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Ligand-Exchange Reactions of Some Five-Coordinated Nickel(II) Complexes

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The neutral-ligand-exchange reaction for the five-coordinate cyanide systems $NiL_3(CN)_2$ proceeds *via* a dissociative mechanism. The rate-controlling step is

$$NiL_3(CN)_2 \overset{k_1}{\rightleftharpoons} NiL_2(CN)_2 + L$$

The magnitudes of k_1 vary according to L = Ph_2POEt (2.9×10^4 sec^{-1}) > $P_3(OEt)_3$ (1.0×10^4 sec^{-1}) > $PhPMe_2$ (4.7×10^3 sec^{-1}) > $PhP(OEt)_2$ (2.9×10^3 sec^{-1}). The dissociative mechanism is predicted by Tolman's rules. Difficulties were encountered in examining the analogous halide systems $Ni(PhPMe_2)_3X_2$, where $X^- = Br^-$ or Cl^-, because the four-coordinate intermediate in the exchange reaction undergoes the rapid isomerization reaction NiL_2X_2(square planar) $\rightleftharpoons$ NiL_2X_2(tetrahedral). The introduction of the tetrahedral paramagnetic species into the system creates a three-site system which has not been interpretable quantitatively. It appears that the exchange reaction proceeds *via* the same square-planar four-coordinate intermediate as encountered in the cyanide systems. Qualitatively it can be concluded that the variation of k_1 (referred to above for the $Ni(PhPMe_2)_3X_2$ exchange reaction) follows the ordering $X^- = CN^- < Br^- < Cl^-$.

Introduction

The occurrence of neutral ligand exchange in systems containing the five-coordinate complexes NiL_3X_2, where L = various phosphines or phosphites and $X^- = CN^-, Cl^-$, or Br^-, was first reported by Verkade, *et al.*[1] They described the temperature dependence of the nmr spectra of the complex $Ni(P(OMe)_3)_3(CN)_2$ in acetone, both with and without excess $P(OMe)_3$, in a qualitative manner. This reaction can be described by the equation

$$NiL_3X_2 + {}^*L \rightleftharpoons NiL_2{}^*LX_2 + L \quad (1)$$

The two sites of free and complexed ligand are magnetically inequivalent, and the rate of this exchange for these nickel systems is such that the rates can be determined by nmr methods.

There are two major mechanistic alternatives to be considered for the reaction of a five-coordinate complex. Such a species can react *via* an SN1, or dissociative, mechanism, where the intermediate is a four-coordinate species. The rate-controlling step can also be an associative, or SN2, reaction. This mechanism involves a six-coordinate intermediate. A double-path mechanism, where both routes operate simultaneously, can also be envisioned. Since coordination numbers 4 and 6 are both well known for nickel(II), both SN1 and SN2 paths would *a priori* seem equally probable. In the light of some recent discussion by Tolman,[2] however, this may not be true. Tolman has proposed the following rules for organometallic complexes and their reactions.

(1) Diamagnetic organometallic complexes of transition metals may exist in a significant concentration at moderate temperatures only if the metal's valence shell contains 16 or 18 electrons. A significant concentration is one that may be detected spectroscopically *or kinetically* and may be in the gaseous, liquid, or solid state.

(2) Organometallic reactions, including catalytic ones, proceed by elementary steps involving only intermediates with 16 or 18 metal valence electrons.

Since the five-coordinate nickel(II) complexes in this study are diamagnetic, they should obey these rules. Using Tolman's postulates to determine the reaction mechanism, the dissociative path is the only allowed route. Equation 2

$$\underset{18\text{ e}}{NiL_3X_2} \rightleftharpoons \underset{16\text{ e}}{NiL_2X_2} + L \quad (2)$$

$$\underset{18\text{ e}}{NiL_3X_2} + L \rightleftharpoons \underset{20\text{ e}}{NiL_4X_2} \quad (3)$$

shows the rate-determining step for a dissociative mechanism. It contains only 16- and 18-electron moieties. The associative pathway is shown in eq 3, and it contains a "forbidden" 20-electron species.

The chief rationale for undertaking the present study was to obtain information on the kinetic behavior of five-coordinate complexes. While the number of known five-coordinate complexes is increasing rapidly, very few kinetic studies have been reported. Previous studies of ligand substitution reactions of five-coordinate platinum(II) and palladium(II) complexes have been explained by SN2 mechanisms[3] and by SN1 mechanisms.[4] Ligand substitution reactions of the five-coordinate maleonitriledithiolate (mnt) complex of Co(III)[5]—$Co(mnt)_2PPh_3$—proceed *via* both an associative and a dissociative pathway. Finally, the substitution reaction of $Fe(CO)_4(CH_2{=}CHX)$ with CO[6] occurs through a dissociative, or SN1, mechanism, with $Fe(CO)_4$ as an intermediate.

Experimental Section

Materials. Dichloromethane was refluxed over and distilled from phosphorus pentoxide under a nitrogen atmosphere and stored under nitrogen. All phosphine ligands were distilled under vacuum prior to use. $Ni(CN)_2$, $NiBr_2$, and $NiCl_2 \cdot 6H_2O$ were obtained as reagent grade materials and were used without further purification.

Preparation of Complexes. All preparative work was done under an atmosphere of dry nitrogen. All of the syntheses followed the general procedure of adding a stoichiometric amount of the phosphine to the nickel salt in either acetone or ethanol, followed by refluxing and isolation of the product. These syntheses have been described in detail by other authors.[1,7,8] The complexes made were $Ni(PhP(OEt)_2)_3(CN)_2$, $Ni(P(OEt)_3)_3(CN)_2$,[7] $Ni(Ph_2POEt)_2(CN)_2$,[7] $Ni(PhPMe_2)_3X_2$ ($X^- = CN^-$,[8] Br^-), and $Ni(PhPMe_2)_2X_2$, ($X^- = Cl^-$, Br^-).[8] Excellent analyses were obtained for all complexes previously made. No analysis for $Ni(P(OEt)_3)_3(CN)_2$, which is an oil, was pre-

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(1) K. J. Coskran, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, 90, 5437 (1968).

(2) C. A. Tolman, *Chem. Soc. Rev.*, 1, 1337 (1972).

(3) R. G. Pearson, M. M. Muir, and L. M. Venanzi, *J. Chem. Soc.*, 5521 (1965).

(4) T. D. B. Morgan and M. L. Tobe, *Inorg. Chim. Acta*, 5, 563 (1971).

(5) D. A. Sweigart and D. G. DeWit, *Inorg. Chem.*, 9, 1582 (1970).

(6) G. Cardaci and V. Narcisco, *J. Chem. Soc., Dalton Trans.*, 2289 (1972).

(7) B. B. Chastain, E. A. Rick, R. L. Pruett, and H. B. Gray, *J. Amer. Chem. Soc.*, 90, 3994 (1968).

(8) E. C. Alyea and D. W. Meek, *J. Amer. Chem. Soc.*, 91, 5761 (1969).

viously reported. *Anal.* Calcd: C, 39.39; H, 7.39; N, 4.60. Found: C, 38.93; H, 7.66; N, 4.48. The complex $Ni(PhPMe_2)_3Br_2$ is reported here for the first time. *Anal.* Calcd: C, 45.53; H, 5.27; Br, 25.25. Found: C, 45.81; H, 5.92; Br, 25.18.

Sample Preparation. Samples for the ligand-exchange reactions were prepared in 1-ml volumetric flasks by adding a weighed amount of complex to a weighed amount of ligand in a flask and diluting to the mark with CH_2Cl_2. The solution was transferred to a nitrogen-filled nmr tube and capped. The samples for the isomerization reactions were made by dissolving a weighed amount of complex in 1 ml of solvent, followed by transfer to a nitrogen-filled tube. All samples containing halide complexes were transferred to amberized nmr tubes provided with a glass insert to exclude as much atmosphere as possible. These precautions prevented the decomposition of these complexes in solution that otherwise occurred.

Nmr Spectra. Spectra were obtained in CH_2Cl_2 solution using a Varian A-60 spectrometer equipped with a variable-temperature probe and a Bruker 90-MHz spectrometer with a variable-temperature probe and ^{31}P broad-band decoupling capabilities. Temperatures were obtained using an nmr probe thermometer. The Varian instrument was used for the ligand-exchange reactions of $Ni(P(OEt)_3)_3(CN)_2$ and $Ni(PhP(OEt)_2)_3(CN)_2$, while the Bruker instrument was used for the rest of the ligand-exchange and the isomerization reactions. In all work with the phenyldimethylphosphine complexes, the ^{31}P decoupling unit was employed.

Analyses. Carbon, hydrogen, and nitrogen analyses were carried out in these laboratories by Miss H. E. Beck on an F & M carbon-hydrogen-nitrogen analyzer, Model 185. Halide analyses were done using the Radiometer automatic titration assembly with a silver-mercury-mercurous sulfate electrode for the titration with $AgNO_3$.

Formation Constants. Evaluation of formation constants for the reaction

$$NiL_2X_2 + L \overset{K_f}{\rightleftharpoons} NiL_3X_2$$

in systems where the extinction coefficients of both the four- and five-coordinate species were not known was accomplished using the method of Rose and Drago.[9] Alyea and Meek[8] have previously used this approach for such systems successfully. Measurements of absorption intensities were made using the Beckman DU-2 spectrophotometer.

pK_a Measurements. Streuli[10] has shown that the half-neutralization potentials measured in CH_3NO_2 of phosphines can be related to their pK_a values. Attempts were made to measure such potentials using a Radiometer automatic titrator with a ground-glass sleeve calomel electrode. Fisher Certified reagent grade CH_3NO_2 was used. Attempts to measure the pK_a's of mixed phosphites were not successful since readable inflection points on the titration curve were not obtained.

Physical Measurements. Visible-uv spectra were collected using a Cary 14 spectrophotometer, and the Cary 14 diffuse reflectance accessory, Model 1411, was used to obtain solid-state spectra in this region. Infrared spectra were obtained with a Beckman IR-9 instrument.

Results

Ligand Exchange in the System $Ni(PhP(OEt)_2)_3(CN)_2$-$PhP(OEt)_2$. The ^1H nmr spectrum of the ligand $PhP(OEt)_2$ shows the expected pattern, with the methyl resonance a triplet ($J = 7$ Hz) resulting from the splitting of the methyl protons of the ethoxy groups by the two adjacent methylene protons. No splitting from ^{31}P is seen in the methyl resonance; the chain is evidently too long for transmission of this spin information. The spectrum of the $Ni(PhP(OEt)_2)_3(CN)_2$ complex is the same as that for the free ligand, but it is shifted 5.5 Hz upfield from it.

When free $PhP(OEt)_2$ is added to a solution of its corresponding complex, a rapid exchange of the free and complexed ligand can be deduced from observation of the nmr spectra. At room temperature only one triplet is seen at a weighted-average position. As the temperature is lowered, the signal broadens, coalesces about −25°, and is resolved into the two overlapping triplets which give the appearance of a distorted quadruplet. The spectra were similar to those for the $P(OEt)_3$ system reported below and shown in Figure 1.

Table I shows the effect of varying the concentration of free ligand on the rate constant $1/\tau_C$, where τ_C is the mean lifetime of the complexed ligand solution. Complete temperature runs were made for each concentration change so that the sensitivity of τ_C to changes in ligand concentration could be evaluated in regions of both fast and slow exchange. The rate constants $1/\tau_C$ were corrected to 25° for the tables. If the reaction is dissociatively controlled, the rate-determining step is

$$NiL_3X_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NiL_2X_2 + L \qquad (4)$$

and the expression for $1/\tau_C$ is

$$1/\tau_C = k_1 \qquad (5)$$

If the reaction is associative in nature, the rate-controlling step is

$$NiL_3X_2 + L \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} NiL_4X_2 \qquad (6)$$

and

$$1/\tau_C = k_1'(L) \qquad (7)$$

If both associative and dissociative paths operate, the expression for $1/\tau_C$ is

$$1/\tau_C = k_1 + k_1'(L) \qquad (8)$$

The results in Table II show that there is no linear dependence of $1/\tau_C$ on the free ligand concentration. The variations in the rate constant are random and the conclusion to be drawn from these data is that the mechanism of the reaction is dissociative (SN1).

The values of $1/\tau_C$ were obtained from the Piette-Anderson equations.[11,12] In the region above coalescence where the exchange is rapid

$$\tau = \frac{T_2\left(\frac{1}{T''} - \frac{1}{T_2}\right)}{\sigma T_2 - \left(\frac{1}{T''} - \frac{1}{T_2}\right)} \qquad (9)$$

where T_2 is the transverse relaxation time, $T'' = \pi\Delta\nu$, where $\Delta\nu$ is the line width at half-length, and σ is the second moment of the separate resonance lines

$$\sigma = P_C(\omega_C - \langle\omega\rangle)^2 + P_F(\omega_F - \langle\omega\rangle)^2 \qquad (10)$$

The subscripts C and F denote complexed and free ligand, respectively, $\langle\omega\rangle$ is the resonance frequency of the averaged signal, and P represents the relative populations of each species. Using the definition that

$$\tau_C = \tau/P_F \qquad (11)$$

the desired rate constants can be obtained.

Below coalescence, in the slow-exchange region

$$\pi\Delta\nu = \frac{1}{T_{2C}} + \frac{1}{\tau_C} \qquad (12)$$

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(9) N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, **81**, 6138 (1959).

(10) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

(11) L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).

(12) L. H. Piette, *NMR EPR Spectrosc., Pap. Varian's Annu. Workshop.*, **3**, 145 (1960).

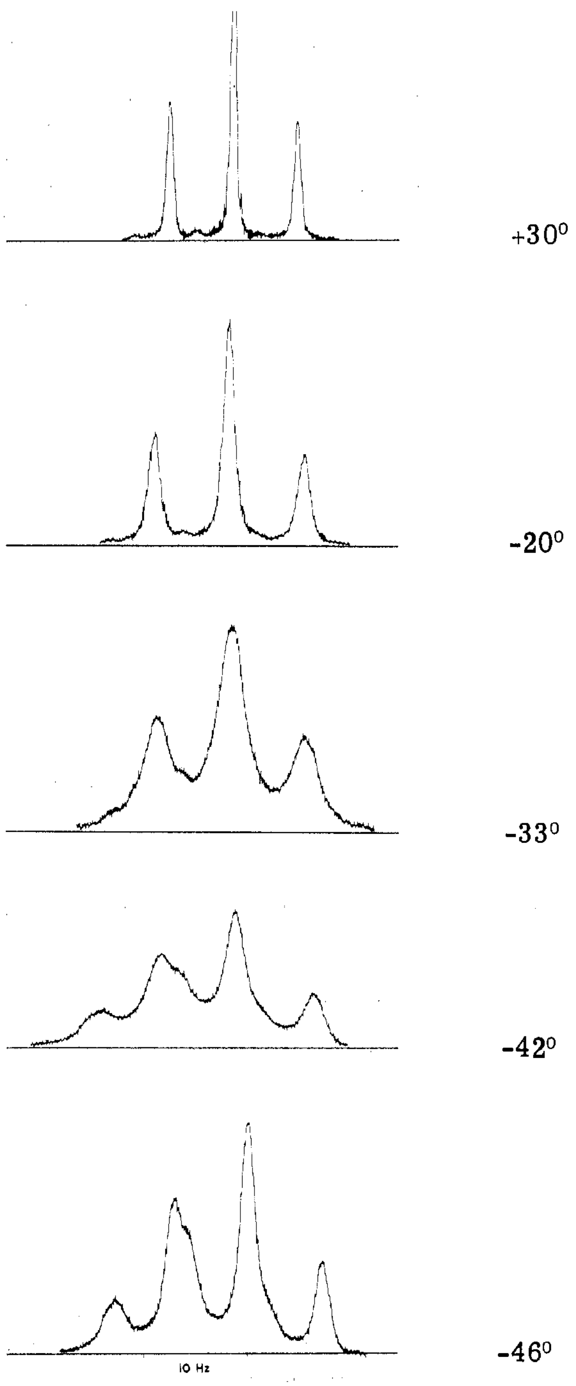

Figure 1. Temperature dependence of the nmr spectrum of Ni-$[P(OEt_3]_3(CN)_2$ + $P(OEt)_3$ in CH_2Cl_2.

Table I. Exchanging System: $Ni(PhP(OEt)_2)_3(CN)_2$ + $PhP(OEt)_2$ in CH_2Cl_2 [a]

(Complex), *M*	(Ligand), *M*	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$10^{-3}/\tau_C^{298\,°K}$, sec^{-1}
0.0981	0.3158	14.3	5.1	2.37
0.2015	0.4495	14.4	5.5	2.52
0.1029	0.5954	14.2	5.4	3.54
0.1809	0.4263	14.4	5.6	2.52
0.1869	0.8451	14.5	6.4	3.38
0.2040	1.5666			2.95

[a] $k_1^{av,298\,°K} = 2.88 \times 10^3\ sec^{-1}$, $\Delta H^{\ddagger} = 14.4$ kcal/mol ± 0.1σ, and $\Delta S^{\ddagger} = 5.6$ eu ± 0.4σ (σ is one standard deviation unit).

Table II. Exchanging System: $Ni(P(OC_2H_5)_3)_3(CN)_2$ + $P(OC_2H_5)_3$ in CH_2Cl_2 [a]

(Complex), *M*	(Ligand), *M*	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$10^{-3}/\tau_C^{298\,°K}$, sec^{-1}
0.1016	0.1035	13.8	6.0	8.7
0.2003	0.2027	15.0	10.8	14.8
0.2114	0.8209	13.8	5.6	8.7
0.2030	0.9900	14.8	9.2	8.1

[a] $k_1^{av,298\,°K} = 10.3 \times 10^3\ sec^{-1}$, $\Delta H^{\ddagger} = 14.4$ kcal/mol ± 1σ, and $\Delta S^{\ddagger} = 8.6$ eu ± 2.5σ (σ is one standard deviation unit).

The activation parameters in Table I were obtained from a conventional Arrhenius plot in which the best straight line has been determined by a least-squares analysis. A typical Arrhenius plot for this system is shown in Figure 2. The activation energy of 15.0 kcal/mol is a reasonable value, since $\Delta H°$ values for the reverse of eq 1 are known to range from −8.9 to −18.0 kcal/mol in dichloroethane.[13] The activation energy for the dissociation must be at least as great as $-\Delta H°$. The entropy of activation is positive, as expected for a dissociative reaction.

The System $Ni(P(OEt)_3)_3(CN)_2$-$P(OEt)_3$. The ^1H nmr spectra of this phosphite and its corresponding five-coordinate nickel(II) complex are the same in the methyl region as the $PhP(OEt)_2$ system described above. The signal of the complex in this case is shifted 5.7 Hz downfield from the ligand signal. The coalescence temperature is about −35°, but the qualitative description of the spectra is the same as for the previous system. Figure 1 shows spectra for this system as a function of temperature.

Table II shows that the variations in the rate constant are random, indicating a dissociative mechanism. The activation parameters for the reaction are reasonable in magnitude.

The System $Ni(Ph_2POEt)_3(CN)_2$-Ph_2POEt. Again, the ^1H nmr spectra of this complex in the methyl region corresponds with those of the other two systems described above. The signal of the complex is shifted 19.1 Hz upfield from the free ligand signal on the 90-MHz instrument.

No detailed concentration study was done for this complex, since the dissociative mechanism had been twice verified for analogous systems. The activation energy and entropy of activation are given in Table III. Measurement of $\Delta H°$ for the reverse of eq 1 yielded a value of −10.9 kcal/mol, which shows that $E_A = 10.9$ kcal/mol is a possible value. The entropy of activation for this system is a small negative value but since an error of 1 kcal in E_A could bring this value to zero, this is not regarded as particularly significant.

The System $Ni(PhPMe_2)_3(CN)_2$-$PhPMe_2$. The ^1H nmr spectrum of the phosphine $PhPMe_2$ in CH_2Cl_2 in the methyl region consists of a sharp doublet ($J = 3$ Hz). The methyl protons are split by the ^{31}P ($S = {}^1/_2$) to which they are directly bonded. When free $PhPMe_2$ is added to a solution of $Ni(PhPME_2)_3(CN)_2$ in CH_2Cl_2 at 25°, only one signal in the methyl region is seen—a broad singlet at an average position. If this solution is warmed to 70°, the singlet splits into a sharp doublet at the average position (Figure 3). When the solution is cooled below 25°, the peak first sharpens, reaching a maximum height at about 0°, then broadens, and resolves into a broad peak and a sharp doublet, the signals of which are separated by 13 Hz (Figure 3). It would appear that the following is occurring. At 70° the exchange between free and complexed ligand is so rapid that the methyl groups "see" only the spin of the ^{31}P nucleus to which they are attached. As the temperature is lowered to 0°, the ^{31}P is effectively decoupled from the methyl groups attached to it

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(13) P. Rigo, G. Guastalla, and A. Turco, *Inorg. Chem.*, 8, 375 (1969).

Table III. Some Kinetic and Thermodynamic Parameters for $NiL_3(CN)_2$ Systems

L	k_1,[a] sec^{-1}	$K_f^{298°K}$ [a]	k_2,[b] M^{-1} sec^{-1}	$\Delta H°$,[a] kcal/mol	E_A,[a] kcal/mol	ΔS,‡ eu
Ph_2POEt	2.9×10^4	18	5.18×10^5	10.9	10.9	−3.7
$PhPMe_2$	4.7×10^3	13,500	6.31×10^7	14.0	15.2	7.0
$P(OEt)_3$	1.0×10^4	900	1.02×10^7		15.1	8.7
$PhP(OEt)_2$	2.9×10^3	1,500	4.33×10^6		15.0	5.6

[a] For the reaction $NiL_3(CN)_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NiL_2(CN)_2 + L$ at 298°K.

[b] $K_f = k_2/k_1$.

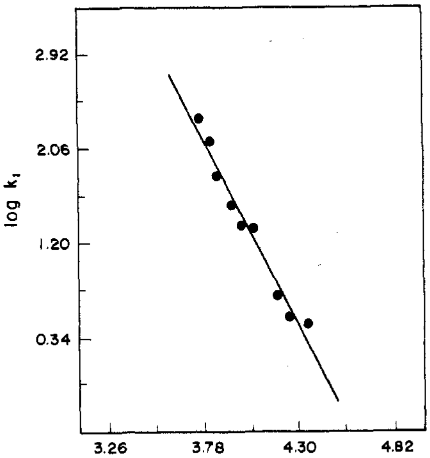

Figure 2. Arrhenius plot for the reaction $Ni[PC_6H_5(OC_2H_5)_2]_3(CN)_2 \rightarrow Ni[PC_6H_5(OC_2H_5)_2]_2(CN)_2 + PC_6H_5(OC_2H_5)_2$ in CH_2Cl_2.

through some mechanism unknown at present.[14] As the temperature is lowered to −53° the reaction rate is reduced to the slow-exchange limit, and signals for the free and complexed ligand emerge. The sharp doublet at the upfield position is due to the free phosphine, and the broad, unresolved signal 13 Hz downfield is the spectrum of the complex, in which the methyl groups are coupled directly to the ^{31}P to which they are attached and "virtually" to the other two ^{31}P atoms in the trigonal plane.[15] The broad signal would then be an envelope for a complex signal. In order to verify this, the spectra were taken while operating a broadband ^{31}P decoupling unit in conjunction with the 90-MHz nmr spectra. These spectra are also shown in Figure 3.

As expected, a single sharp peak resulted at the average position for temperatures above 0°. Below that, the peak broadened and resolved into two signals, one for the free and one for the complexed ligand. The free ligand peak was very sharp, while the other signal was broader, an anticipated phenomenon for decoupled spectra. The decoupled spectra were used to evaluate rate constants by the line-broadening method. In the region of slow exchange, the completely decoupled free ligand line widths were used to evaluate τ's.

Activation parameters for the dissociation are shown in Table III. Again, a complete concentration study was not made. E_A = 15 kcal/mol is reasonable, since $\Delta H°$ for the reverse reaction was determined to be −14 kcal/mol. The $\Delta S^‡$ value is positive, as expected.

Exchange of CN^-. ^1H nmr spectra make it easy to verify the phosphine ligand exchange discussed above. When the question of whether the cyanide groups exchange arises, however, the matter is not so easily settled. The experiment of adding excess CN^- to a solution of $NiL_3(CN)_2$ and checking the nmr spectrum for evidence of exchange is not possible. Cyanide ion attacks the $NiL_3(CN)_2$ complexes in a rapid reaction that gives $Ni(CN)_4^{2-}$. The product was identified by its vis-uv spectrum but the reaction is too fast to observe on the stopped-flow apparatus.

As mentioned earlier, conductivity data do not show the existence of measurable amounts of ionic dissociation products, *i.e.*, $NiL_3(CN)^+ + CN^-$, but it is possible that the equilibrium exists. In an attempt to acquire information on this subject, the reaction of $Ni(Ph_2POEt)_3(CN)_2$ with *p*-toluenesulfonic acid in ethanol was studied. When the acid is added to a pale yellow solution of the complex, the resulting solution gradually decolorizes. The shoulder at 340 nm characteristic of the complex decreases in absorbance, and the product is presumably solvated Ni(II). The half-time of the reaction ranges from 475 min in 0.025 *M* acid to 12 min in 1.0 *M* acid, the complex concentration being about 3×10^{-4} *M*. The reaction is first order in $[H^+]$ and first order in complex.

The exact details of this reaction need not concern us. The important information to be extracted from this experiment is that the cyanide groups dissociate slowly (relative to the very rapid dissociation of the phosphine ligands) even when attacked by acid. If the cyanide groups were undergoing a rapid dissociation equilibrium, one would expect the above reaction to proceed equally rapidly, since the acid would react with the dissociated CN^-.

The Systems $Ni(PhPMe_2)_3X_2$-$PhPMe_2$; $X^- = Br^-, Cl^-$. The ^{31}P-decoupled methyl resonance of the ligand $PhPMe_2$ is a sharp singlet. The spectrum of $Ni(PhPMe_2)_3Br_2$ alone cannot be obtained because of the large amount of dissociation ($K_f = 510$). When enough excess $PhPMe_2$ is added to a solution of the complex to suppress the dissociation to a few per cent of the total (complex ~0.05 *M*, ligand ~0.4 *M*), the ^{31}P-decoupled signal seen in the methyl region is one broad peak (Figure 4). (^{31}P decoupling in both the Br^- and Cl^- systems makes little difference in the spectra. Below about −30° the coupled spectra show some slight broadening, presumably due to ^{31}P coupling in the ligand, and splitting of the peak due to free ligand below the coalescence temperature.) As the temperature is lowered, this peak sharpens, reaching a minimum line width at about −2°. Lowering the temperature still further results in a broadening of this line. At temperatures lower than about −40°, the peak begins to sharpen again, and two small, broad asymmetric peaks appear at either side of the major peak. At the low-temperature limit for CH_2Cl_2 (about −82°), the main peak is sharpened still more, and the two smaller peaks do not become perceptibly larger. It was assumed that the temperature range below −40° was below the coalescence point and that for some reason the signal of the five-coordinate complex is spread into the smaller peaks.

In the chloro system, as in the bromo complex, the methyl signal for the exchanging system is a broad singlet, which sharpens to a minimum line width at about −5° and then broadens below this temperature. The broadening continues until about −62°. At −71° the line width appears to be smaller, and again two small peaks appear flanking the central peak, which is due to free $PhPMe_2$.

The curious behavior of the nmr spectra described above led to a more thorough investigation of the solution behavior of the corresponding four-coordinate complexes, since these species are probably present in the exchanging five-coordinate system. The complexes $Ni(PhPMe_2)_2X_2$, $X^- = Cl^-$ or Br^-, are diamagnetic in the solid state.[8] On the other hand, the

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(14) E. J. Lukosius and K. J. Coskran, private communication, have observed similar behavior.

(15) J. P. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, 91, 1941 (1969).

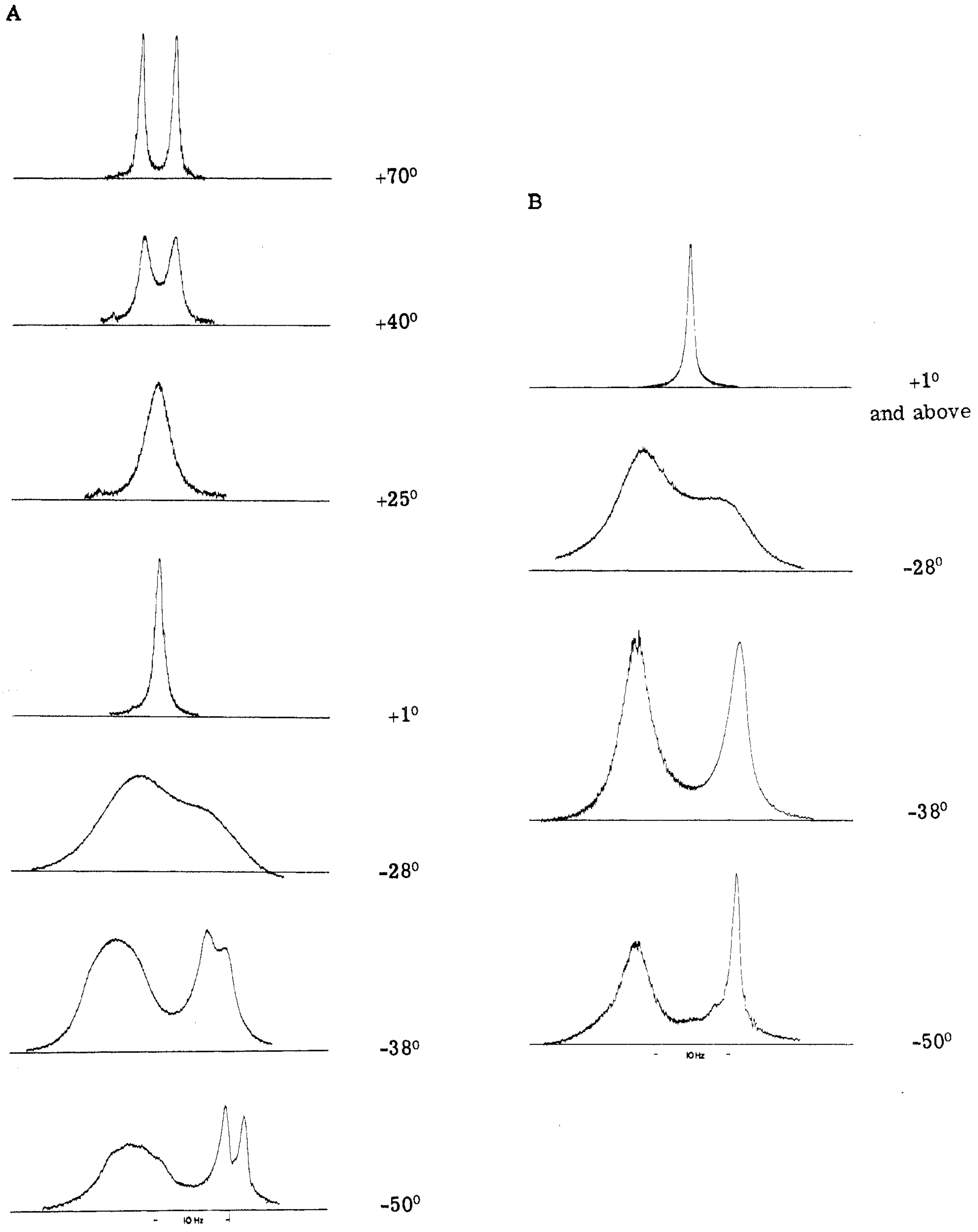

Figure 3. Temperature dependence of the nmr spectrum of Ni[$PC_6H_5(CH_3)_2$]$(CN)_2$ + $PC_6H_5(CH_3)_2$ in CH_2Cl_2: A, no ^{31}P decoupling; B, ^{31}P decoupled.

nmr spectra of solutions of these complexes show contact shifts of the proton signals, indicating the presence of paramagnetic species in solution. These nmr spectra show patterns of temperature dependence typical of planar–tetrahedral equilibria in the four-coordinate complexes[16-18] NiL_2X_2, where L is a di- or triarylphosphine. Venanzi, *et al.*,[19] first noted the existence of solution paramagnetism in these com-

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[16] L. H. Pignolet and W. DeW. Horrocks, Jr., *J Amer. Chem. Soc.*, 91, 3976 (1969).

[17] L. H. Pignolet, W. DeW. Horrocks, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, 92, 1855 (1970).

[18] G. N. LaMar and E. O. Sherman, *J. Amer. Chem. Soc.*, 92, 2691 (1970).

[19] M. C. Browning, J. R. Mellor, D. J. Morgan, S. A. J. Pratt, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 693 (1962).

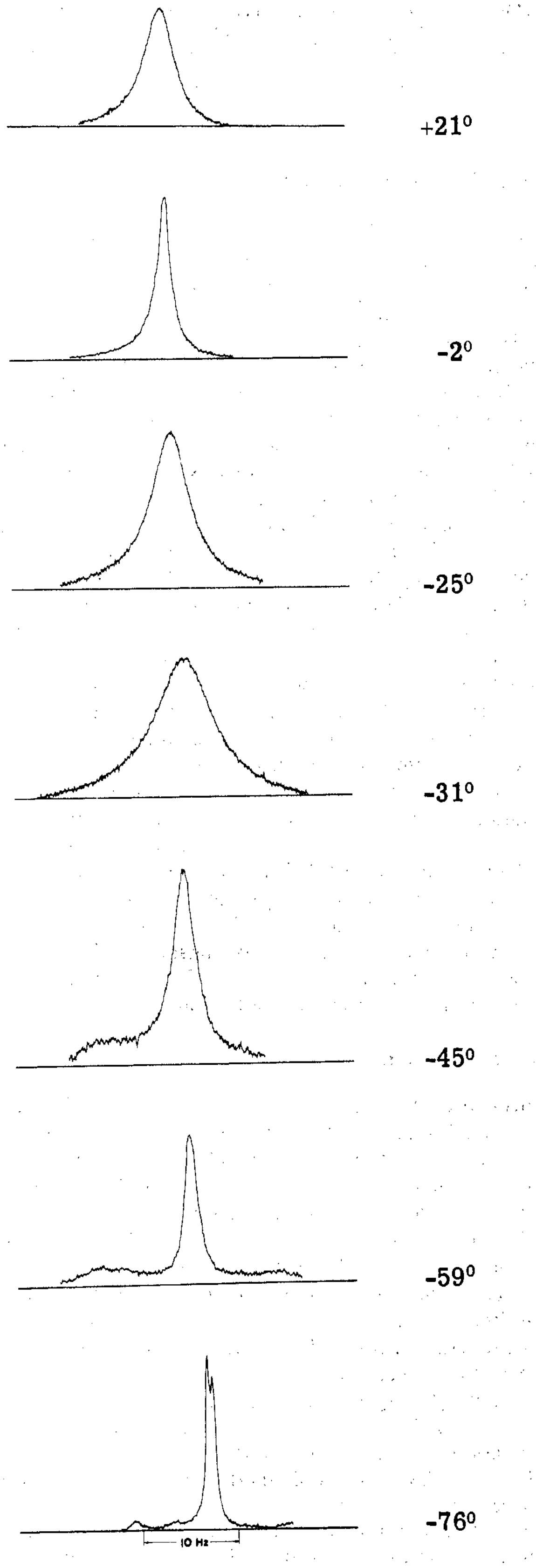

Figure 4. Temperature dependence of the nmr spectrum of Ni-$[PC_6H_5(CH_3)_2]_3Br_2 + PC_6H_5(CH_3)_2$ in CH_2Cl_2.

plexes, concluding that the more aryl groups on the phosphine ligand, the greater the fraction of paramagnetic tetrahedral species present, with monoarylphosphine complexes showing no detectable paramagnetism. We have verified the last statement using the method of Evans.[20] The fraction of tetrahedral isomer was so small that essentially no bulk paramagnetism was detected. This is doubtless the reason that this work represents the first report of planar-tetrahedral isomerism in a monoarylphosphine complex of this type.

At room temperature the methyl group signal for Ni$(PhPMe_2)_2X_2$ appears at about −8.3 ppm (*vs.* TMS) for $X^- = Br^-$ and at about −3.5 ppm for $X^- = Cl^-$. As the temperature is lowered, this signal shifts upfield toward the position of the diamagnetic ligand and broadens simultaneously, finally disappearing into the noise. At about −25° a signal begins to emerge at the diamagnetic complex position and sharpens.

The isotropic shift, $\Delta\nu$, for the signal of a methyl group attached to phosphorus is very large. For the complex $Ni((p\text{-}ClC_6H_4)_2PMe)_2Cl_2$ $\Delta\nu$ has been estimated to be −99 ppm (*vs.* TMS), and a very rough estimate of $N_t^{25°}$, the fraction of tetrahedral isomer in solution, was made using this value. Both the chloro and bromo complexes have less than 7% of the total species present in the paramagnetic tetrahedral form. In accord with the observations of ref 17, the order of stability of the tetrahedral species is $Ni(PhPMe_2)_2Cl_2 < Ni(PhPMe_2)_2Br_2$.

Kinetic parameters for the isomerization were obtained from line-broadening studies of the methyl resonance of the diamagnetic planar species under slow-exchange conditions. Treatment of data was the same as in ref 17 and yielded linear plots of log k_s *vs.* $1/T$. Table IV contains the definitions of rate constants and the activation parameters obtained. These $Ni(PhPMe_2)_2X_2$ systems exhibit no unique features when the values of k_t are compared to the results of Horrocks, *et al.*,[17] and those of LaMar and Sherman.[18] Values for k_t are all of the order of 10^5 sec^{-1} in magnitude, and the ordering of the k_t values is $X^- = Cl^- > Br^-$, as found in the previous work.

Discussion

For the reaction

$$NiL_3(CN)_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NiL_2(CN)_2 + L \qquad (13)$$

where $k_1 = 1/\tau_C$ in Tables I-III, the values for k_1 follow the order $L = Ph_2POEt$ (2.9×10^4 sec^{-1}) > $P(OEt)_3$ (1.1×10^4 sec^{-1}) > $PhPMe_2$ (4.7×10^3) > $PhP(OEt)_2$ (2.9×10^3). Other authors[21] have suggested that if metal-ligand bond breaking is the dominant process, the rates should correlate with the formation constants of the five-coordinate complexes; *i.e.*, the greater K_f, the smaller k_1. Reference to Table III for K_f and k_1 values shows that if K_f were the only factor involved, the ordering of k_1 should be $Ph_2POEt > P(OEt)_3 \sim PhP(OEt)_2 > PhPMe_2$. The ordering is, in fact, $Ph_2POEt > P(OEt)_3 > PhPMe_2 > PhP(OEt)_2$.

The order of basicity in the ligands cannot by itself explain the ordering of rates either. Thorsteinsen[22] has measured the pK_a of $P(O\text{-}n\text{-}Bu)_3$ which is 3.4, and his data also show that other trialkyl phosphites have very similar basicities. Even though our attempt to measure the pK_a's of $PhP(OEt)_2$ and Ph_2POEt was not successful, the pK_a's of these two ligands and $P(OEt)_3$ can be estimated. From Thorsteinsen's data on trialkyl phosphites and knowledge of the pK_a of Ph_3P (2.73),[10] the three ligands of interest must have pK_a's of about 3. $PhPMe_2$ must be the most basic

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Table IV. Kinetic Parameters for NiL_2X_2 Planar–Tetrahedral Inversion in CH_2Cl_2

$$NiL_2X_2(\text{planar}) \underset{k_t}{\overset{k_s}{\rightleftharpoons}} NiL_2X_2(\text{tetrahedral})$$

	$Ni(PhPMe_2)_2Br_2$	$Ni(PhPMe_2)_2Cl_2$
$N_t^{298°K}$, %	7	2
$\Delta H^{\ddagger}$, kcal/mol	15.1 ± 0.2	14.1 ± 0.7
$\Delta S^{\ddagger}$, eu	11.3 ± 0.7	6.5 ± 2.8
$k_s^{298°K}$, sec^{-1}	$17 \times 10^3 \pm 0.2$	$7.6 \times 10^3 \pm 0.7$
$k_t^{298°K}$, sec^{-1}	$2.4 \times 10^5 \pm 0.2$	$3.7 \times 10^5 \pm 0.7$

phosphine used since its pK_a has been measured as 6.50.[10] Lukosius and Coskran[14] have also found an "anomalous" ordering of rates in studies of the exchange reactions of analogous complexes. Their work resulted in the order of decreasing lability $PMe_3 > P(OMe)_3 > MeP(OMe)_2 > MeOPMe_2$. Since PMe_3 complexes are more stable than those with the less basic ligands, the slowest rate of exchange would have been expected for the $Ni(PMe_3)_3(CN)_2$ complex on the basis of formation constants.

For the four systems described herein there is only a factor of 10 between the fastest and slowest rates. Since there is a factor of 10^3 in basicities and K_f values among these systems, and considering that the two systems whose basicities and K_f's are very similar ($P(OEt)_3$ and $PhP(OEt)_2$) have disparate rates, it is doubtful that the differences in k_1 can be interpreted in any meaningful way.

In the halide systems, knowledge of the paramagnetic species present makes the general behavior of the nmr spectra explicable. At low temperatures there is little of the four-coordinate species present at equilibrium and only a small fraction will be paramagnetic. In this range the halide system should behave like the diamagnetic cyanide system. The line width will increase as the temperature decreases (below 0°, Figure 4). At higher temperatures line width is controlled by the effect of ligand substitution in the paramagnetic species. Since the fraction of paramagnetic species, N_t, increases as the temperature increases, the normal behavior is now that line width will increase as temperature increases.[23] This is the behavior seen above 0° in Figure 4.

The data for $Ni(PhPMe_2)_3Br_2$ below the presumed coalescence temperature were analyzed according to 9, which assumes no role for the paramagnetic tetrahedral complex. When $1/\tau_C$ was plotted against $1/T$ on a semilog plot, a good straight line was obtained with $E_A = 5.5$ kcal/mol.

An attempt was made to use the high-temperature data for both the bromo and chloro complexes. The assumption was made that all the line broadening was due to the paramagnetic species and that the isomerization reaction was infinitely rapid. Thus the rate-determining step would be dissociation of the ligand from the five-coordinated complex. Using the equations of Pearson and Lanier,[23] the bromo system gave rate data at high temperatures consistent with that obtained below coalescence (described above), with $E_A = 5.5$ kcal/mol. The chloro system gave $E_A = 7.5$ kcal/mol.

A direct test of the acceptability of these values was made by measuring K_f directly for the equilibrium

$$Ni(PhPMe_2)_2Cl_2 + PhPMe_2 \rightleftharpoons Ni(PhPMe_2)_3Cl_2$$

over a range of temperatures. The results are shown in Table V. The value of $\Delta H° = -16.5$ kcal is reasonable in comparison to data on similar systems.[8] Obviously values of E_A in the 5–7 kcal range are unacceptable since E_A must be $\geq |\Delta H°|$.

Table V. Temperature Dependence of K_f for the Reaction $Ni(PhPMe_2)_2Cl_2 + PhPMe_2 \rightleftharpoons Ni(PhPMe_2)_3Cl_2$[a]

T, °C	K_f
8	133
15	59
25	24

[a] $\Delta H° = -16.5$ kcal/mol in CH_2Cl_2.

An attempt was next made to solve the exchange-modified Bloch equations for a three-site system, following the lead of Swift and Connick.[24] Unfortunately it was found that no simplifying assumptions could be made in the case of the halo complexes. The equations were very complex and contained too many parameters to allow any quantitative conclusions. What can be said is that the exchange rates for the complexes $Ni(PhPMe_2)_3X_2$ have the ordering $CN^- < Br^- < Cl^-$. This can be rationalized on the basis of the ordering of K_f's for these systems. The cyanide complex, which has the largest formation constant and is therefore the strongest complex, would be expected to exchange phosphines at a slower rate than the weaker halide complexes, which bind the phosphines less strongly. Since the phosphine is the same in all three cases, largely eliminating the factors of steric interactions and basicities encountered in the four cyanide systems, this would seem to be a reasonable rationale.

There have been some observations on the halide systems. Pignolet and Horrocks[25] reported a kinetic study of phosphine exchange with some four-coordinate nickel(II) and cobalt(II) complexes ML_2X_2, where M = Ni, Co; $X^- = Cl^-$, Br^-, and I^-; and L = triphenylphosphine (TPP), tri-*p*-tolylphosphine (TTP), and *n*-butyldiphenylphosphine (BPP). In systems containing such bulky ligands as TTP, TPP, and BPP, no significant amounts of the five-coordinate species can be found, and the rate-controlling step is

$$ML_2X_2 + L \overset{k_2}{\rightleftharpoons} ML_3X_2 \tag{14}$$

This appears to be simply the reverse of eq 4. The data obtained for a few of these systems are contained in Table VI, and comparison of these data with the kinetic and thermodynamic parameters for the $NiL_3(CN)_2$ systems listed in Table III is of some interest.

The second-order rate constants k_2 for the cyanide systems are on the whole quite a bit greater than the k_2 values for the halide systems. In the cyanide systems, $\Delta H°$ and E_A for dissociation (rate constant k_1) are equal within experimental error in cases where both have been measured. This means that the activation energy for the bimolecular reaction, k_2, of $NiL_2(CN)_2$ with L must be nearly zero. The $\Delta H^{\ddagger}$ values in the halide systems show that the corresponding activation energies are substanital, certainly not near zero. This raises the question of whether the same mechanism is operating in both cases.

In the four-coordinate halide systems the predominant species present is the tetrahedral form. It was reasonably assumed by Pignolet and Horrocks[25] that this was the reactive species. In other words k_2 referred to the attack

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Table VI. Kinetic Parameters for Ligand Exchange with ML_2X_2 [a] in $CDCl_3$ at 25° (L = TPP = Triphenylphosphine)

Complex	k_2, M^{-1} sec^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
NiL_2Cl_2	3.2×10^5	8.1 ± 0.8	-7 ± 4
NiL_2Br_2	6.9×10^3	4.7 ± 0.4	-25 ± 2
NiL_2I_2	6.4×10^2	6.9 ± 0.6	-23 ± 3

[a] From ref 25.

of a free phosphine molecule on the tetrahedral ML_2X_2. In the cyanide systems the dominant four-coordinate species is the planar isomer. It has been assumed that k_2 relates to attack of a free phosphine on this planar species.

The differences in activation parameters and rate constants are consistent with these two assumptions. Alternatively, if attack were always on the planar form, even for the halide complexes, the slower rates and larger activation energies could be explained. The activation energies would be largely due to the value of $\Delta H°$ relating the high-energy planar form to the low-energy tetrahedral form.

It is of interest to note that the structures of the five-coordinated cyano complexes are well established with the cyano groups trans.[26] This is just what would be expected for addition of a third phosphine to *trans*-$NiL_2(CN)_2$. The three L ligands lie in an approximately trigonal plane.[18] As part of this study the comparison of solution and solid-state infrared and visible-uv spectra showed that in solution these complexes have the same trans structure as that determined in the crystals.

The structures of the five-coordinated halo complexes are not known. From spectral data it has been argued that $Ni(PMe_3)_3X_2$ is both cis[27] and trans.[28] If a phosphine attacked a tetrahedral complex in the usual SN2 mechanism, the intermediate NiL_3X_2 would have both halide ligands in the trigonal plane, and hence cis to each other.

The structure of PdL_3Br_2,[29] where L = 2-phenylisophosphindoline, is in fact square pyramidal, with Br axial. This lends support to the argument that the structures and behavior of the five-coordinated nickel(II)-cyano and -halo complexes are indeed different.

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Registry No. $Ni(PhP(OEt)_2)_3(CN)_2$, 15282-55-0; $Ni(P(OEt)_3)_3(CN)_2$, 49756-79-8; $Ni(Ph_2POEt)_3(CN)_2$, 50322-08-2; $Ni(PhPMe_2)_3(CN)_2$, 24419-46-3; $Ni(PhPMe_2)_3Br_2$, 49756-80-1; $Ni(PhPMe_2)_2Cl_2$, 25456-42-2; $Ni(PhPMe_2)_2Br_2$, 25456-40-0.

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Nuclear Magnetic Resonance Studies of Configuration and Ligand Conformation in Paramagnetic Octahedral Complexes of Nickel(II). IX. 1,3-Diamine Chelates

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Proton nuclear magnetic resonance spectra have been utilized in detailing the stereochemistry of six-membered rings formed by chelation of nickel(II) ion with selected 1,3-diamines. A correlation between the magnitude of observed contact shifts for the $CH_2(NH_2)$ protons and their Ni-N-C-H dihedral angle analogous to that reported in the 1,2-diamine-nickel(II) chelates has been found. In addition, the existence of a definite angular dependence of the contact shifts across four bonds to the central methylene group protons has been elucidated. Rapid conformational interconversion of these chelate rings allows the utilization of the ligand proton contact shifts as a sensitive probe of chelate ring conformations in solution. As in other saturated six-membered rings, the chair conformation is found to be most stable; however, the skew-boat conformer lies at relatively low energy, with respect to the chair, ΔG = 1.4 kcal/mol in the tetraaquo-1,3-diaminopropane-nickel(II) chelate. Data reveal that accommodation of alkyl groups in an axial environment of the chair conformation can engender unfavorable steric interactions, and this destabilization can introduce significant amounts of twist conformer in the equilibrium distribution; tetraaquo-*rac*-2,4-diaminopentanenickel(II) ion, for instance, exists in an essentially equal distribution of skew-boat and chair conformers at 300°K. The bis chelate of this latter ligand is found to be engaged in an octahedral square-planar equilibrium in solution, with octahedral species containing chelate rings of both chair and skew-boat conformations being identified. Tris(1,3-diaminopropane)nickel(II) ion is found to racemize rapidly on the nmr time scale, and this rate is estimated to be 1.1×10^4 sec^{-1} at 72°; the free energy of activation for this process is 14 kcal/mol at that temperature.

Introduction

The proton magnetic resonance spectra of pseudooctahedral paramagnetic nickel(II) complexes have recently been shown to contain a wealth of stereochemical information.[1,2] With the appreciation of the dihedral angular dependence of contact shift across the Ni-N-C-H moiety,[1,3] an extremely sensitive configurational and conformational probe has been elucidated for these chelates, and a number of useful applica-

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