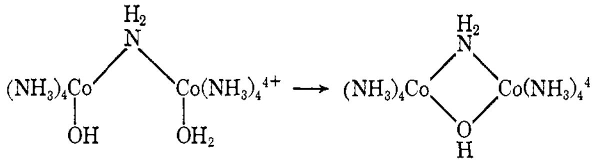
formed directly at pH 7.5 (0.45 sec^{-1} at 4°). This showed that the intermediates **2A** and **2B** at the two pH's are related by some simple (and scheme 6 indicates an acid–base) equilibrium, and that they are not radically different species. The pK values for the intermediate are 10.9 and <7.0 and these do not seem unreasonable in view of the values for the mononuclear α-*cis*-Co(trien)$(H_2O)_2^{3+}$ ion (7.6 and 5.3).[13] The higher value for the intermediate, however, presents a slightly disturbing feature to our explanation. At pH 9.0 there should be virtually no pH change for the second stage, since only condensation with removal of an H_2O molecule occurs. We observe a small pH increase and can only conclude that this small pH change is a result of some unknown secondary reaction. The rate constant for the transformation **2A** → **3** (2.0 sec^{-1} at 25°) might be considered high for the reaction of a cobalt(III) complex, but for reaction 8 the relatively high value of 0.013 sec^{-1} has been measured.[14] In order to estimate this value it is necessary to use the measured pK of 6.2 for the reactant. The second pK must be much higher and this behavior resembles our system. Reaction 8 shows an anchiomeric effect, the NH_2 bridge holding the two cobalt-coordinated OH and H_2O groups close together for reaction. Such an effect can also be envisaged with reaction 6, one of the Co-O_2 bonds easily rotating from the normal Co-O-O-Co staggered conformation.[15] The low rate constant for **2B** → **3** ($\approx$0.012 sec^{-1}) reflects the difficulty of replacement of an hydroxy group compared with coordinated water.



(8)

The product **3** slowly changes color from brown to strawberry pink. This takes about 2 weeks at room temperature at pH ~12, but very much longer at lower pH's. The spectra of the pink product indicates that it contains the mononuclear cobalt(III) complex *cis*-β-Co(trien)$(OH)_2^+$ ion,[16] the production of which from the bridged species must be base-catalyzed. It is not yet known whether the final β configuration of the trien is also in the double bridged **3**, or whether it results from isomerization processes involving the mononuclear complex. The *cis* is preferred to the *trans* configuration with the tetramine, trien.[19]

Acknowledgment. We thank Drs. S. Fallab and R. B. Martin for information prior to publication, and we acknowledge, with gratitude, the support of this work by a National Science Foundation Grant (No. GP-8099), and a Union Carbide Fellowship (to F. M.).

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[13] D. A. Buckingham, J. P. Collman, D. A. R. Happer, and L. G. Marzilli, *J. Amer. Chem. Soc.*, **89**, 1082 (1967).

[14] M. B. Stevenson, R. D. Mast, and A. G. Sykes, *J. Chem. Soc., A*, 937 (1969).

[15] W. P. Schaefer, *Inorg. Chem.*, 7, 725 (1968).

[16] Acidifying the pink solution to pH 3.0 produces an orange-pink colored ion, with a maximum at 493 mμ (ϵ_M 123) to be compared with the *cis*-β-Co(trien)$(H_2O_3)^{3+}$ ϵ_{487}^{max} 122, and the *cis*-α form, ϵ_{500}^{max} 87.[17] The *trans*-Co(trien)$(H_2O)_2^{3+}$ ion has only a shoulder at 495 mμ.[18]

[17] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).

[18] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *ibid.*, **6**, 1032 (1967).

[19] See B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc., A*, 1331 (1966), for a discussion of this point.

A Proton Nuclear Magnetic Resonance Investigation of the Kinetics of Tetrahedral $\rightleftharpoons$ Planar Isomerization of Bis(*n*-alkyldiphenylphosphine)nickel(II) Dihalides

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Abstract: The rates of tetrahedral, paramagnetic $\rightleftharpoons$ planar, diamagnetic isomerization have been determined for a series of bis(*n*-alkyldiphenylphosphine)nickel(II) dihalides, $(RP(Ph)_2)_2NiX_2$ (R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9; X = Cl, Br, I), by analysis of the proton magnetic resonance line-width dependence on temperature. The first-order kinetics, ~10^5–10^6 sec^{-1} at 25°, depend on both R and X. In the presence of excess ligand, an additional second-order ligand-exchange mechanism also contributes to the rate of isomerization. Although some reproducible trends in rate constants appear to characterize the variables, such as I > Cl > Br for fixed R, and C_2H_5 > *n*-C_4H_9 $\gtrsim$ *n*-C_3H_7 > CH_3 for fixed X, no simple relationship between ligand steric and/or electronic properties was found. Though the thermodynamics are more regular, some differences between expected and observed trends are also noted. Some reasons for the complex dependence of the rate of isomerization on R and X are discussed.

It is now well established[1–4] that a number of four-coordinated nickel(II) complexes possess sufficiently similar ground-state free energies for the pseudotetrahedral, paramagnetic, and planar, diamagnetic configurations so that both states are appreciably

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[1] Salicylaldimines: L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Amer. Chem. Soc.*, 85, 411 (1963).

[2] (a) Salicylaldimines: R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, 86, 379 (1964); (b) aminotroponimines: D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, 85, 397 (1963); (c) naphthaldimines: A. Chakravorty and R. H. Holm, *Inorg. Chem.*, 3, 1010 (1964); (d) β-ketoimines: G. W. Everett, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, 87, 2117 (1965); (e) pyrrol-3-aldimines: R. H. Holm, A. Chak-

populated in solution at ambient temperatures. The equilibrium for such a structural interconversion can be represented as

$$\text{planar } (S = 0) \overset{\Delta G}{\rightleftharpoons} \text{tetrahedral } (S = 1)$$

where ΔG is the free-energy change accompanying the conversion. A similar equilibrium has also been reported[5] between the $S = {}^1/_2$ and $S = {}^3/_2$ states of four-coordinated cobalt(II).

One of the most convenient and accurate techniques for characterizing the thermodynamics of this type of equilibrium has been the detection[2] of large isotropic shifts for the mixture of isomers in solution, which result from delocalization[2,6] of unpaired spin in the paramagnetic isomer. Thus a knowledge of the coupling constant A_i in the tetrahedral isomer allows one to obtain the fraction of paramagnetic isomer, N_t, at any temperature using the well-known equation[2]

$$\left(\frac{\Delta H}{H}\right)_i = -A_i \frac{\gamma H}{\gamma e}\frac{g\beta S(S + 1)}{6SkT} N_t \qquad (1)$$

where all notations are standard.

Extensive investigations of the thermodynamics[2] of this equilibrium for a large number of nickel complexes has established that the planar state is nearly always electronically more stable, but is readily depopulated in favor of the tetrahedral configuration by steric ligand–ligand interactions. Thus for a number of bis chelates bonded through nitrogen, the stability of the tetrahedral isomer was markedly enhanced[2a–h] as the nitrogen substituents increased in size or bulkiness.

Although steric interactions tend to dominate the position of the equilibrium, electronic effects are also operative, as evidenced by a series of N-phenylaminotroponimine[2b] chelates, where increasing electronegativity of the *para* phenyl substituent tended to favor the planar isomer. For the bis(tertiary phosphine)-nickel dihalides,[3,4] it has been proposed that the weakening of the ligand field as one passes from $R_3P \rightarrow R_2P(C_6H_5) \rightarrow RP(C_6H_5)_2 \rightarrow P(C_6H_5)_3$ accounts for the increased tendency to populate the tetrahedral isomer, which appears to conflict with the observations[2b] on the aminotroponimines.

Thus, although the thermodynamics for this equilibrium are now well characterized,[2] almost nothing is known about the kinetics of this novel isomerization. Since the proton spectra exhibit only completely averaged shifts, a lower limit for the interconversion rate, k, of $>10^5$ has been obtained.[7] The complete resolution of the optical spectra for the two isomers dictates that $k \ll 10^{14}$ sec^{-1}. In principle, analysis of nmr line widths[8,9] could yield information on this kinetic process if k^{-1} is comparable to the isotropic shift. However, lowering the temperature to the experimental limit has failed to produce[2] detectable line broadening which could be attributed to the kinetics of the equilibrium in any of the previously reported complexes.

The bis(*n*-alkyldiphenylphosphine)nickel dihalides, designated $(RP(Ph)_2)_2NiX_2$, have been shown,[3] using optical and magnetic data, to also participate in this structural equilibrium. Recently we gave a preliminary report[10] that for $(CH_3P(Ph)_2)_2NiBr_2$ and $(CH_3P(Ph)_2)_2NiI_2$, although only averaged proton nmr spectra were observed at ambient temperatures, lowering the temperature had the effect of increasing the line widths until for each ligand position, the averaged peak split into two resonances, one for the tetrahedral isomer and one for the planar isomer. This was the first example of the direct observation of the kinetics of this isomerization. We wish to report here a more extensive investigation of the kinetics and thermodynamics of this equilibrium for R = methyl, ethyl, *n*-propyl, and *n*-butyl, and X = Cl, Br, and I complexes using proton magnetic resonance.

Experimental Section

Complexes and Sample Preparation. Preparation of the bromo and iodo complexes was carried out according to the method of Venanzi[11] in which a stoichiometric amount of the alkyldiphenylphosphine in hot butanol is added to a hot butanol solution of the nickel halide. The chloro complexes were prepared in a similar manner but with ethanol as solvent. All the compounds were synthesized in a Vacuum Atmospheres Corp. Dri-Lab to prevent oxidation of the ligand. Upon cooling of the reaction mixture the complex was obtained in good yield (60–80%) as crystalline solids. The complexes were purified by a double recrystallization from either dry butanol or ethanol. The analytical results are given in Table I.

Ethyldiphenylphosphine was obtained commercially (Orgmet, Inc.). The remaining phosphines were prepared by the reaction of diphenylphosphorus chloride (Wilshire Chemical Co.) with a suitable alkyl Grignard reagent (Peninsular ChemResearch). This reaction was carried out in ether under an argon atmosphere in the conventional manner. Purification of all the phosphines was accomplished by fractional distillation at reduced pressure. Infrared spectra and proton magnetic resonance spectra served to substantiate the identity and purity of the distilled products.

The solutions for the nuclear magnetic resonance measurements were prepared in the drybox in a 1-ml volumetric flask. A weighed portion of complex was made up to the mark with dry d_2-methylene chloride (Merck Sharp and Dohme) and a small amount of tetramethylsilane was added. The solution was transferred to resonance tubes; the tubes were capped and the caps tightly taped with Teflon tape. Initially the tubes were sealed with a torch under a nitrogen stream. However, the high volatility of the solvent, even at low temperatures, always caused a carbon deposit to be formed at the seal. Some of this deposit often dropped into the sample during the measurements and caused appreciable line broadening. Taping the cap to tube joint prevented this contamination and allowed no sample oxidation. No change in the observed magnetic resonance spectra was detected in a 12-hr period with the taped caps.

For the magnetic susceptibility measurements the sample was prepared in a manner similar to that used for the magnetic resonance samples using AR grade methylene chloride.

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ravorty, and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966); (f) 2-acetimodimedones: S. Y. Shaw and E. P. Dudek, *ibid.*, 8, 1360 (1969); (g) β-iminothiones: D. H. Gerlach and R. H. Holm, *J. Amer. Chem. Soc.*, **91**, 3454 (1969); (h) 3-aminomethylenecamphor: C. R. Powers and G. W. Everett, Jr., *ibid.*, **91**, 3468 (1969); (i) ditertiary phosphines: G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1968 (1966); a review of some of the above systems is found in R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966).

(3) Alkyldiphenylphosphines: (a) C. R. Coussmaker, M. H. Hutchinson, J. R. Mellor, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 2705 (1961); (b) R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, **4**, 1701 (1965).

(4) Allyldiphenyl- and benzyldiphenylphosphines: 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).

(5) G. W. Everett, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 2442 (1966); *Inorg. Chem.*, **7**, 776 (1968).

(6) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

(7) D. R. Eaton, *J. Amer. Chem. Soc.*, **90**, 4272 (1968).

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 10.

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

(10) G. N. La Mar and E. O. Sherman, *Chem. Commun.*, 809 (1969); a similar observation was also reported by L. H. Pignolet and W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, **91**, 3976 (1969).

(11) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

Table I. Elemental Analyses

Complex	Calcd, %				Found, %			
	C	H	P	X	C	H	P	X
$(CH_3P(Ph)_2)_2NiCl_2$[a]	58.91	4.94	11.69	13.38	59.1	5.0		13.3
$(CH_3P(Ph)_2)_2NiBr_2$	50.45	4.23	10.01	25.82	50.1	4.4		25.5
$(CH_3P(Ph)_2)_2NiI_2$	43.80	3.68	8.69	35.60	44.0	3.9		35.1
$(C_2H_5P(Ph)_2)_2NiCl_2$	60.26	5.42	11.1	12.71	60.3	5.3	11.7	12.4
$(C_2H_5P(Ph)_2)_2NiBr_2$	51.98	4.67	9.57	24.70	51.8	4.9	9.9	24.0
$(C_2H_5P(Ph)_2)_2NiI_2$	45.38	4.08	8.36	34.25	45.5	4.2	8.9	
$(n\text{-}C_3H_7P(Ph)_2)_2NiCl_2$	61.47	5.85	10.57	12.10	61.4	5.8	11.3	12.3
$(n\text{-}C_3H_7P(Ph)_2)_2NiBr_2$	53.38	5.08	9.18	23.68	53.3	5.0		23.2
$(n\text{-}C_3H_7P(Ph)_2)_2NiI_2$	46.85	4.46	8.06	33.00	46.6	4.4	8.6	33.0
$(n\text{-}C_4H_9P(Ph)_2)_2NiCl_2$	62.58	6.24	10.09	11.54	62.0	6.2	10.0	12.3
$(n\text{-}C_4H_9P(Ph)_2)_2NiBr_2$	54.66	5.45	8.81	22.73	54.2	5.4		23.0
$(n\text{-}C_4H_9P(Ph)_2)_2NiI_2$	48.22	4.80	7.77	31.84	47.2	4.7	7.9	32.0

[a] In the formulas for the complexes, Ph represents phenyl, C_6H_5.

Nmr Spectra. The proton nmr spectra were recorded on a Varian HR-100 spectrometer modified to operate with variable modulating frequency. TMS was used as the internal reference and the shifts were calibrated by the conventional audio side-band technique. The sample temperature was controlled by a Varian V 4343 temperature control unit which was precalibrated with methanol. The solvent for all spectra was d_2-methylene chloride, which had the advantages over *d*-chloroform of better solubility and lower freezing point, both of which were necessary for our investigation.

All sample concentrations were 0.07 *M*, except where otherwise noted, and except for $(C_2H_5P(Ph)_2)_2NiI_2$, whose maximum solubility was 0.046 *M*. A number of samples were run at both 0.07 and 0.04 *M* to determine any concentration effects on the spectra.

The spectra of each complex were recorded between $\sim +40$ and $\sim -80°$ in intervals of 3–10°, with the smaller intervals used in the region where exchange broadening was detected. The temperature dependence of both the shifts and line widths was recorded for all resolved peaks. Owing to the severe overlap of the *o*-H and *p*-H peak and most of the alkyl peaks, it was possible to obtain reliable data only for the *m*-H resonance. For the observed line width, defined as the peak width at half-height, the lowest practical power levels were employed. Line-width and shift data were also obtained at $-60°$ for 0.06 *M* $(CH_3P(Ph)_2)_2NiBr_2$ solutions containing 0.00, 0.0012, and 0.0018 *M* excess ligand, and for a 0.04 *M* solution of this complex with 0.0012 *M* excess ligand.

The line widths, given in Hz at 100 MHz, represent the average of four traces and are accurate to ±10%. The isotropic shifts are reported in ppm, referenced against the diamagnetic, planar bromide isomer of each ligand, whose shifts were obtained from the low-temperature traces in the limit of very slow isomer interconversion; upfield shifts are defined as positive.

The solution magnetic susceptibilities were determined by the method of Evans,[12] using a Varian A-60 spectrometer.

Treatment of Data

Isotropic Shifts and Thermodynamic Parameters. The proton–electron coupling constants were obtained directly from the shift data[13] of the tetrahedral isomer in the limit of slow exchange using eq 1. For four complexes (X = Cl, R = CH_3; X = I, R = C_2H_5, *n*-C_3H_7, and *n*-C_4H_9), the limit of slow exchange was not attainable experimentally, and their coupling constants were estimated by assuming[14] the same relative *p*-H coupling constants as a function of alkyl group as observed for the X = Br complexes.

The fraction of paramagnetic isomer, N_t, for each complex in solution was obtained from the ratio of the observed averaged *m*-H isotropic shift in the limit of rapid isomerization to the shift for the tetrahedral isomer at that temperature. The latter shift was obtained by extrapolating the low-temperature Curie behavior (as shown in Figures 2 through 4). N_t was also estimated from the solution magnetic moment, μ_{eff}, by the equation[2]

$$N_t = (\mu_{\text{eff}}/\mu_t)^2 \qquad (2)$$

where μ_t is the moment for the tetrahedral isomer.

ΔG for the equilibrium was obtained[2,6] by

$$N_t = (\exp(\Delta G/RT) + 1)^{-1} \qquad (3)$$

using the N_t obtained from the shift data. Since $\Delta G = \Delta H - T\Delta S$, ΔH and ΔS were obtained from a plot of ΔG *vs.* $1/T$. The uncertainty in ΔH and ΔS values are ±10% and ±0.5 eu, respectively, and arise primarily from temperature and shift uncertainties.

Line Widths and Kinetic Parameters. In the limit of fast exchange, the line widths were analyzed by the conventional equation[8]

$$\frac{1}{T_2} = \frac{N_t}{T_{2t}} + \frac{N_s}{T_{2s}} + N_t^2N_s^2(\omega_t - \omega_s)^2(\tau_t + \tau_s) \qquad (4)$$

where N_s is the fraction planar isomer, T_{2t} and T_{2s} are the transverse relaxation times in the absence of exchange for the tetrahedral and square-planar complexes, respectively, and T_2 is related to the observed line width by $\pi\delta_{1/2} = 1/T_2$, $\omega_t - \omega_s$ is the isotropic shift for the tetrahedral isomer, and τ_t and τ_s are the lifetimes of the tetrahedral and planar isomers, respectively. The lifetimes are related[9] to the rate constants

$$\text{tetrahedral} \underset{k_s}{\overset{k_t}{\rightleftarrows}} \text{planar}$$

by $k_t = \tau_t^{-1}$ and $k_s = \tau_s^{-1}$.

$1/T_{2t}$ was estimated from the line widths of the *m*-H peak of the tetrahedral isomer at low temperature, where there is no contribution from exchange, and from the observed data in the limit of very rapid exchange at high temperatures, by dividing the observed widths by N_t. The line width as a function of temperature was represented by a straight line connecting the low- and high-temperature points on a log plot, as is observed[15,16]

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(12) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(13) The diamagnetic resonances for the planar complexes at $\sim -75°$ are *o*-H = -7.80 ± 0.03, *m*-H and *p*-H = -7.45 ± 0.05, α-$CH_{2,3}$ = -2.20 ± 0.10, β-CH_2 = 1.50 ± 0.10, β-CH_3 = 1.20 ± 0.03, γ-CH_2 = 1.45 ± 1.03, γ-CH_3 = 0.95 ± 0.03, δ-CH_3 = 0.90 ± 0.03, referenced against TMS, where the α carbon is attached to the phosphorus. The shifts of the diamagnetic complexes differ from those of the free ligand in that the ring protons are shifted downfield by 0.2–0.4 ppm, and the *o*-H resonance is resolved from the *m-H* and *p*-H peaks.

(14) Since the *p*-H hyperfine coupling constants for the bromo complexes varied only ~5% with R, as shown in Table III, our estimate should yield valid results.

(15) G. N. La Mar, *J. Phys. Chem.*, **69**, 3212 (1965).

(16) L. H. Pignolet and W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, **90**, 922 (1968).

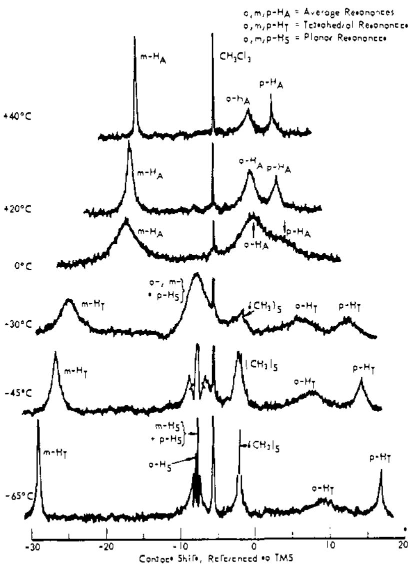

Figure 1. Proton nmr traces of $[CH_3P(C_6H_5)_2]_2NiBr_2$ in CD_2Cl_2 as a function of temperature.

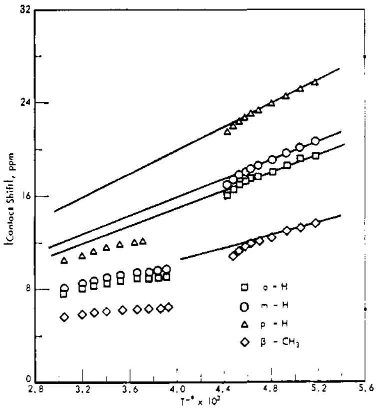

Figure 2. Curie plot for 0.07 M $[(C_2H_5)P(C_6H_5)_2]_2NiBr_2$ in CD_2Cl_2.

in related complexes where exchange effects are absent. A dotted line in Figure 5A gives the dependence of $1/(\pi T_{2t})$ on temperature for $(CH_3P(Ph)_2)_2NiBr_2$. Although the low-temperature line widths in the absence of exchange were not attainable for any but the bromide complexes, similar plots of $(T_{2t}\pi)^{-1}$ *vs.* T^{-1} were obtained for the remaining complexes by drawing lines parallel to that for the analogous bromide complex through the averaged line width (divided by N_t) in the limit of very rapid exchange, which were accessible for all complexes. Similar parallel lines have been observed for the related triphenylphosphine complexes[15,16] of Ni(II) and Co(II).

The diamagnetic *m*-H line width was estimated as ~5 Hz as observed for the aromatic peaks at −75° for $(CH_3P(Ph)_2)_2NiBr_2$. Proton spin–spin coupling in the diamagnetic isomer was not observed.[17] Those data points used in the kinetic analyses had contributions from exchange one to two orders of magnitude greater than the maximum diamagnetic line width. Since $\tau_t N_s = \tau_s N_t$,[9] $k_t = \tau_t^{-1} = [(\tau_t + \tau_s)N_t]^{-1}$.

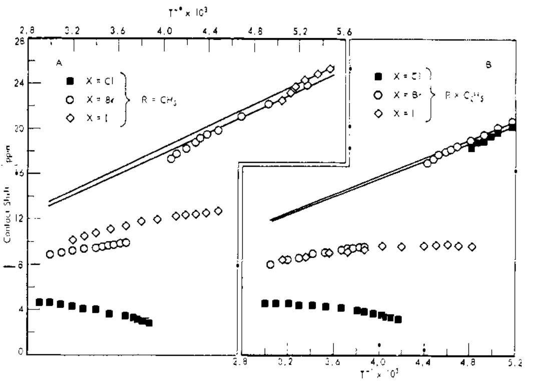

Figure 3. Curie plots for *m*-H contact shift for 0.07 M CD_2Cl_2 solutions of (A) $[(CH_3)P(C_6H_5)_2]_2NiX_2$ and (B) $[(C_2H_5)P(C_6H_5)_2]_2$-NiX_2.

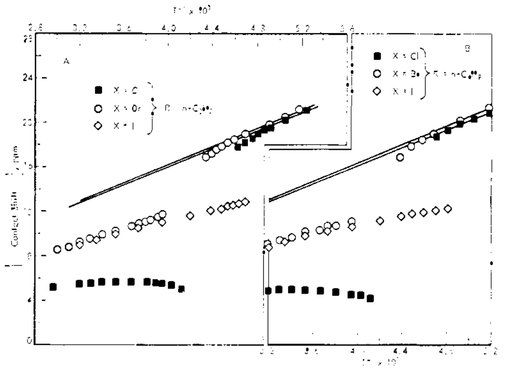

Figure 4. Curie plots for *m*-H contact shift for 0.07 M CD_2Cl_2 solutions of (A) $[(n\text{-}C_3H_7)P(C_6H_5)_2]_2NiX_2$ and (B) $[(n\text{-}C_4H_9)P$-$(C_6H_5)_2]_2NiX_2$.

In the limit of slow exchange, the applicable equation[8] for the observed line width for the tetrahedral isomer is

$$\pi\delta_{1/2} = \frac{1}{T_t} = \frac{1}{T_{2t}} + \frac{1}{\tau_t} = \frac{1}{T_{2t}} + k_t \qquad (5)$$

The method of shifts,[18] used successfully in analyzing the line width in the intramolecular rearrangements, was not practical here since the diamagnetic ring protons overlapped too severely to detect any change in their position previous to collapse of the two spectra upon raising the temperature. The deviations from Curie behavior for the tetrahedral shifts just before collapse of the spectra are noticeable (see eq 2–4).

Assuming the Eyring equation is valid[19] for the isomerization

$$k_t = \frac{kT}{h}\exp(-\Delta F^{\ddagger}/RT) = \frac{kT}{h}\exp(\Delta H^{\ddagger}/RT)\exp(\Delta S^{\ddagger}/R) \qquad (6)$$

using standard notation, the kinetic data were analyzed by plotting log k_t/T *vs.* $1/T$ to obtain $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$.

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[17] Even the free ligand exhibited aromatic resonances which, though they consisted of a number of very closely spaced lines, the total width or spread for either the *o*-H or *p*-H and *m*-H peaks did not exceed ~10 Hz at 100 MHz.

(18) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(19) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp 195, 196.

Table II. Proton Hyperfine Coupling Constants for the Pseudotetrahedral $[RP(C_6H_5)_2]_2NiX_2$ Complexes[a]

		Ligand coupling constants, A_i						
R	X	o-H	m-H	p-H	α-$CH_{2,3}$	β-$CH_{2,3}$	γ-$CH_{2,3}$	δ-CH_3
CH_3	Cl[b]	−0.033	0.041	−0.049	0.38			
	Br	−0.0347	0.0424	−0.0488	0.38			
	I	−0.0365	0.0444	−0.0503	0.36			
C_2H_5	Cl	−0.0345	0.0365	−0.0466	0.45	0.0161		
	Br	−0.0376	0.0397	−0.0498	0.46	0.0243		
	I[b]	−0.038	0.041	−0.052	0.40	0.026		
n-C_3H_7	Cl	−0.0343	0.0407	−0.0478	0.51	−0.0086	0.0091	
	Br	−0.0380	0.0417	−0.0512	0.47	−0.0094	0.0124	
	I[b]	−0.037	0.041	−0.050	0.40	−0.0035	0.014	
n-C_4H_9	Cl	−0.0335	0.0381	−0.0468	0.42	−0.0066	0.0082	0.0037
	Br	−0.0376	0.0398	−0.0503	0.43	−0.0095	0.0083	0.0054
	I[b]	−0.035	0.037	−0.045	0.34	−0.0078	0.0082	0.0049

[a] A_i given in gauss. g in eq 1 was obtained from magnetic moments in Table III using $\mu = \sqrt{S(S+1)}$. [b] The proton spectrum of the pure tetrahedral isomer not observed. A_i was estimated by assuming the same relative p-H coupling constants with R as observed for X = Br.

Results

The effect of temperature on the ligand shifts and line widths for $(CH_3P(Ph)_2)_2NiBr_2$ in CD_2Cl_2 is illustrated in Figure 1. The temperature at which the two spectra coalesce is −13°. Figure 2 exhibits the Curie plot for all but the α-CH_2 ligand protons for $(C_2H_5P(Ph)_2)_2NiBr_2$ in CD_2Cl_2. The Curie plots for the m-H shifts for each of the twelve complexes are reproduced in Figures 3 and 4. The observed coupling constants for each complex are listed in Table II.

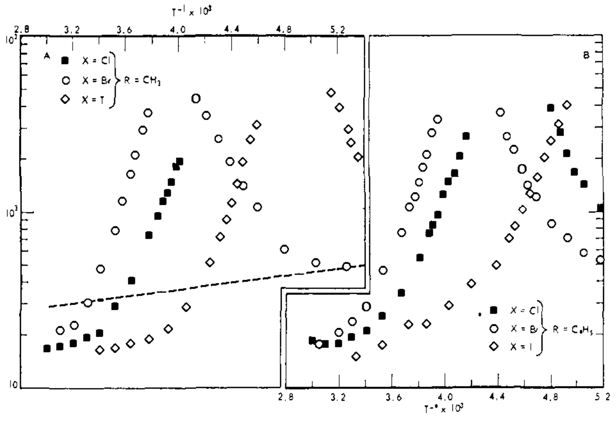

Figure 5. Plot of observed line width vs. reciprocal temperature for 0.07 M CD_2Cl_2 solutions of (A) $[(CH_3)P(C_6H_5)_2]_2NiX_2$ and (B) $[(C_2H_5)P(C_6H_5)_2]_2NiX_2$.

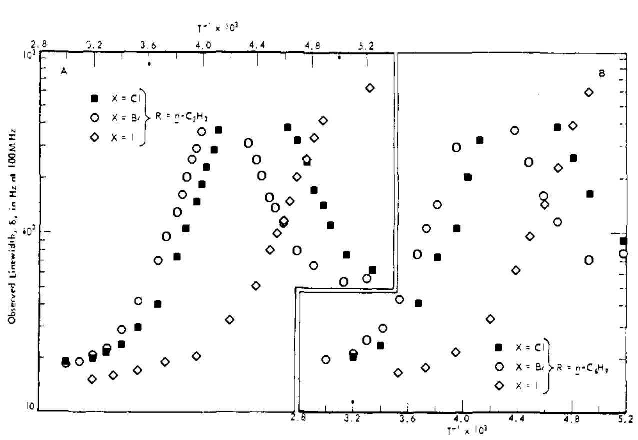

Figure 6. Plot of observed line width vs. reciprocal temperature for 0.07 M CD_2Cl_2 solutions of (A) $[(n\text{-}C_3H_7)P(C_6H_5)_2]_2NiX_2$ and (B) $[(n\text{-}C_4H_9)P(C_6H_5)_2]_2NiX_2$.

In Figures 5 and 6 we present the effect of temperature on the observed m-H line width for each complex. The dotted line in Figure 5A represents the line width of the tetrahedral $(CH_3P(Ph)_2)_2NiBr_2$ isomer in the absence of exchange broadening.

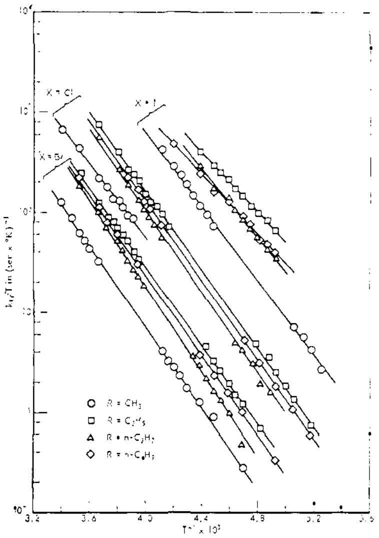

Figure 7. Log (k_t/T) vs. T^{-1} plot for 0.07 M $[RP(C_6H_5)_2]_2NiX_2$ complexes in CD_2Cl_2.

The thermodynamic parameters resulting from the analysis of the shifts and the kinetic parameters from the conventional analysis of the line widths are listed in Tables III and IV, respectively. The linearity of the plots of log (k_t/T) vs. $1/T$ is illustrated in Figure 7. The solution magnetic moments are also included in Table III.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are estimated to be accurate to ±0.4 kcal/mol and ±3 eu, respectively, for those complexes for which line-width data were available in both the slow- and fast-exchange regions. The errors are more sizable, ±1.5 kcal/mol and ±6 eu, respectively, for the remaining complexes. Also included in Table IV are the extrapolated rate constants at 298°K, k_t^{298} for all complexes. Due to the large errors in $\Delta H^{\ddagger}$ for complexes with X = I and R = C_2H_5, n-C_3H_7, and n-C_4H_9, only lower limits to k_t^{298} are given.

Table III. Thermodynamic Parameters for Tetrahedral ⇌ Planar Interconversion of 0.07 M [$RP(C_6H_5)_2]_2NiX_2$ Complexes in CD_2Cl_2

R	X	Magnetic susceptibility data[a] μ_{solid}	μ_{soln}	% T_d	Nmr shift data % T_d	ΔG	ΔH	ΔS
CH_3	Cl		1.82	30 ± 3	32 ± 3	+540	2210[b]	5.6[b]
	Br	3.37	2.58	59 ± 6	65 ± 1	−320	650	3.3
	I	3.32	2.72	67 ± 7	69 ± 1	−480	540	3.4
C_2H_5	Cl		2.06	44 ± 5	36 ± 1	+420	1460	3.5
	Br	3.2	2.69	71 ± 7	67 ± 1	−400	430	2.8
	I[c]	3.1	2.51	66 ± 7	70 ± 5	−500	780[b]	4.2[b]
n-C_3H_7	Cl		2.18	49 ± 5	44 ± 1	+190	820	2.1
	Br	3.1	2.80	82 ± 9	71 ± 9	−550	−190	1.2
	I	3.06	2.67	76 ± 8	72 ± 5	−570	210[b]	2.6[b]
n-C_4H_9	Cl		2.17	46 ± 5	39 ± 1	+320	970	2.2
	Br	3.30	2.64	64 ± 6	70 ± 1	−500	90	2.0
	I	3.18	2.61	67 ± 7	70 ± 5	−500	290[b]	2.6[b]

[a] μ_{solid}, in BM, obtained from ref 3. μ_{soln} and % T_d at 40°. [b] Data from shifts only approximate, since direct estimates of tetrahedral complex shifts were not obtainable. [c] Solution only 0.046 M.

Table IV. Kinetic Parameters for Tetrahedral ⇌ Planar Interconversion of 0.07 M [$RP(C_6H_5)_2]_2NiX_2$ in CD_2Cl_2[a]

R	X	$k_t^{298} \times 10^{-5}$ sec	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu	$\Delta F^{\ddagger}_{298}$, kcal
CH_3	Cl	2.6	~9[b]	~−4[b]	~10.1[b]
	Br	0.45	9.3	−6.1	11.1
	I	29	8.5	−0.6	8.7
C_2H_5	Cl	9.2	9.0	−1.0	9.3
	Br	1.6	9.0	−4.7	10.4
	I	>10[c]	~7[b]	~−5[b]	~8.5[b]
n-C_3H_7	Cl	6.6	9.4	−0.6	9.6
	Br	1.3	9.8	−2.4	10.5
	I	>10[c]	~8[b]	~−3[b]	~8.9[b]
n-C_4H_9	Cl	7.5	9.1	−1.3	9.5
	Br	1.4	9.2	−4.3	10.5
	I	>10[c]	~7[b]	~−5[b]	8.5[b]

[a] Parameters defined as in eq 5, with the subscript or superscript 298 designating the absolute temperature. [b] Only approximate, since spectra in the limit of slow exchange were not attainable. [c] $\Delta H^{\ddagger}$ too approximate to allow meaningful extrapolation from ~220° to 298°, though lower limit is given.

Discussion

For each of the 12 complexes studied, the room-temperature proton nmr spectra are characterized by a single peak per set of equivalent ligand protons, with isotropic shifts of approximately the same relative magnitudes and the same signs as previously reported[20,21] for analogous triphenylphosphine, $P(Ph)_3$, complexes. However, the shifts are smaller and more variable with X. The reduced isotropic shifts, which are probably contact in nature, as was shown[20] for the $P(Ph)_3$ complexes, are consistent with the previous observations[3] that these complexes also participate in a tetrahedral ⇌ planar equilibrium, such that the observed shifts are averaged over both species. In agreement with these findings, lowering the temperature produces averaged contact shifts which do not obey the Curie law, tending to increase more slowly than the predicted $1/T$ behavior.

As the temperature is lowered, in addition to the expected shifts, the line widths for each resonance increase markedly, and then split into two separate peaks, as shown in Figure 1 for $(CH_3P(Ph)_2)_2NiBr_2$. One peak is temperature independent and is centered at nearly the same position as for the diamagnetic ligand,[13] while the other peak, which obeys the Curie law, is centered at approximately the position found[20] for the completely tetrahedral $P(Ph)_3$ complexes. Figure 2 demonstrates the effect of the temperature on each ligand resonance as the temperature is varied (the α-CH_2 peak is not shown), for $(C_2H_5P(Ph)_2)_2NiBr_2$. The Curie behavior of the m-H shift for all other complexes exhibit similar behavior,[22,23] as shown in Figures 3 and 4. The temperature at which the line width from exchange is first detected or where the spectra split upon lowering the temperature varies with both X and R, as shown in Figures 3–6.

For $(CH_3P(Ph)_2)_2NiCl_2$, the separate spectrum of the paramagnetic isomer was not observed, since the complex reverts almost exclusively to the square-planar form below −30°. For the three complexes with X = I and R = C_2H_5, n-C_3H_7, and n-C_4H_9, sufficiently low temperatures (<−85°) were not attainable to freeze out the separated spectra. However, for each of these four complexes, it is possible to produce spectra in the intermediate exchange region, as shown in Figures 3 and 4, such that the lifetime of the isomers could be determined from eq 4. For the bromides, the separated spectra in the limit of very slow isomerization were readily attainable, while for the chlorides, although the separate spectra are observed, sizable exchange con-

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[20] (a) G. N. La Mar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964); (b) E. A. LaLancette and D. R. Eaton, *J. Amer. Chem. Soc.*, **86**, 5145 (1964).

[21] The aromatic peaks were easily identified on comparison with the analogous triphenylphosphine complexes (ref 20). The alkyl peaks were assigned on the basis of intensities and on comparison of complexes with different R. The aromatic proton shifts are indicative of delocalized π spin density, though this may not be evidence for dπ–dπ bonding. The alkyl proton shifts are consistent with primarily σ spin delocalization. The upfield β-CH_2 (though the β-CH_3 is downfield) shifts are more likely to arise from some polarization effects within the σ framework (as observed for the amino protons (R. S. Milner and L. Pratt, *Discuss. Faraday Soc.*, **34**, 88 (1962)), than from π spin density on the phosphorus.

[22] For some complexes, the tetrahedral complex shifts in Figures 3 and 4 seem to deviate very slightly from Curie behavior, tending to increase very slightly faster with decreasing temperature than the predicted $1/T$. Our extrapolated Curie behavior used to obtain the N_t values in the fast-exchange region was made to pass through zero. Thus if the deviations are real, our calculated N_t values will be only lower limits. The low-temperature tetrahedral shifts are not observable over a sufficiently wide temperature range to independently establish the slope on the line.

[23] A notable exception to the Curie behavior appears to be the β-CH_2 shift in the n-propyl and n-butyl complexes. Although the aromatic protons and remaining alkyl protons obey the Curie law at low temperatures, the β-CH_2 shift appears to increase faster than predicted. This anomaly is also noticeable in the fast-exchange region, where the shift doubles in size during a temperature range where the remaining contact shifts change by only ~20%. Thus some temperature-dependent conformational change for the alkyl chain is indicated. Whether this behavior is associated with the unexpected positive β-CH_2 shifts is not known at this time.

tributions to the observed line widths persist to low temperatures.

The fact that the observed line widths can be successfully interpreted by a kinetic process, as discussed above,[8] with definite activation parameters, indicates that the process which we are observing must exchange the phosphine ligands between a diamagnetic and paramagnetic environment. That the paramagnetic isomer is the pseudotetrahedral complex is well established.[2-4] The two possible diamagnetic environments would be either the planar isomer or the uncoordinated ligand. The first case would represent the tetrahedral $\rightleftharpoons$ planar equilibrium,[2-4] while the latter case would involve only bulk ligand exchange, a process which has been characterized for a number of related Ni(II) and Co(II) phosphine complexes.[16]

That the kinetic process we are observing cannot be simple ligand exchange and must therefore be the isomer interconversion process is strongly supported by the following.

(a) In a noncoordinating solvent such as methylene chloride, it is very unlikely that the complexes would dissociate appreciably, since a three-coordinated Ni(II) complex should not be stable. Integration of the diamagnetic alkyl peaks relative to the paramagnetic *m*-H peaks in the limit of slow exchange indicates that between ~30 and ~90% of the ligands exist in a diamagnetic environment. Such extents of dissociation are highly improbable. Moreover, the quality of the elemental analyses preclude the presence of any detectable excess ligand over the stoichiometric amount.

(b) The effective magnetic moments (in Table III) as well as optical studies prove the presence of the diamagnetic, planar isomer in solution. The fractions of paramagnetic isomer, N_t, obtained from the contact shift and the solution magnetic moments[24] agree within experimental error. Also, the partial loss of paramagnetism in solution cannot be explained by ligand exchange.

(c) The integration of the low-temperature paramagnetic *m*-H peaks and the diamagnetic alkyl protons for four of our complexes yielded populations of the tetrahedral configuration within experimental error of those predicted by the thermodynamic data obtained from the high-temperature fast-exchange region. The complexes, their N_t^* values from the integration, and the N_t values from the parameters in Table III respectively are: $(CH_3P(Ph)_2)_2NiBr_2$ at $-55°$, 0.45 ± 0.1, 0.52 ± 0.05; $(C_2H_5P(Ph)_2)_2NiBr_2$ at $-75°$, 0.50 ± 0.10, 0.55 ± 0.05; $(C_2H_5P(Ph)_2)_2NiCl_2$ at $-80°$, 0.10 ± 0.03, 0.11 ± 0.03; $(n\text{-}C_3H_7P(Ph)_2)_2NiBr_2$ at $-80°$, 0.65 ± 0.08, 0.70 ± 0.05.

(d) The presently observed trend of this kinetic process with halogen is not consistent with the trends observed[16,20b] for ligand-exchange reactions.

Mechanism of Isomerization. In dilute solutions of noncoordinating solvents, the mechanism for this tetrahedral $\rightleftharpoons$ planar isomerization can be readily envisaged as an intramolecular first-order process, effected by a torsional distortion along one of its vibrational normal modes, where the dihedral angle oscillates between ~0° (planar) and ~90° (pseudotetrahedral). The presence of first-order kinetics in our system is evidenced by the fact that the exchange contributions to the line widths[8,9] in the limit of slow exchange, and hence k_t, are essentially independent of the concentration of the complex between 0.04 and 0.07 *M* for $(n\text{-}C_3H_7P(Ph)_2)_2NiX_2$ with X = Cl, Br, and I.[25]

Upon the addition of as little as 15 mol % excess ligand, the tetrahedral $\rightleftharpoons$ planar averaging process is increased sufficiently so as to make resolution of the spectra of the two isomers impossible even at $-85°$ for $(CH_3P(Ph)_2)_2NiBr_2$, which has the slowest isomerization rate in the absence of free ligand. Thus some rapid ligand-exchange process must be operative which averages the spectra of the two isomers. At <5% excess ligand the observed line-width contribution at $-60°$ for $(CH_3P(Ph)_2)_2NiBr_2$ (in the limit of slow exchange) in excess of that observed in the absence of uncoordinated ligand was found to be essentially proportional to the free-ligand concentration, indicating a ligand-exchange process which is second order with respect to the ligand, L. On the other hand, decreasing the complex concentration at fixed free-ligand concentration did not noticeably decrease the observed line width. That the effect of free ligand in speeding up the planar–tetrahedral isomerization arises from ligand exchange rather than some catalytic effect is suggested by the fact that the free-ligand resonances are averaged with both the diamagnetic, planar peaks as well as the paramagnetic, tetrahedral peaks. This would arise only if the "free" ligand is bonded to the paramagnetic nickel during the reaction. Thus the rate of tetrahedral $\rightleftharpoons$ planar averaging in the presence of excess ligand at 60° can be described by the expression

$$k = k_t + k_2[L] \qquad (-60°)$$

where $k_t = 60\ \text{sec}^{-1}$ and k_2 is estimated as $3 \pm 2 \times 10^5$ l./(sec mol).

Since the ligand-exchange process completely averages the tetrahedral and planar isomers, the mechanism of the reaction probably proceeds *via* a five-coordinated transition state, which could decompose into either the tetrahedral or planar isomer. The second-order ligand-exchange reaction appears to be much faster in these complexes than for the analogous triphenylphosphine complexes,[16] probably because coordination of the fifth ligand is facilitated by the relatively less bulky alkyldiphenylphosphine ligands. The effect of halogen and alkyl groups on this ligand-exchange contribution to the interconversion rate is currently being investigated.

Effect of R and X on Thermodynamic Parameters. The thermodynamic parameters derived from the data in Figures 3 and 4 are listed in Table III. The fraction of tetrahedral isomer follows the orders $CH_3 < C_2H_5 < n\text{-}C_3H_7 \sim n\text{-}C_4H_9$ for fixed X, and generally Cl < Br < I for fixed R, although for the last two alkyl groups, N_t for Br and I are nearly the same. These trends are

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(24) The magnetic moments for the butyl complexes (ref 3a) do not fit into the smooth pattern established for the moments for the remaining alkyl substituents (ref 3b). It seems unlikely that sizable differences are real. Our values for N_t using eq 2 were thus based on moments for the butyl complexes approximately equal to the propyl complexes. Similarly, the magnetic moments for the chloride complexes were approximated by the data for the bromide complexes, inasmuch as only qualitative agreement between N_t from eq 1 and 2 was desired.

(25) The observed average contact shifts were slightly concentration-dependent, increasing by ~3% as the sample concentration was varied from 0.04 to 0.07 *M*. Thus the tetrahedral isomer appears to be favored at higher concentrations. Attempts to determine whether enthalpy or entropy terms were responsible for the change in ΔG produced values which were always within experimental error of each other, with no obvious trend.

consistent with the increasing steric requirements of the ligands, which are expected to increase Cl < Br < I and $CH_3 < C_2H_5 < n\text{-}C_3H_7 < n\text{-}C_4H_9$. The lower N_t for R = $n\text{-}C_4H_7$, observed for each X, plus the lower N_t of some iodides relative to the bromides indicate that electronic effects as well as steric effects are probably operative. The anomalous position of R = $n\text{-}C_4H_9$ complexes is also evident in the ΔH and ΔS values as well as in the magnetic data. Generally, both ΔH and ΔS decrease Cl > Br > I for fixed R, and follow the order $CH_3 > C_2H_5 > n\text{-}C_3H_7 \gtrless n\text{-}C_4H_9$ for fixed X. Enthalpy effects generally appear to dominate, since comparing two complexes indicates that $\Delta\Delta H > T\Delta\Delta S$.

The ligand-field strength of the halogens increases I < Br < Cl. A shift of the $^3T_1(F) \rightarrow {}^3A_2$ ligand field bands to longer wavelength with increasing alkyl chain length indicates[3b] that the effective ligand field strengths of the ligands in these complexes are $CH_3 > C_2H_5 > n\text{-}C_3H_7 > n\text{-}C_4H_9$. It is thus apparent that the thermodynamic parameters are not simple functions of either of these ligand properties. A more detailed interpretation of the data must await a separation of the steric and electronic contributions.[26]

Effect of R and X on Kinetic Parameters. As the data in Table IV and Figure 7 demonstrate, the rate of the isomerization is a sensitive function of both R and X, though the effect of X is generally greater than R. Some definite trends are apparent; for fixed R, k_t^{298} always follows the order Br < Cl < I, while the obscure ordering $CH_3 < n\text{-}C_3H_7 < n\text{-}C_4H_9 < C_2H_5$ persists for fixed X. The effect of halogen is quite different from that noted for simple ligand exchange, whose order was shown[16,20b] to be a more predictable Cl > Br > I. The values of $\Delta H^{\ddagger}$ are sufficiently close for all complexes that clear trends are not observed, though there is a tendency for $\Delta H^{\ddagger}$ to also parallel the rate constant, Br > Cl > I for fixed R. For a given X, the only observation is that $\Delta H^{\ddagger}$ tends to be largest for $n\text{-}C_3H_7$, and smallest for C_2H_5. The entropy of activation, $\Delta S^{\ddagger}$, is always small and negative, -3 ± 3 eu, with a tendency for R = CH_3 to exhibit the most negative value. The values for $\Delta S^{\ddagger}$ cannot be reliably estimated for those complexes for which line-width data were not available in both the slow- and fast-exchange regions, due to the large uncertainties in $\Delta H^{\ddagger}$.

Thus, although some definite and characteristic trends in k_t^{298} with both R and X are apparent, the differences cannot be unambiguously traced to changes in $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$, though both parameters appear to change. The lack of any simple correlation between k_t, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ with any obvious steric or electronic properties of the ligands indicate that not only are both effects operative, but more likely, the two effects are inseparable.

The lack of any simple correlation between observed kinetics and simple ligand properties is hardly unexpected when one considers the complex effects on the electronic and molecular structure of the whole complex upon altering either R or X. Thus it has been demonstrated through X-ray diffraction studies[27,28] that when Cl is replaced by Br in the complex $(P(Ph)_3)_2NiX_2$, not only is the effective ligand field around the metal decreased, but the X–Ni–X angle increases from 123 to 126°, and even the P–Ni–P angle decreases from 117 to 110°. Although it might be reasonable to expect a monotonic dependence of the kinetic parameters on either the ligand-field strength of X for fixed structure, or on a change in the X–Ni–X or P–Ni–P angles for fixed ligand-field strength, it seems very unlikely that the simultaneous operation of all three effects will allow a realistic interpretation of the observed kinetic parameters in terms of just ligand properties. A further complication could be that the Ni–P bond lengths change with X, and the Ni–X bond lengths change with R. Even purely "electronic" effects may induce significant structural alterations in these complexes, so as to obscure any meaningful interpretation.

An interesting question that arises at this point is why the kinetics of isomerization are so much slower in this system than for all previously reported[2] systems exhibiting this equilibrium. The fact that some bis(iminothione)nickel(II) complexes[2g] do not exhibit any exchange contributions to the observed line width of peaks with contact shifts of 3×10^4 Hz at −93° indicates that $k_t(180\text{°K}) > 10^7\ \text{sec}^{-1}$, although $k_t(180\text{°K})$ for the present complexes is only $\sim 1\text{–}10^2\ \text{sec}^{-1}$. This difference of 10^5 in rate constants is unlikely to arise only from differences in activation enthalpy, which would imply that $\Delta H^{\ddagger}$ for the iminothione complexes < 4 kcal/mol. A recent analysis[7] of this isomerization using Woodward–Hoffmann[29] rules has indicated that the interconversion is allowed, suggesting that this may account for the previously reported rapid equilibria. Thus more or less comparable kinetics might be predicted for all of the four-coordinated nickel(II) exhibiting this equilibrium.

However, it may be significant that all previous systems exhibiting very rapid isomerization[2] have been mono or bis chelate complexes. This suggests the possibility that the unexpectedly large difference in kinetics may result from activation entropy rather than enthalpy effects. Equation 5 clearly shows that decreasing $\Delta S^{\ddagger}$ slows down the reaction. $\Delta S^{\ddagger}$ for all complexes studied here was not only very small but negative. Negative entropies of activation in such reactions have been interpreted[30] as arising from severe steric crowding in the transition state, such that internal degrees of motion of the ligands are hampered. At this time we have no evidence that our observed negative $\Delta S^{\ddagger}$ do indeed arise from such an effect, since nothing is known about the role of the solvent in the transition state. However, such an effect could well account for the much slower isomerization of complexes containing complicated unidentate ligands, such as our present system, than for similar complexes with rigid, planar bidentate ligands, such as those previously studied.[2] The latter complexes have many fewer internal degrees of freedom which could be hampered even if the same degree of crowding existed in the transition state. It is therefore possible that even

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[26] A recent study of the thermodynamics of this equilibrium for a series of related complexes with variable ring substituted diarylmethylphosphine shows that decreasing phosphine ligand-field strength favors the planar isomer: L. H. Pignolet, W. D. Horrocks, Jr., and R. H. Holm, private communication.

[27] G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963).

[28] J. A. Jarvis, R. H. B. Mais, and P. G. Owston, *ibid.*, 1473 (1968).

[29] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, 87, 2046, 4388, 4389 (1965).

[30] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1959, pp 181, 182.

though such an isomerization is symmetry allowed[7] (implying only a relatively low activation enthalpy) and, therefore, predicted to be fairly rapid, variable entropy effects could cause enormous variations in the observed rate constants for apparently closely related sets of complexes.

Further understanding of the factors determining the kinetics may result from current studies of the effect of other ligand substituents, and of the effect of solvent on the isomerization rate.

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The Kinetics of an Oxidative Addition of Some Silicon Hydrides to an Iridium(I) Complex

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Abstract: The kinetics of the oxidative addition of the silicon hydrides $(CH_3)_n(C_2H_5O)_{3-n}SiH$ to bis(bis-1,2-diphenylphosphinoethane)iridium(I) tetraphenylborate have been investigated. The rate laws for the forward and back reactions were shown to be $-d[Ir^I]/dt = k_1[Ir^I][SiH]$ and $-d[Ir^{III}]/dt = k_{-1}[Ir^{III}]$, respectively. For n = 0, 1, and 2, the values of $\Delta H_{-1}^{\ddagger}$ varied systematically with increasing methyl substitution on the silicon (25.3, 22.7, and 19.2 kcal for n = 0, 1, and 2 in acetonitrile solvent; 23.6 and 21.8 for n = 0 and 1 in tetrahydrofuran). The values $\Delta S_{-1}^{\ddagger}$ were all small and positive, or close to zero, and showed no systematic variation. The mechanism of the reaction is discussed in terms of these results.

Oxidative addition reactions have received a great deal of attention both as an interesting class of reaction of transition complexes and as an important step in several homogeneous catalytic reactions.[1] Our interest in this reaction stems from an earlier postulate that oxidative addition of silicon hydrides to certain d^8 complexes was a key factor in the ability of the latter to catalyze the hydrosilation of unsaturated organic compounds.[2] More recently Sommer and Lyons have demonstrated that stereospecific exchange reactions of optically active silicon hydrides and deuterides are catalyzed by complexes of cobalt and iridium.[3] These reactions also almost certainly involve oxidative addition as the key step in the reaction sequence. In fact such exchange reactions have been proven to proceed *via* oxidative addition when catalyzed by hydridocarbonyltris(triphenylphosphine)iridium(I), **1**.[4] When chlorocarbonylbis(triphenylphosphine)iridium(I), **2**, is used as catalyst,[3] it is undoubtedly converted to the hydrido derivative.[5]

Two distinct types of mechanistic behavior have been observed in oxidative addition reactions.[6] The addition of homopolar diatomic molecules to **2** proceeds with a moderate activation enthalpy ($\Delta H^{\ddagger}$) and a moderately large negative activation entropy ($\Delta S^{\ddagger}$), but the addition of methyl iodide to **2** was shown to occur with an extraordinarily large $\Delta S^{\ddagger}$. This latter fact, in addition to a large dependence of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ on solvent polarity, led Chock and Halpern[6] to speculate that oxidative addition of methyl iodide involved a highly polar transition state analogous to that previously proposed for the Menschutkin reaction. On the other hand, the activation parameters for hydrogen were not inconsistent with a three-center transition state in which both addend atoms interact simultaneously with the metal ion.

An earlier study[4] showed that, at least in the case of the iridium complex **1**, addition of Si–H to Ir(I) occurs in a *cis* fashion. It was inferred that *cis* addition supported a three-center rather than an SN2 mechanism. The present paper describes the kinetics of the reactions of the series of silicon hydrides $(CH_3)_n(C_2H_5O)_{3-n}SiH$ with bis(bis-1,2-diphenylphosphinoethane)iridium(I) tetraphenylborate, **3**, and discusses the results in terms of the two alternative mechanisms.

Results

The silicon hydrides $(CH_3)_n(C_2H_5O)_{3-n}SiH$ were found to undergo a readily reversible oxidative addition reaction with the ionic complex **3**. The qualitative order

$$(CH_3)_n(C_2H_5O)_{3-n}SiH + (diphos)_2Ir^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (diphos)_2[(CH_3)_n(C_2H_5O)_{3-n}Si]HIr^+ \quad (1)$$

of stabilities was the same as that observed previously for additions of silicon hydrides to d^8 complexes.[2,4,7] At −10° the equilibrium of eq 1 lay almost completely to the right for n = 0 and almost completely to the left for n = 3. The low stabilities of the reaction products

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