

TABLE 2. EQUILIBRIUM CONSTANT K_1 AT 22°C AND THERMODYNAMIC DATA FOR THE COORDINATION OF SOLVENT WITH $\mathrm{Ni(C_2H_5)_2(bpy)}$

Solvent[a)]	K_1[b)] (l/mol)	$\Delta F_1°$ (kcal/mol)	$\Delta H_1°$ (kcal/mol)	$\Delta S_1°$ (e.u.)
Acetonitrile	8.0×10^{-2}	1.5	−4.3	−20
N,N-Dimethylformamide	9.1×10^{-2}	1.4	−3.7	−17
Acetone	5.9×10^{-2}	1.7	−3.1	−16
Tetrahydrofuran	2.3×10^{-2}	2.2	−3.7	−20

a) Protons of solvents are deuterated. b) The value of [**2**]/[**1**] is divided by the molarity of the neat solvent.

TABLE 3. CHEMICAL SHIFTS OF 2,2′-BIPYRIDINE PROTONS OF **1** AND **2** IN NON-AROMATIC SOLVENTS (ACETONITRILE, *N,N*-DIMETHYLFORMAMIDE, ACETONE, AND TETRAHYDROFURAN)[a]

Compound	3-H and 4-H[b]	5-H	6-H
1	8.0±0.1m	7.5t	9.0d
2	8.4±0.1m	7.8t	8.9d

a) In ppm from TMS (downfield positive). The assignment of the 2,2′-bipyridine protons in 1,2-dimethoxyethane has been given elsewhere;[8] d: double, t: triplet, m: multiplet.

b) Signals of 3-H and 4-H were not separated from each other at 100 MHz.

independence of the chemical shift of CH_3 protons in non-aromatic solvents, both chemical shifts of CH_2 and CH_3 protons are temperature dependent in aromatic solvents. The chemical shifts of CH_2 and CH_3 in toluene at various temperatures are given in Table 4.

TABLE 4. CHEMICAL SHIFT OF CH_2 AND CH_3 SIGNALS IN TOLUENE[a]

Temp. (°C)	CH_2	CH_3
−60	1.66	1.94
−20	1.60	1.87
20	1.57	1.65
40	1.60[b]	
60	1.52[b]	

a) In ppm from TMS (downfield positive).

b) CH_2 and CH_3 signals overlap with each other.

In benzene-d_6 the CH_2 and CH_3 signals are resolved at 20 °C or below (Fig. 3), although at 40 °C or above they overlap each other even at 220 MHz. At 40 °C and 59 °C the ^1H-NMR spectra of the ethyl region show an A_2B_3 pattern where the chemical shift difference between A and B is comparable to the coupling constant between A and B (Figs. 3b, 3c).[10,11] At 76 °C in benzene the chemical shifts of CH_2 and CH_3 coincide to give a sharp singlet peak (Fig. 3d). Further increase in the temperature led to the decomposition of the ethyl nickel complex.

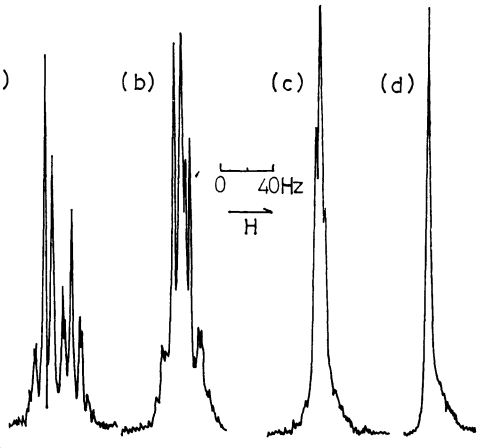


Fig. 3. NMR spectra of the ethyl protons of Ni(C_2H_5)$_2$(bpy) in benzene-d_6 at 220 MHz. (a) 20 °C, (b) 40 °C, (c) 59 °C, and (d) 76 °C.

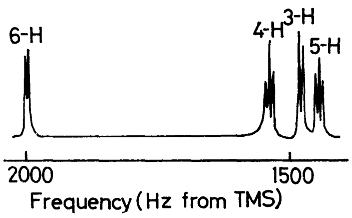


Fig. 4. NMR spectrum of bipyridine protons of Ni(C_2H_5)$_2$(bpy) in benzene-d_6 at 220 MHz (at 20 °C).

Signals of 3-H and 4-H of 2,2′-bipyridine, which overlap each other in the non-aromatic solvent, separate in the aromatic solvents (Fig. 4). The enhancements of higher field portions of the 6-H doublet and 4-H triplet and lower field portion of the 3-H doublet and 5-H triplet are consistent with the coupling between 5-H and 6-H, 3-H and 4-H, and 4-H and 5-H.

The ^1H-NMR spectrum of Ni(C_2H_5)$_2$(bpy) in pyridine or styrene is essentially the same as that in benzene or toluene, suggesting a coordination of pyridine and styrene with nickel through the aromatic π-ring. However, in contrast to the considerable stability of **1** even in boiling benzene,[6a] standing of the pyridine or styrene solution at room temperature for some time (30 min or more) caused a scission of Ni–C_2H_5 bonds to form butane.[6c]

TABLE 5. ^{13}C-NMR SPECTRUM OF Ni(C_2H_5)$_2$(bpy) IN BENZENE AT 68 °C (25.15 MHz)

Chemical shift (ppm from TMS)	$J(^{13}C\text{-}H)$ (Hz)	Assignment
10.63	132	CH_2
15.97	128	CH_3
120.3∼147.6		2,2′-bipyridine carbons

Although CH_2 and CH_3 signals of **1** in aromatic solvents overlap each other in ^1H-NMR at 40 °C or above, the ^{13}C-NMR at 68 °C in benzene gave well separated CH_2 and CH_3 signals at 10.63 and 15.97 ppm from TMS, respectively. The good separation of CH_2 and CH_3 signals in ^{13}C-NMR is considered to be due to a difference of anisotropic character between CH_2 and CH_3 positions to which the ^{13}C-NMR is more sensitive than ^1H-NMR.[12] The ^{13}C-NMR spectroscopic data are listed in Table 5. The magnitude of $J(^{13}C\text{-}H)$ indicates that the electronic configuration of carbon is essentially sp^3 both in CH_2 and CH_3 groups of the ethyl nickel complex suggesting a covalent bond between Ni and C_2H_5 rather than an ionic bond.

Ni(CH_3)$_2$(bpy) and Ni(C_3H_7)$_2$(bpy). The ^1H-NMR spectrum of Ni(CH_3)$_2$(bpy) in non-aromatic solvent at 100 MHz showed a singlet at δ 0.10 ppm for CH_3, a multiplet at 8.18 ppm for 3-H and 4-H protons of 2,2′-bipyridine, a triplet at 7.62 ppm for 5-H, and a doublet at 8.96 ppm for 6-H. The ^1H-NMR spectrum of Ni(CH_3)$_2$(bpy) in aromatic solvents showed the aromatic induced solvent shifts. The NMR spectroscopic data for Ni(CH_3)$_2$(bpy) both in non-aromatic and aromatic solvents are listed in Table 6 together with those for Ni(C_3H_7)$_2$(bpy).

TABLE 6. ^{1}H-NMR SPECTRA OF $Ni(CH_3)_2(bpy)$ AND $Ni(C_3H_7)_2(bpy)$ AT 24 °C (100 MHz, ppm from TMS)[a]

$Ni(CH_3)_2(bpy)$	CH_3	2,2′-bipyridine			
		3-H	4-H	5-H	6-H
In acetone-d_6	−0.10 s	8.18m[b]		7.62t	8.96 d
In toluene-d_8	0.74 s	6.81 d	8.52t	6.60t	9.00 d

$Ni(C_3H_7)_2(bpy)$	α-CH_2	CH_3	β-CH_2	2,2′-bipyridine			
				3-H	4-H	5-H	6-H
In N,N-dimethylformamide-d_7	0.8t	1.05t	1.52m	8.27m[b]		7.71t	8.99 d
In benzene-d_6	1.7∼1.8m[b]		2.23m	6.78 d	7.07t	6.65t	9.16 d

a) s=singlet, d=doublet, t=triplet, m=multiplet. b) Unresolved.

^{1}H-NMR spectrum of $Ni(C_3H_7)_2(bpy)$ showed signals of β-methylene at the lowest field amongst the signals of the propyl group similar to the NMR spectrum of $Al(C_3H_7)_3$. No signals assignable to $Ni(i\text{-}C_3H_7)_2(bpy)$, which might be formed through a thermal isomerization of $Ni(C_3H_7)_2(bpy)$, were observed in the NMR spectrum. Chemical shift of each signal of $Ni(CH_3)_2(bpy)$ and $Ni(C_3H_7)_2(bpy)$ showed temperature dependence which may be accounted for on the basis of the solvation of the methyl and propyl nickel complexes as in the case of the ethyl nickel complex.

$Ni(C_2H_5)_2(bpy)$–Olefin System. On addition of olefins (acrylonitrile and acrylaldehyde) to the deep green tetrahydrofuran solution of $Ni(C_2H_5)_2(bpy)$ at −70 °C the color of the solution turned deep red, the NMR spectrum of the **1**–olefin system showing the CH_3 signals of C_2H_5 at higher field than CH_2 signals in contrast to the NMR spectrum of **1** in tetrahydrofuran without olefin. On warming the solution, the coloration turned from deep red to deep green *via* black, the chemical shift of CH_2 and CH_3 signals changing with the coloration (Figs. 5 and 6).

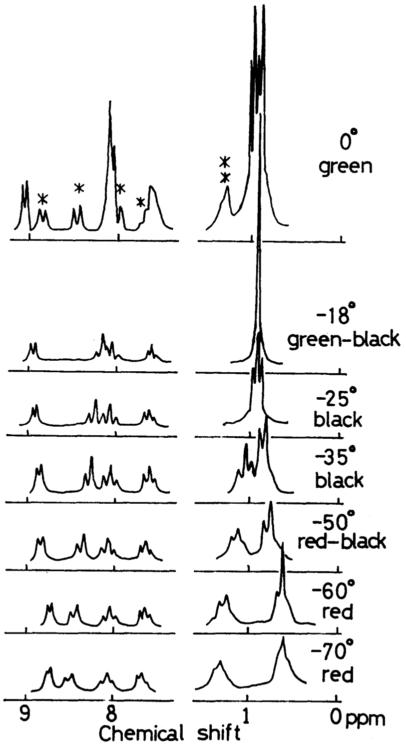


Fig. 5. Temperature dependence of the NMR spectrum of the **1**–acrylonitrile system in tetrahydrofuran-d_8. [acrylonitrile]=1.4 mol/l. [**1**]+[**3**]=0.2 mol/l. At 0 °C the partial scission of the Ni–C_2H_5 bonds takes place to give Ni(bpy)(acrylonitrile) and C_4H_{10}. The signals with * and ‡ show bpy signals of Ni(bpy)(acrylonitrile) and CH_2 signals of butane evolved, respectively.

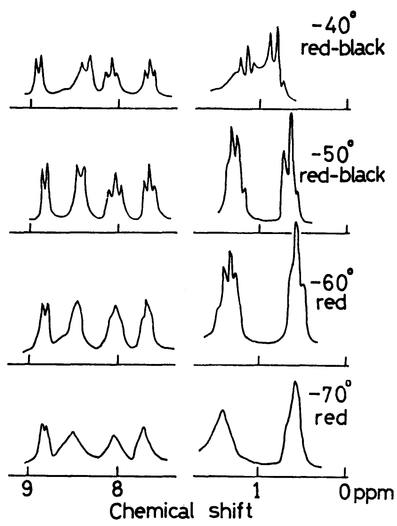


Fig. 6. Temperature dependence of the NMR spectrum of the **1**–acrylaldehyde system in tetrahydrofuran-d_8. [acrylaldehyde]=2.3 mol/l. [**1**]+[**3**]=0.2 mol/l.

Dialkyl(2,2′-bipyridine)nickel (deep green) forms complexes of the type $NiR_2(bpy)(olefin)$ (deep red) with acrylonitrile and acrylaldehyde at low temperatures.[1,6c] By a visual method based on the change of the color from deep red to deep green on warming the $NiR_2(bpy)$–olefin system, the equilibrium constant expressed by Eq. (4) was estimated.[1]

$$\underset{\mathbf{1}}{NiR_2(bpy)} + olefin \rightleftharpoons \underset{\mathbf{3}}{NiR_2(bpy)(olefin)} \tag{3}$$

$$K_2 = \frac{[NiR_2(bpy)(olefin)]}{[NiR_2(bpy)][olefin]} \tag{4}$$

From the change of the NMR spectrum of the **1**–olefin system at various temperatures we can estimate the equilibrium constants more accurately than with the visual method. Corresponding to the color change, the NMR spectrum of the **1**–olefin system varies with temperature and the variation of the chemical shifts can

TABLE 7. VALUES OF [**3**]/[**1**] AND K_2 CALCULATED FROM THE DATA IN FIG. 7[a)]

[Acryonitrile]=6.5 mol/l				[Acrylonitrile]=1.4 mol/l			
Temp. (°C)	(ppm)	[**3**]/[**1**]	K_2 (l/mol)	Temp. (°C)	(ppm)	[**3**]/[**1**]	K_2 (l/mol)
−50	0.51	14	2.2	−70	0.52	11	7.9
−40	0.53	9.0	1.4	−60	0.54	7.6	5.4
−30	0.57	5.0	0.77	−50	0.60	3.6	2.6
−20	0.63	2.8	0.43	−42	0.72	1.4	1.0
−10	0.69	1.7	0.26	−35	0.77	1.0	0.72
				−18	0.50	0.4	0.29

a) Solvent=tetrahydrofuran-d_8

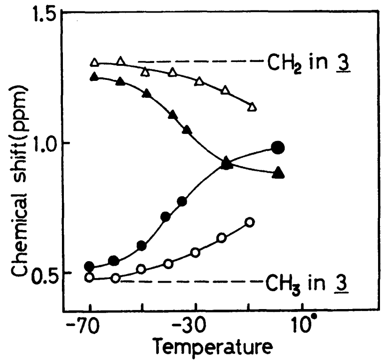


Fig. 7. Chemical shifts of CH_2 and CH_3 protons of the **1**–acrylonitrile systems in tetrahydrofuran-d_8 at various temperatures. ○CH_3 and △CH_2 for [acrylonitrile]=6.5 mol/l, ●CH_3 and ▲CH_2 for [acrylonitrile]=1.4 mol/l.

be explained in terms of a 1 : 1 adduct (**3**) formation and its rapid exchange with the uncoordinated ethylnickel complex **1**. At lower temperatures the olefin-coordinated complex **3** is predominant and the chemical shifts of the CH_3 and CH_2 protons approach the limiting values 0.47 and 1.3 ppm, respectively, corresponding to $Ni(C_2H_5)_2(bpy)(acrylonitrile)$ as shown in Fig. 7. On warming the solution, the CH_3 signals shift to lower field and the CH_2 signals to higher field. The extent of the shifts depends on the concentration of acrylonitrile in the solution. In a system containing a lower concentration of acrylonitrile (1.4 mol/l in Fig. 7), the crossing of two signals was observed and the CH_3 and CH_2 protons appeared as a sharp singlet at −18 °C with identical chemical shift values for the CH_3 and CH_2 protons. The CH_3 and CH_2 signals separate again with the CH_3 signals at a lower field than the CH_2 signals by raising the temperature to 0 °C. Further increase of the temperature caused the decomposition of the ethylnickel complex. The decomposition set in at a lower temperature when a higher concentration of acrylonitrile was employed.

From the temperature dependence of the chemical shifts of CH_2 and CH_3 one can calculate the ratio of the concentration of **3** to that of **1**. The ratio [**3**]/[**1**] is calculated from the chemical shift of $CH_3(\delta_{CH_3})$ of the **1**–olefin system at the temperature as

$$\frac{[\mathbf{3}]}{[\mathbf{1}]} = \frac{\delta_{CH_3}(\text{in } \mathbf{1})-\delta_{CH_3}}{\delta_{CH_3}-\delta_{CH_3}(\text{in } \mathbf{3})} = \frac{1.07-\delta_{CH_3}}{\delta_{CH_3}-0.47} \quad (5)$$

In the equation 1.07 and 0.47 are the limiting chemical shifts of the CH_3 protons in the uncoordinated and fully coordinated ethylnickel complexes **1** and **3**.

The values of [**3**]/[**1**] for **1**–acrylonitrile system at various temperatures as well as the equilibrium constant expressed by Eq. (4) are given in Table 7.

The plot of log K_2 against $1/T$ gives a straight line (Fig. 8).

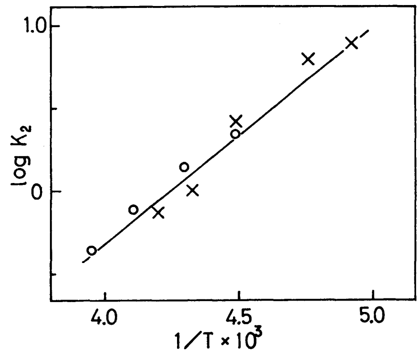


Fig. 8. log K_2 *vs.* $1/T$ for the coordination of acrylonitrile with **1**. ○ for [acrylonitrile]=6.5 mol/l, ● for [acrylonitrile]=1.4 mol/l.

The temperature dependence of the 2,2′-bipyridine signals of the **1**–acrylonitrile system is also accounted for by assuming the equilibrium expressed by Eq. (3).

The 2,2′-bipyridine signals observed at −70 °C can be assigned to those of **3**. On warming, the chemical shift of each 2,2′-bipyridine signal approaches that of **1** (Table 3).

A similar temperature variation of ^1H-NMR spectrum to that for the **1**–acrylonitrile system was observed for **1**–acrylaldehyde system. The stability constants of the complexes of the type $Ni(C_2H_5)_2(bpy)(olefin)$ and the thermodynamic data for the coordination of olefin with **1** are given in Table 8.

TABLE 8. STABILITY CONSTANT OF $Ni(C_2H_5)_2$-(bpy)(olefin) K_2 AT −50 °C AND THERMODYNAMIC DATA

Olefin	log K_2	$\Delta F_2°$ kcal/mol	$\Delta H_2°$ kcal/mol	$\Delta S_2°$ e.u.
Acrylonitrile	0.38	−0.4	−6.4	−27
Acrylaldehyde	0.080	−0.1	−7.4	−31

The enthalpy changes for the coordination of olefin are fairly large as compared with those of solvents (*cf.* Table 2).

In the case of **1**–acrylaldehyde system both ethyl and

2,2′-bipyridine signals showed a broadening at low temperatures (−50— −70 °C).

Since the signals of solvent impurities (tetrahydrofuran-d_7's) and TMS did not show any broadening at low temperatures, the broadening of the ethyl and 2,2′-bipyridine signals is not considered to be due to the increase of viscosity of the solution but to the decrease of the exchange rate between **1** and **3** at the low temperatures. At −40 °C or above, both the ethyl and 2,2′-bipyridine signals are sharp and the half widths of the signals are constant.

Approximate rates of the coordination and dissociation of olefin and, consequently, the rate constants k_1 and k_{-1} in the following equation have been calculated from the half widths of C_2H_5 and 2,2′-bipyridine signals.[13)]

$$\underset{\mathbf{1}}{Ni(C_2H_5)_2(bpy)} + \text{acrylaldehyde} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\mathbf{3}}{Ni(C_2H_5)_2(bpy)(\text{acrylaldehyde})} \qquad (6)$$

The values of k_1 and k_{-1} are *ca.* 1×10^3 l/mol·s and 1×10^3 s^{-1} at −60 °C respectively.

Electronegativities of Nickel in 1 and 3. As for the NMR spectrum of an ethyl group bonded with various atoms Narasimhan and Rogers[14)] proposed the straight-line correlation

$$\chi = 0.62\Delta + 2.07 \qquad (7)$$

where χ is the electronegativity of M for M–C_2H_5 compounds and Δ is the chemical shift difference between the CH_2 and CH_3 singals ($\Delta=\delta_{CH_2}-\delta_{CH_3}$).

When Eq. (7) is applied to the present nickel complexes, the electronegativities of the nickel in **1**, $Ni(C_2H_5)_2$(bpy)(acrylonitrile), $Ni(C_2H_5)_2$(bpy)(acrylaldehyde) are 1.89, 2.58, and 2.65, respectively (Table 9).

Table 9. Electronegativity of nickel in complexes calculated according to Eq. (7)

Complex	Δ	χ
$Ni(C_2H_5)_2$(bpy)	−0.30	1.89
$Ni(C_2H_5)_2$(bpy)(acrylonitrile)	0.83	2.58
$Ni(C_2H_5)_2$(bpy)(acrylaldehyde)	0.94	2.65

The electronegativity of nickel in **1** is close to Pauling's electronegativity of nickel (χ=1.7).[6b)] When an olefin is coordinated with **1**, the electronegativity of nickel markedly increases almost to the value of carbon (χ= 2.5—2.6); the chemical shifts of CH_3 and CH_2 of **3** are close to those of butane. The increase of the electronegativity of nickel by the coordination of olefin can be interpreted as due to the back-donation of electron from nickel to the olefin. The result is consistent with the lowering of the highest occupied energy level of nickel by coordination of olefin with **1** as observed in the strong blue shift of a charge-transfer band (Ni→bpy).[1,6c)]

The coordination of olefin with **1** makes a homolytic scission of Ni–C_2H_5 bond much easier by a factor of 10^{11} at room temperature than without the coordination of olefin.[15)] Since the nickel–carbon bond of **1** is considered to be polarized as $Ni^{\delta+}$—$C^{\delta-}$, the homolytic scission of the nickel-carbon bond in **1**, leading to liberation of an electrically neutral molecule butane, seems to require the migration of electron from carbon to nickel.[16)] The scission of the Ni–C bond in **3**, however, may require only a minor migration of electron because of minor polarization of the Ni–C bond as judged from the small difference in electronegativity between Ni and C in **3**. This may account for the easier scission of Ni–C bond by the coordination of olefin.

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15) The first-order rate constant k for the thermolysis of **1** obtained at high temperature (97—113 °C), $\mathbf{1}\xrightarrow{k}$Ni(bpy)+$C_4H_{10}$, is extrapolated to 20 °C to give a value of *ca.* 1×10^{-11} s^{-1}.[6c] The stability constant K_2 at 20 °C for Ni$(C_2H_5)_2$(bpy)-(acrylaldehyde) is estimated from the thermodynamic data (Table 8) to be *ca.* 1×10^{-2} l/mol, while the rate constant k_2K_2 for the reaction, $\mathbf{1}$+acrolein$\overset{K_2}{\rightleftharpoons}\mathbf{3}\xrightarrow{k_2}$Ni(bpy)(acrylaldehyde) +butane, is *ca.* 1×10^{-2} l/mol·s at 20 °C,[6c] which gives the value of k_2, the rate constant for the splitting of Ni–C_2H_5 bond in Ni$(C_2H_5)_2$(bpy)(acrylaldehyde), 1×10^{0} s^{-1}. Therefore we obtain the value of 1×10^{11} for the ratio of k_2 to k.

16) The migration of electron was represented as a promotion of electron from σ_{Ni-C} orbital to the lowest vacant orbital of nickel.[6c]