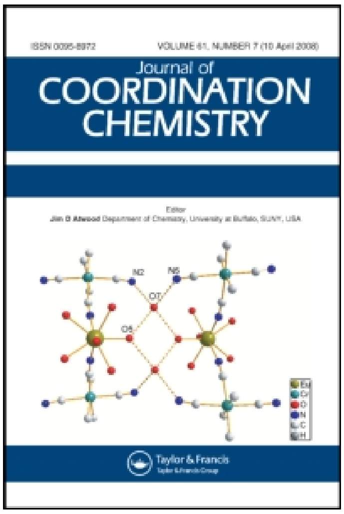

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RATE OF EXCHANGE OF SUBSTITUTED PYRIDINES WITH THEIR BIS(β-DIKETONATO)NICKEL(II) ADDUCTS

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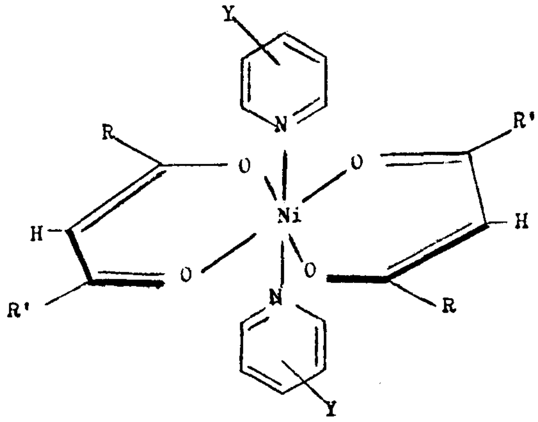
The exchange rates of various substituted pyridines coordinated with a bis-(β-diketonato)nickel(II) complex and the corresponding uncomplexed ligands are first order over a wide ligand concentration range. They decrease slightly in nonpolar solvents and decrease only slightly and irregularly with increase in pyridine base strength. These results lend further support for a dissociative mechanism in these reactions.

Picoline exchange in several bis(β-diketonato)-bis-(4-picoline)nickel(II) complexes, **1** $Y = 4\text{–}CH_3$, as given by equation (1),[1] was studied recently in the presence of a relatively large excess of uncomplexed ligand using nuclear magnetic resonance techniques.[2] as well as bond breaking, the I_D or I_A mechanisms.[6] Additional studies on the effects of ligand concentration, solvent, and pyridine substituents have now been made in order to more firmly establish the dissociative mechanism for this process.

P +



$= Ni(AA)_2P_2 + P$ (1)

1

The exchange rates were found to be first order in chelate and independent of the 4-picoline concentration and to decrease with increasing electron withdrawal by the substituents on the β-diketone chelate rings. These observations were interpreted in terms of a dissociative mechanism, the generally postulated pathway for reactions of hexacoordinate nickel(II).[3,4,5] However the presence of a large excess of 4-picoline made it impossible to rule out a bimolecular process in which development of the transition state involves significant bond making

EXPERIMENTAL SECTION

Preparation of Complexes

All of the ligands were purchased except for 4-nitropyridine[7] and 4-methoxypyridine[8] which were prepared from the available N-oxides by reduction. Typical of the procedures used to prepare the adducts is the synthesis of bis(2,4-pentanedionato)-bis(4-nitropyridine)nickel(II). To 1 g (8.1 mmol) of 4-nitropyridine dissolved in 20 ml of benzene was added 1 g (3.4 mmol) of nickel acetylacetonate dihydrate. The mixture was boiled to remove the water azeotropically and the hot solution filtered. The crystalline product which formed upon cooling was recrystallized from benzene to produce green needles which turned yellow after washing with petroleum ether. The product was dried one hour at 56° *in vacuo*. This and other complexes used in this study are characterized in Table I.

TABLE I

Characterization of the complexes $Ni(AA)_2P_2$, **1**

$Ni(AA)_2P_2$, **1**					$\bar{\nu}_{max}$ cm^{-1}(ϵ $M^{-1}cm^{-1}$)		Anal. calcd			Anal. found		
R	*R′*	*Y*	color	mp	A_{2g}–T_{2g}	A_{2g}–T_{1g}	%C	%H	%N	%C	%H	%N
CH_3	CH_3	4–$N(CH_3)_2$	blue	—	—	—	57.50	6.84	11.18	57.32	6.67	11.16
CH_3	CH_3	4–OCH_3	blue	200–201°	10,150 (5.0)	17,100 (6.7)	55.60	5.94	5.90	55.29	5.81	—
CH_3	CH_3	3–CH_3	violet-blue	191–193°	—	—	59.62	6.37	6.32	59.19	6.38	—
CH_3	CH_3	4–CH_3	blue	208–211°dec	10,200 (5.7)	17,000 (8.5)	59.62	6.37	6.32	59.84	6.33	—
CH_3	CH_3	H	violet blue	191–193°	10,200 (6.7)	17,100 (6.6)	57.86	5.83	6.74	58.02	5.92	6.93
CH_3	CH_3	4–CN	lt. blue	dec 250°	—	—	56.80	4.77	12.04	57.03	5.02	12.04
CH_3	CH_3	4–NO_2	yellow	dec 225–227°	10,250 (4.6)	17,700 (6.3)	47.55	4.39	11.09	47.69	4.44	—
C_6H_5	CH_3	4–$N(CH_3)_2$	green	243–245°	10,100 (8.5)	16,950 (13.8)	65.29	6.13	9.19	65.30	6.22	—
C_6H_5	CH_3	4–CH_3	green	191–192°	10,100 (7.7)	17,050 (13.1)	67.75	5.69	4.94	67.52	5.73	4.97
C_6H_5	CH_3	H	green	~170°(164)	10,150 (7.9)	16,950 (13.3)	66.81	5.23	5.21	66.48	5.22	—
C_6H_5	CH_3	4–CN	green	212–214°	10,250 (8.8)	17,250 (15.6)	65.21	4.45	9.51	65.84	4.63	—

The melting points of these compounds are dependent on the time and rate of heating. The data reported in Table I were obtained by inserting a capillary containing the compound in an oil bath at approximately 5–10° below the point where liquifaction becomes rapid, and heating at the rate of 3–4° per minute. All compounds liquified partially below the given range owing to ligand release. Bubbling due to released ligand was noted in the compounds **1**, $R = R' = CH_3$, $Y = H$ and 4-CH_3. The solution electronic spectra reported in Table I were obtained in methylene chloride 0.5–2.0 *M* in base and .04–.08 *M* in complex. In addition nujol mull spectra were obtained but the exact maxima could not be reproducibly obtained from these owing to the broadness of the lower energy peak and the difficulty of obtaining base lines. However all samples showed maxima at 950 ± 25 mμ and 575 ± 10 mμ except $Ni(AcAc)_2P_2$ Y = 4–NO_2 which showed shoulders in these regions. The difference in colors of the adducts appears to be due to tailing into the visible region of strong ultraviolet absorptions. The adducts were also characterized by infrared spectroscopy which in each case showed the complex to be free of water. In addition to nmr resonances reported elsewhere, the following isotropic shifts in cps were observed at −60° in a $CDCl_3$ solution: $Ni(AcAc)_2P_2$ Y = 4–CHO_3, $CH_3O + 37$; $Ni(AcAc)_2P_2$ Y = 3-CH_3, 3-CH_3 −525, γ-H −620; $Ni(AcAc)_2P_2$ Y = H, γ-H–650; $Ni(BzAc)_2P_2$ Y = 4-$(CH_3)_2N$, $(CH_3)_2N + 220$; $Ni(BzAc)_2P_2$ *Y* = H, γ-H −650. Where comparison can be made these values are in agreement with the previously reported shifts or shift ratios[9a] and the transmission of spin density through linking heteroatoms.[9b] Low temperature integrated intensities of the complexed and uncomplexed ligand resonances indicated all complexes to have the $Ni(AA)_2P_2$ stoichiometry in solution.

Kinetics

Nmr data were obtained using an extended range Varian A-60 NMR Spectrometer with tetramethyl silane as an internal standard and calibration by the sideband technique.[2] Negative values indicate isotropic shifts downfield from the reference. Solvents were purchased commercially; the deuterated solvents were dried over molecular sieves, the other solvents were distilled and then dried before use. The concentrations of ligand varied from

0.8–2.5 M and the mole fraction of complexed pyridine varied from 0.03 to 0.085. At least three samples were used to obtain the averaged curves such as those shown in figure 2; these were nominally 0.05 M complex, 1 M base; 0.05 M complex, 2M base; 0.025 M complex, 1 M base. Exceptions included the experiments with acetone as a solvent, where solubility restrictions necessitated the use of lower complex concentration. Data obtained from samples made from anhydrous $Ni(AA)_2$ or preformed $Ni(AA)_2P_2$ gave comparable results.

RESULTS

As in the previous work,[2] most of the exchange rates were obtained principally from nmr line shift data, using the predominantly uncomplexed ligand proton resonance at temperatures intermediate between those where resonances of both the free and complexed ligands can be observed (slow exchange) and those where only a single time-averaged set of resonances are found (fast exchange). The Swift and Connick analysis of such data is given by equation 2[10] where $\Delta\omega_f$ is the observed

$$\Delta\omega_f = \frac{P_m \Delta\omega_m}{[(\tau_m/T_{2m}) + 1]^2 + (\tau_m \Delta\omega_m)^2} \qquad (2)$$

shift from the free ligand position, P_m is the mole fraction of ligand complexed, $\Delta\omega_m$ is the shift calculated for the pure paramagnetic complex in the absence of exchange, T_{2m} is the transverse relaxation time of the proton in the pure paramagnetic complex which can be obtained from the half-width at half-height of the resonance in radians/sec, and τ_m is a characteristic exchange time so that for first order kinetics $1/\tau_m = k_1$, where k_1 is the first order rate constant for the exchange. Since there are two ligands the rate for the reaction (1) is 2 (k_1). A number of corroborative rates were also calculated from the line width of this resonance.[10]

TABLE II

Effect of solvent on exchange rate of 4–Picoline with bis(Benzoylacetonato)-bis-(4–Picoline)nickel(II)[1b]

Solvent	Viscosity[a]	Dielectric[b] Constant	k × 10^{-4} sec^{-1}(25°)	ΔH† Kcal	ΔS† eu	$\Delta\omega_m$(cps) 4–CH_3(–60°)	10^{-3}Slope[c]
CCl_4	0.89	2.24*	2.3	13	4	(860)	.398
Toluene d^8	0.56	2.3	3.4	14	8	864	.380
$CDCl_3$	0.55	4.8*	3.7	12	3	858	.376
Acetone d^6	0.32	20.7	4.7	12	4	860	.348
CH_3OH	0.56	33.1*	4	—	–	875	.36
$HCON(CH_3)_2$	0.80	36.7	3.6	12.5	4	860	.392

[a] Centipoise. N. A. Lange, *Handbook of Chemistry*, Handbook Publishers Inc., Sandusky, Ohio, 6th Ed., p. 1571. P. G. Sears, R. K. Wolford and L. R. Dawson, J. Electrochem. Soc. 103, 633 (1956). (25°)

[b] C. P. Smyth, *Dielectric Behaviour and Structure*, McGraw-Hill Book Co., Inc., New York, N. Y., 1955. *Handbook of Chemistry and Physics*, Chemical Rubber Co., Cleveland, Ohio, 45th Ed., p. E–30. Those marked * at 20°, other at 25°.

[c] slope of linear plot of log (full line width at half height cps) against reciprocal absolute temperature; a measure of $1/T_{2m}$.

In the study of the effect of solvent on the exchange rate, Table II, the observed differences are quite small so additional details on the measurements and calculations will be presented. In all cases the shift of the 4–CH_3 protons resonance was followed. The solubility of $Ni(BzAc)_2P_2$ $Y = 4\text{–}CH_3$ in some of the solvents such as acetone is low and in these cases the complex was dissolved hot, and the low temperature studies were made on supersaturated solutions. The average molar shifts of the 4–CH_3 proton resonances are plotted against reciprocal temperature in Figure 2. Datum points for the $CDCl_3$ experiments are included to show the reproducibility achieved. The data for N,N-dimethyl formamide are somewhat less reliable than the rest, since undeuterated solvent was used and the solvent peaks interfered with the determination of the exact position of the ligand resonances. The isotropic shifts of the pure paramagnetic complex, $\Delta\omega_m$, were measured with respect to the 4–CH, resonance in the uncomplexed ligand. Within experimental error, $\Delta\omega_m$ was found to be invariant with respect to solvent. The line, shown in part in Figure 2, which joins the experimentally observed slow exchange values of $\Delta\omega_m$ and the calculated fast exchange points $\Delta\omega_f/P_m$ was used to obtain the intermediate temperature values. This line has a $1/T = 0$ intercept of ~ 0 in agreement with a Curie behavior for the complex. While the uncomplexed ligand resonances usually show but slight variation in position, 2–4 cps, with respect to concentration, temperature, and solvent, the toluene and 4-picoline pair proved an exception. The 4–CH_3 resonance in the uncomplexed picoline is shifted upfield by up to 0.5 ppm at low temperatures. The β proton resonance also shifts slightly upfield but the α proton resonance is shifted downfield. The logs of the observed diamagnetic resonance positions (in cps relative to TMS) of the picoline proton resonances are linear with respect to reciprocal absolute temperature over most of the temperature range studied. The slopes and $1/T = 0$ intercepts for these lines are 4–CH_3, -21.5, log(136.5 cps); β-H, -4.75, log(416 cps); α –H, 2.69, log(495 cps). These shifts indicate the formation of a solute-solvent complex such as that found in the pyridine benzene system.[11] Although the data are accommodated by the previously proposed model having the solute dipole axis perpendicular to the solvent π orbital plane with the positive end of the dipole nearest to the orbital, it can also be accommodated by an ordering of the solute in the solvent in which the ring planes are parallel and the 4–CH_3 group lies near the center of the toluene ring. The CH_3 linewidths in the pure paramagnetic complex, necessary for estimating T_{2m}, are solvent dependent, varying with the solution viscosity as evidenced by the order of decreasing line widths at -40 to $-60°$; $CCl_4 > DMF > \text{Toluene} > CDCl_3 > \text{Acetone}$ (Table II). The relaxation times for resonances in other nickel complexes have been shown to be dependent on the Debye rotational correlation time for solute tumbling in solution,[12] a parameter which is viscosity dependent. For the purpose of reducing the resonance shift data to rate data the log of the full line width at half-height of the proton resonance in the paramagnetic complex was assumed to vary linearly with reciprocal absolute temperature and the $1/T = 0$ intercept of this line was arbitrarily assigned a value of zero. This approximation is justified since even line widths half as large as those predicted by this slope and intercept produced less than a 3% change in the exchange rate. The slopes of the lines obtained for the various solvents are given in Table II.

In the study of the effect of the pyridine substituent on the rate of exchange, the resonance shifts of the β protons were generally followed. The positions of the β proton nmr resonances of the uncomplexed ligands at 40° are (cps downfield from TMS in $CDCl_3$): 4–$N(CH_3)_2$, 388; 4–OCH_3, 403(CCl_4 solvent); 3–CH_3, 436; 4–CH_3, 425; H, 436; 4–CN, 453; 4–NO_2, 482. These values change by 1–2 cps over the studied temperature range and are also very slightly affected by the presence of paramagnetic solute (observations made under slow exchange conditions). Attempts were made to correct for these effects by interpolating and extrapolating the available data. In $CDCl_3$ solutions, the line widths of β proton resonances of the pure paramagnetic complexes are all comparable and a values of 0.455×10^3 was used for the slope of the log of the full line width at half-height (cps) against reciprocal absolute temperatures plot with the $1/T = 0$ intercept again being set at zero in all cases. The number of different pyridines which could be studied in the $Ni(AA)_2P_2$ systems is limited by factors such as complicating steric effects, complex insolubility and the absence of nmr resonances suitable for study. Steric factors have a large effect on the exchange rate, for example 2-picoline exchange is too fast to measure in the temperature range studied here. Contrasting with the relative solubility of $Ni(AcAc)_2P_2$ Y = 4–NO_2 and $Ni(BzAc)_2P_2$ Y = 4–$N(CH_3)_2$ is the insolubility in $CDCl_3$ of the complexes $Ni(BzAc)_2P_2$ $Y =$ 4–NO_2 and $Ni(AcAc)_2P_2$ $Y =$ 4–$N(CH_3)_2$ which preclude their measurement in our instrument. The presence of interfering peaks is illustrated by the pyridine data in which there is an overlap of β and γ proton resonances in most of the kinetically significant range. Attempts were made to follow both peaks with temperature change and to interpret the shifts kinetically, but the results for the two sets of data differed significantly, particularly in the slopes of the log (k_1/T) against $1/T$ plots. A comparison of the 4–CH_3 and β–H proton resonance data for 4-picoline exchange shows much better agreement. Partly for the reason of interference in the spectrum and partly for solubility concentration effects, the exchange rates for 3-picoline were evaluated using data from the 3–CH_3 resonance line shifts.

DISCUSSION

Use of the Swift and Connick equation to study exchange rates requires the use of a large excess of uncomplexed ligand, and under these conditions, first order kinetics can be observed even though the incoming ligand may be participating in the bond breaking process. Equation 3,[13] which describes the broadening of the paramagnetic resonance (T_{2mp} is the observed half-widths at half-height in radians/sec of the complexed ligand

$$(T_{2mp})^{-1} = (T_{2m})^{-1} + (\tau_m)^{-1} \qquad (3)$$

resonance) is free of concentration limitations and can be used to determine kinetic order. Figure 1, which provides data on 4-picoline exchange in bis(benzoylacetonato)-bis(4-picoline)nickel(II) using the 4-CH_3 resonance of complexed picoline, shows that over a wide range of added picoline, the line width broadening due to exchange and hence the rate of exchange is independent of free ligand concentration. A similar result was obtained using the β proton resonance in the exchange of 4-nitropyridine with bis(2,4-pentanedionato)bis(4-nitropyridine)nickel(II). Although large variations in ligand concentration will change the polarity of the reaction medium and might therefore affect the rate, in this system such solvent effects are small (*vide infra*). This concentration independence of the exchange broadening, even at free ligand to complex ratios of less than one, indicates the presence of an intermediate in the reaction pathway which is long-lived relative to the approach of uncomplexed ligand molecules to the reaction site. It rules out the alternative interchange mechanism I_D in which the solvation shell is preferentially occupied by the incoming ligand molecule.

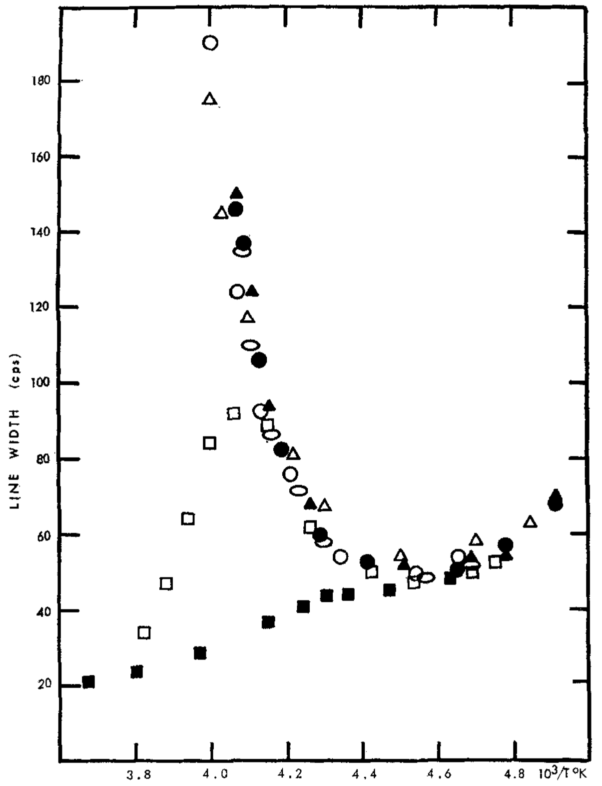


FIGURE 1 The effect of 4-picoline concentration on the variation with reciprocal absolute temperature of the full linewidth at half height of 4-CH_3 picoline proton resonance for 0.10 *M* $Ni(BzAc)_2P_2Y$ = 4-CH_3 in $CDCl_3$. Molarity of excess picoline: ● 0.83, ▲ 0.35, ○ 0.20, ⬭ 0.13, △ 0.05, □ 0.014, ■ 0.00.

The postulated intermediate in the reaction pathway can be either a solvent-complex adduct in which a solvent molecule has entered the coordination sphere, or simply a pentacoordinate species.[14] In order to assess the role of the solvent in the exchange process, a study of the system $Ni(BzAc)_2P_2$ and 4-picoline in various solvents was made. Table II and Figure 2 shows that changing the solvent from nonpolar to polar or from noncoordinating to coordinating has but little effect on the 4-picoline exchange rate. The small differences do show a trend to slower exchange in low dielectric and poorly solvating media. This supports the dissociative mechanism,[5,6] as effective solvation should aid the dissociation of $Ni(AA)_2P_2$ to $Ni(AA)_2P + P$. Since in this case no highly polar species are formed, the observed changes can be expected to be quite small. It also rules against an interchange mechanism since in nonpolar solvents the free 4-picoline would be expected to solvate the complex and the preferential solvation of the complex by the ligand should result in rate enhancement in an interchange process. While the presence of an intermediate with rapidly exchanging solvent in the coordination shell cannot be rigorously excluded, the absence of any signficant rate enhancement in a coordinating solvent such as *N*,*N*-dimethyl formamide suggests that as the leaving group vacates the coordination site, the molecule distorts to prevent coordination sphere occupation of the vacated site by the solvent. Recent work on ligand exchange of NiL_6^{2+} complexes in mixed solvents has also led to the postulation of such intermediates.[14,15]

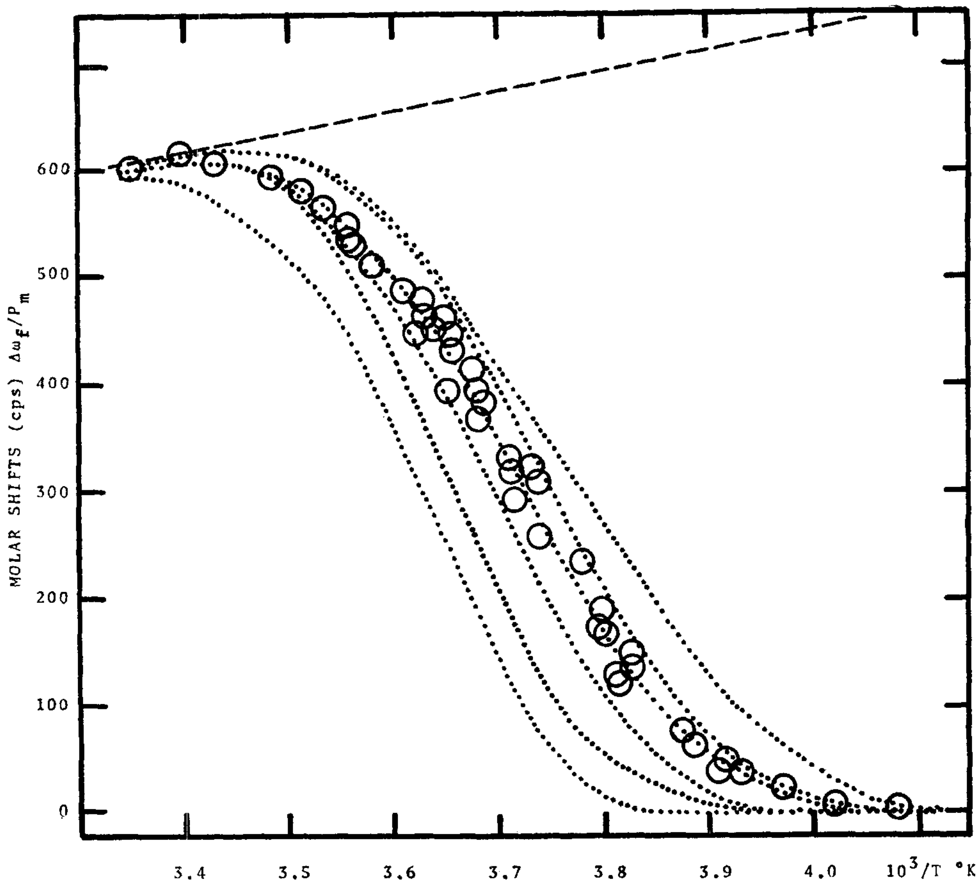


FIGURE 2 Temperature dependence of molar isotropic shifts of 4–CH_3 proton resonance in 4-picoline and bis(benzoylacetonato)-bis(4-picoline)nickel(II) mixtures in various solvents. From left to right: CCl_4, $C_6D_5CD_3$, $HCON(CH_3)_2$, $CDCl_3$, CD_3COCD_3, CH_3OH. ○ represent experimental data points in $CDCl_3$. — — — — represents isotropic shift of 4–CH_3 resonance of pure complex.

TABLE III

Rate of exchange of substituted pyridines in $Ni(AA)_2P_2$ 1[b]

$Ni(AA)_2P_2$			*p*Ka of	$k_1 \times 10^{-5}$	ΔH‡	ΔS‡	$\Delta\omega_m$(cps) of
R	*R′*	*Y*	Base[a]	$sec^{-1}(25°)$[b]	Kcal.	eu	Proton at −60°
CH_3	CH_3	4–CH_3O	6.58	0.46	10.3	−2.5	−2325
CH_3	CH_3	3–CH_3	5.67	1.33[c]	11.4[c]	4.1[c]	−2775
CH_3	CH_3	4–CH_3	6.03	0.94	11.9	4.4	−2545
CH_3	CH_3	H	5.21	0.8–1.4	—	—	−2660
CH_3	CH_3	4–NO_2	1.39	0.59	8.7	−7.2	−2315
C_6H_5	CH_3	4–$(CH_3)_2N$	9.12[d]	0.26	11.0	−1.4	−2375
C_6H_5	CH_3	4–CH_3	6.03	0.35	10.7	−1.4	−2610
C_6H_5	CH_3	H	5.21	0.4–0.6	—	—	−2705
C_6H_5	CH_3	4–CN	1.86	0.48	10.7	−1.4	−2505

[a] Reference 16. [b] Kinetic data derived from β proton resonance except as noted.
[c] Data derived from frequence shifts of 3–CH_3 protons. [d] Data for 4–aminopyridine.

In a final series of experiments the effect of pyridine substituents Y on the exchange rate was studied. Changing the pyridine ring substituent Y has a marked effect on the ligand's basicity[16] and to the extent such effects are electronic in nature, they may be expected to produce opposing changes in the exchange rates in the present system. Other things being equal, the stronger the base the less effective it is as a leaving group.[17] But the stronger bases are more electron donating and will labilize the other ligands.[2,18] In $\mathrm{Ni(AA)_2P_2}$, a change in the substituent Y affects not only the leaving group but also the residual chelate as well as the incoming group, so that the tendency for a stronger base to exchange more slowly in a dissociative mechanism is at least partially offset by the labilizing effect of the second pyridine group. The observed results, Table III, show only a small difference in the rates of base exchange, reflecting these two opposing effects. The data also indicate that both enthalpy and entropy of activation differences contribute to the rate changes, but these numbers are not sufficiently accurate to make an exact analysis meaningful.

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