show similar values and $HBPEDA^+$ shows a slightly larger value, due presumably to the rest of the molecule as a substituent in the 2 position of the pyridine ring. Phenanthroline shows a rather low value in view of the fact that the second ring cannot rotate out of the way during initial bonding as is the case with the others. This may suggest some type of accelerating effect due to the close proximity of the second nitrogen during initial bonding.

Comparison of Formation Rates of Ni(II) with BPEDA, TKED, EDDA, and trien. The ligands BPEDA, TKED, EDDA, and trien can all be considered as N-substituted ethylenediamines. The position of the rate-determining step, either initial bond formation or ring closure, depends on the values of k_{-1} and k_2 in eq 11. With the exception of trien, all k_2 values should be about the same since only coordinated nitrogens appear to have a sizable effect on nickel-water loss[10] and since rotational barriers would be similar. Thus, the magnitude of the dissociation constant for the N-substituted dentate group really determines the position of the rate-determining step. The strong nickel-nitrogen bonds, $k^{Ni(py)}$ and k^{NiNH_3}, compared to weak nickel-oxygen bonds, k^{NiOAc} and k^{NiOR}, coupled with the relative inaccessibility of secondary and tertiary nitrogens cause a shift in the rate-determining step from first to second bond formation as k_{-1} increases. BPEDA having $k_{-1} = 38$ sec^{-1} fits the mechanism well.

Comparison of BPEDA with AMP and DPA. The formation reactions of Ni(II) with both free and protonated forms of 2-aminomethylpyridine, AMP, and di(2-picolyl)-amine, DPA, have been measured. Again, assuming no ICB effect to be present in the protonated cases, E_s values can be calculated and are listed in Table III. Since the monoprotonated forms of both ligands involve aliphatic nitrogen protonation, the E_s values reflect steric factors for attack at the aromatic nitrogens. The value for $HDPA^+$ is similar to that for $HBPEDA^+$ as would be expected but that for $HAMP^+$ is abnormally low.

Calculations of E_s for AMP and DPA result in anomously large values. In the case of DPA, pK_{HL} is <8[11] and no ICB effect should be present. Thus, E_s must approximate the steric factor for initial attack at either an aromatic nitrogen or an aliphatic one and can be compared to E_s for $HBPEDA^+$ and $HDPA^+$ approximating an aromatic nitrogen or E_s for $HDBEDA^+$ and $H(N,N'\text{-}(Et)_2en)^+$ approximating a secondary aliphatic nitrogen. Although E_s for DPA is higher than E_s for all the above-mentioned ligands, it clearly is closer to those for $HBPEDA^+$ and $HDPA^+$ than those for $HDBEDA^+$ and $H(N,N'\text{-}(Et)_2en)^+$. On this basis it is likely that, like the Ni(II) attack on BPEDA, initial attack on DPA is also through an aromatic nitrogen.

The situation involving AMP is more complex. E_s could reflect initial attack at an aromatic nitrogen but would also include an ICB effect since pK_{HL} is 8.6.[17] Comparison to E_s for $HAMP^+$ would give an ICB effect of 100 which is unreasonable. Conversely, E_s for AMP could reflect initial attack at the aliphatic nitrogen in which case it could not be compared to E_s for $HAMP^+$ because different dentate sites would be involved although no ICB effect would be present. However, ethylamine should have a similar steric factor but comparison of E_s for $EtNH_2$ and AMP shows them to be a factor of 10 apart. Thus, neither mechanism is supported by the data and a clear picture of the mechanism of Ni(II) formation with AMP cannot be established yet.

Registry No. DBEDA, 140-28-3; BPEDA, 4608-34-8; Ni, 7440-02-0; $HDBEDA^+$, 36223-04-8; $HBPEDA^+$, 36223-05-9; H_2BPEDA^{2+}, 36223-06-0; NiDBEDA, 36202-31-0.

Contribution from the Department of Chemistry, University of Minnesota,
Minneapolis, Minnesota 55455

Proton Magnetic Resonance Study of the Stereochemistry of Four-Coordinate Nickel(II) Complexes. Dihalobis(tertiary phosphine)nickel(II) Complexes

LAWRENCE QUE, Jr.,[1] and L. H. PIGNOLET*

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A series of dihalobis(tertiary phosphine)nickel(II) complexes, NiL_2X_2, has been synthesized. The tertiary phosphine ligands include PR_3, PR_2Ph, and $PRPh_2$ types where R is cyclopropyl or cyclohexyl and Ph is phenyl. These tertiary phosphines and several others were selected to test the relative importance of steric and electronic effects on the planar-tetrahedral structural equilibrium exhibited by NiL_2X_2 type complexes. The thermodynamics and kinetics of this interconversion were determined by proton magnetic resonance and magnetic susceptibility measurements in dichloromethane solution. Results show that steric factors are relatively unimportant in affecting the thermodynamics of the structural equilibrium. Electronic effects, however, are extremely important and are interpreted *via* a metal-phosphorus π-bonding scheme. Kinetic parameters were measured by standard pmr line shape techniques and are reported for trialkyl- and dialkylphenylphosphine complexes for the first time. The activation parameters are similar to other NiL_2X_2 complexes where L = alkyldiphenylphosphine.

Introduction

Tertiary phosphines are among the most extensively investigated ligands in coordination chemistry.[2] Reports have appeared which have presented conflicting evidence for the importance of σ and π bonding between these ligands and transition metals.[3] An understanding of the bonding mode is important because phosphine ligands play a significant role in homogeneous catalysis. A sensitive test

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[1] Lubrizol Fellow, University of Minnesota, 1971-1972.

[2] See for example G. Booth, *Advan. Inorg. Chem. Radiochem.*, 6, 1 (1964).

[3] (a) L. M. Venanzi, *Chem. Brit.*, 4, 162 (1968); (b) B. B. Chastain, E. A. Rick, R. I. Pruett, and H. B. Gray, *J. Amer. Chem. Soc.*, 90, 3994 (1968); (c) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

for the type of ligand-metal bonding is the effect of phosphine substituent on the thermodynamic and kinetic parameters for the planar-tetrahedral structural equilibrium I in noncoordinating solvents. This equilibrium is now well

$$\text{planar } (S = 0) \rightleftarrows \text{tetrahedral } (S = 1) \qquad \text{(I)}$$

established for a number of bis-chelate[4] and dihalochelate[5] complexes of nickel(II) and for some dihalobis(tertiary phosphine)nickel(II)[6-10] complexes. Several studies have shown that small electronic and/or steric variations in the ligand moiety can produce marked effects on the position of equilibrium I.[4,7a,11] Two of these studies yielded linear free energy correlations between the position of (I) and the Hammett or Taft substituent constants.[7a,11] These correlations can give evidence for σ and π bonding provided steric effects are not important. Pignolet, Horrocks, and Holm[7a] have reported convincing evidence for π bonding between tertiary phosphines and square-planar nickel(II) in complexes of the type $\mathrm{Ni}[(p\text{-ZC}_6\mathrm{H}_4)(p\text{-Z}'\mathrm{C}_6\mathrm{H}_4)\mathrm{CH}_3\mathrm{P}]_2\mathrm{X}_2$ where $\mathrm{X}^- = \mathrm{Cl}^-$, Br^-, or I^- and Z and Z′ are substituents of varying electronic requirement. The position of (I) was monitored in series of constant halide and various Z and Z′ substituents. A remarkably sensitive electronic substituent effect was observed, *e.g.*, the mole fraction of tetrahedral isomer, $N_\mathrm{t}^{25^\circ}$, changed from 0.10 to 0.77 for $Z = Z' = \mathrm{CF}_3$ and OCH_3, respectively, when $\mathrm{X}^- = \mathrm{Br}^-$. Bonding information was deduced by comparing N_t values with Hammett σ_p values and electronic spectral data.[7a]

Evidence to date on $\mathrm{NiL}_2\mathrm{X}_2$ type complexes indicates that with few exceptions when L = triarylphosphine the complexes have pseudotetrahedral coordination,[12-15] when L = alkyldiarylphosphine equilibrium I is found,[6-10] and when L = dialkylaryl- or trialkylphosphine a planar coordination geometry is observed.[6,16-19] This trend has been rationalized by both steric and electronic arguments. Several exceptions to this scheme have been reported. When L = tricyclopropylphosphine,[20] tricyclohexylphosphine,[10] or dicyclohexylphenylphosphine[10] equilibrium I has been found. These observations result exclusively from solution magnetic susceptibility and electronic spectroscopic data and are subject to error (*vide infra*).

Thermodynamic parameters for (I) are obtained from the temperature dependence of the magnetic moment and/or the pmr shift of a ligand proton.[4] The pmr resonance position is a weighted average over the paramagnetic tetrahedral isomer (which manifests large isotropic shifts) and the diamagnetic planar isomer. Averaged resonances have been observed for the chelate complexes exhibiting (I) down to −90°,[21] whereas the dihalobis(alkyldiarylphosphine)nickel(II) complexes show separate resonances for both isomers at temperatures as high as *ca.* −30°.[7,8] Kinetic parameters for (I) have been measured by standard pmr line shape techniques for several of these complexes. No kinetic trends were found as a function of halide or ligand substituent.[7,8]

We report here results of a pmr study of some dihalobis(tertiary phosphine)nickel(II) complexes in dichloromethane solution. The ligands used were specially selected to shed light on two pertinent problems: (i) to present evidence for or against π bonding by varying the electronic properties of sterically similar phosphine alkyl substituents; (ii) to examine a variety of tertiary phosphine ligands in order to determine the relative importance of electronic and steric effects on the thermodynamics and kinetics of equilibrium I. This work is the first thermodynamic and kinetic analysis of equilibrium I performed on $\mathrm{NiL}_2\mathrm{X}_2$ type complexes in which dialkylaryl- and trialkylphosphine ligands have been employed.

Experimental Section

Preparation of Compounds. (a) Phosphines.[22] With the exception of $\mathrm{PPh_2Cyp}$, $\mathrm{PPhCyp_2}$, $\mathrm{PPh_2Me}$, and $\mathrm{PPh_2Vy}$, all of the phosphines were prepared according to literature syntheses.[23] $\mathrm{PPh_2Cyp}$ and $\mathrm{PPhCyp_2}$ were prepared by the reaction of cyclopropyllithium with the appropriate chlorophosphine in ether and were purified by vacuum distillation, 110–113° (0.5 Torr) and 90–95° (1.5 Torr), respectively. All preparations and manipulations were carried out in a nitrogen atmosphere. The compounds were characterized by pmr spectroscopy. $\mathrm{PPh_2Me}$ and $\mathrm{PPh_2Vy}$ were purchased from the Strem Chemical Co.

(b) **Complexes.** The bromide complexes were synthesized by mixing hot butanolic solutions of the appropriate phosphine and hydrated nickel bromide under nitrogen. The solid complexes which separated immediately or on cooling were filtered, washed with cold butanol, and recrystallized from hot freshly distilled dichloromethane–heptane solution under nitrogen. The crystalline products were collected, washed with heptane, vacuum dried, and stored under nitrogen. In the cases of the trialkyl- and dialkylphenylphosphines the complexes were not recrystallized in order to prevent oxidation or reaction with halogenated solvents which forms paramagnetic products (*vide infra*). The chloride complexes were synthesized by mixing hot ethanolic solutions of the appropriate phosphine and hydrated nickel chloride under nitrogen. The crystalline products which separated immediately were filtered, washed thoroughly with ethanol, and vacuum dried. These com-

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(22) Abbreviations for tertiary phosphine substituents used throughout this paper: Ph, phenyl; Cyp, cyclopropyl; Cyh, cyclohexyl; Vy, vinyl; *t*-Bu, *tert*-butyl; Me, methyl.

(23) The following phosphines were prepared according to the references listed: $\mathrm{PCyp_3}$, D. B. Denney and F. J. Gross, *J. Org. Chem.*, **32**, 2445 (1967); $\mathrm{PCyh_3}$, K. Issleib and A. Black, *Z. Anorg. Allg. Chem.*, **277**, 259 (1964); $\mathrm{P(PhCyh_2)}$ and $\mathrm{P(Ph_2Cyh)}$, K. Issleib and H. Volker, *Chem. Ber.*, 94, 393 (1961); $\mathrm{P(Ph_2\text{-}\mathit{t}\text{-}Bu)_3}$, ref 9a.

Table I. Characterization Data for $\mathrm{NiX_2L_2}$ Complexes

				% C		% H		% P	
X	L	Mp,[a] °C	μ_{eff},[b] BM	Calcd	Found	Calcd	Found	Calcd	Found
Cl	$\mathrm{PCyp_3}$	172	3.15	49.34	49.18	6.90	7.11		
Cl	$\mathrm{PPhCyp_2}$	171–172	Diamag	56.56	56.44	5.93	6.15		
Cl	$\mathrm{PPh_2Cyp}$	157	Diamag	61.86	61.84	5.16	5.33		
Br	$\mathrm{PCyp_3}$	225–228	3.16	41.05	41.20	5.70	5.41	11.77	11.29
Br	$\mathrm{PPhCyp_2}$	162–163	Diamag	48.12	47.76	5.04	5.11		
Br	$\mathrm{PPh_2Cyp}$	202–204	3.17	53.71	54.09	4.48	4.84	9.24	9.14
Br	$\mathrm{PCyh_3}$	245	Diamag	55.48	55.32	7.95	8.14	8.53	8.80
Br	$\mathrm{PPhCyh_2}$	225	Diamag	56.37	56.42	7.05	7.01		
Br	$\mathrm{PPh_2Cyh}$	244	3.14	57.40	57.50	5.60	5.60	7.94	8.24
Br	$\mathrm{PPh_2Vy}$	202–204	3.13	52.30	52.07	4.08	3.98	9.63	9.52
Br	$\mathrm{PPh_2}$-*t*-Bu[c]	215–216	3.31	54.68	54.17	5.41	4.57	8.82	8.42

[a] Uncorrected decomposition points. [b] Measured at 22° for solid complexes (see Experimental Section). [c] Slightly impure.

Table II. Magnetic and Thermodynamic Data[a] for $\mathrm{NiX_2L_2}$ Complexes in Dichloromethane Solution

X	L	μ_{eff}(304°), BM	ΔH, cal/mol	ΔS, eu	ΔG(304°), cal/mol	$N_t^{304°}$	$\Delta\nu^{\mathrm{av}}$(meta),[c] ppm	Curie intercept,[e] ppm
Cl	$\mathrm{PCyp_3}$	2.56	1870	8.20	−600	0.73	−7.92[d]	+3.30[d]
Cl	$\mathrm{PPhCyp_2}$	2.11	1940	5.67	+225	0.41	−4.71	+0.92
Cl	$\mathrm{PPh_2Cyp}$	2.38	1640	5.90	−150	0.56	−7.16	+3.20
Br	$\mathrm{PCyp_3}$	3.04	*b*	*b*	*b*	>0.95	−11.93[d]	+3.60[d]
Br	$\mathrm{PPhCyp_2}$	2.46	1600	6.59	−400	0.66	−8.11	+3.50
Br	$\mathrm{PPh_2Cyp}$	3.01	1210	8.75	−1440	0.92	−11.35	+5.00
Br	$\mathrm{PCyh_3}$	Diamag				0.00		
Br	$\mathrm{PPhCyh_2}$	1.07	*b*	*b*	−1210	~0.12	−16.2	*b*
Br	$\mathrm{PPh_2Cyh}$	2.62	1370	6.31	−550	0.71	−7.34	+2.60
Br	$\mathrm{PPh_2Vy}$	2.55	2190	8.33	−335	0.64	−7.68	+4.00
Br	$\mathrm{PPh_2}$-*t*-Bu	3.06[f]	*b*	*b*	*b*	1.00	−9.20	+3.20
Br	$\mathrm{PPh_2Me}$	2.50	930	4.22	−356	0.64	−9.00	+3.50

[a] See text for calculation of parameters. [b] Equilibrium too far toward tetrahedral or planar isomer for accurate measurement. [c] Observed isotropic pmr shifts at 304°, *i.e.*, averaged over planar and tetrahedral isomers. [d] Cyclopropyl β-$\mathrm{H_2}$ resonance labeled in Figure 1. [e] Intercept at $1/T = 0$ in $\Delta\nu$(meta) *vs.* $1/T$ plot. [f] Slight decomposition noted.

Table III. Ligand Field Spectral Data for $\mathrm{NiX_2L_2}$ Complexes in Dichloromethane Solution

X	L	ν_1[a] (ϵ)[b]	ν_2 (ϵ)	$N_t^{304°}$
Cl	$\mathrm{PCyp_3}$	19,450 (255)	11,900 (109)	0.73
Cl	$\mathrm{PPhCyp_2}$	20,270 (336)	11,680 (74)	0.41
Cl	$\mathrm{PPh_2Cyp}$	19,650 (308)	11,600 (79)	0.56
Br	$\mathrm{PCyp_3}$	17,770 (208)	11,840 (228)	>0.95
Br	$\mathrm{PPhCyp_2}$	18,450 (282)	11,560 (156)	0.66
Br	$\mathrm{PPh_2Cyp}$	17,700 (216)	11,520 (204)	0.92
Br	$\mathrm{PCyh_3}$	16,570 (545)	*c*	0.00
Br	$\mathrm{PPhCyh_2}$	18,300 (380)	11,120 (22)	~0.12
Br	$\mathrm{PPh_2Cyh}$	17,160 (409)	11,360 (150)	0.71
Br	$\mathrm{PPh_2Vy}$	18,000 (263)	11,300 (159)	0.64
Br	$\mathrm{PPh_2}$-*t*-Bu	16,300 (190)	10,800 (185)	1.00
Br	$\mathrm{PPh_2Me}$	18,700 (279)	11,680 (182)	0.64
Br	$\mathrm{PPh_3}$	17,050 (232)	10,980 (254)	1.00

[a] Transitions are accurate within ±40 $\mathrm{cm^{-1}}$. [b] In l. $\mathrm{mol^{-1}\ cm^{-1}}$. [c] This band is due to decomposition in $\mathrm{CH_2Cl_2}$ solution and is absent in toluene solution.

plexes were used without further purification. All complexes were characterized by elemental analysis, magnetic susceptibility, and pmr (Table I).

Pmr Spectra. The pmr spectra were recorded on a Varian XL-100-15 nmr spectrometer equipped with a variable-temperature probe. Temperatures were measured to within ±1° by a thermocouple mounted in an nmr tube. The instrument was operated in the ^{2}H-locked mode using $\mathrm{CD_2Cl_2}$, $\mathrm{CDCl_3}$, or $\mathrm{CD_3C_6D_5}$ as the internal lock. All chemical shifts were measured to within ±1 Hz relative to the internal lock by use of an electronic counter. The thermodynamic and kinetic measurements were made using $\mathrm{CD_2Cl_2}$ solutions *ca.* 0.05 *M* in complex. The samples were made under nitrogen and sealed in nmr tubes. Spectra were recorded within *ca.* 5 hr because slight decomposition was noted after this time.

Magnetic Measurements. Solid magnetic moments were determined *in vacuo* by the Faraday technique at 23° (Table I). Solution moments were determined by the nmr method[24] in $\mathrm{CD_2Cl_2}$ containing *ca.* 5% v/v TMS and were 0.01–0.03 *M* in complex (Table II). Diamagnetic corrections were calculated from Pascals' constants.

Electronic Spectra. Electronic spectra were recorded on a Cary Model 14 spectrophotometer using 10^{-2}–10^{-3} *M* solutions at 22°. The samples were prepared and run under nitrogen using thoroughly degassed $\mathrm{CH_2Cl_2}$ previously treated with anhydrous $\mathrm{K_2CO_3}$. The data are presented in Table III.

Treatment of Data

Thermodynamic Parameters. All of the thermodynamic parameters (ΔH, ΔS, ΔG, and N_t) reported in Table II were determined according to the following procedure. Observed pmr shifts, $\Delta\nu^{\mathrm{av}}$, which are weighted averages of those of the diamagnetic planar isomer ($\Delta\nu_p = 0$) and the paramagnetic tetrahedral isomer ($\Delta\nu_t$),[25] were recorded between +31 and *ca.* 0°. Below *ca.* 0° line broadening occurred due to kinetic exchange between the planar and tetrahedral isomers and below *ca.* −70° separate resonances assignable to both isomers grew in. Figure 1 shows a typical temperature-dependent pmr spectrum for $\mathrm{Ni(PCyp_3)_2Cl_2}$ and Figures 2 and 3 show Curie plots of the observed isotropic shifts for all complexes. The frozen-out isotropic shifts of the paramagnetic isomer indicate linear Curie plots but generally with nonzero intercepts at $1/T = 0$. The least-squares intercepts obtained for all complexes for the *m*-H or cyclopropyl β-$\mathrm{H_2}$ resonances are listed in Table II. The values for $\mathrm{Ni(PPh_2\text{-}}t\mathrm{\text{-}Bu)_2Br_2}$ and $\mathrm{Ni(PPh_3)_2Br_2}$ which are 100% tetrahedral over the entire temperature range are +3.20 and +3.45 ppm, respectively for the *m*-H resonance.[26] These values are in good agreement with those observed for the other complexes with $N_t < 1.0$ where the frozen-out tetra-

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[24] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[25] Isotropic shifts are negative when the resonance is downfield of the diamagnetic position. The diamagnetic resonance positions used in this study were determined from low-temperature frozen-out spectra at −80° (*vide infra*) and are as follows: *m*-H, −2.25 ppm; cyclopropyl β-$\mathrm{H_2}$ resonance defined in Figure 1, +4.30 ppm relative to $\mathrm{CHDCl_2}$.

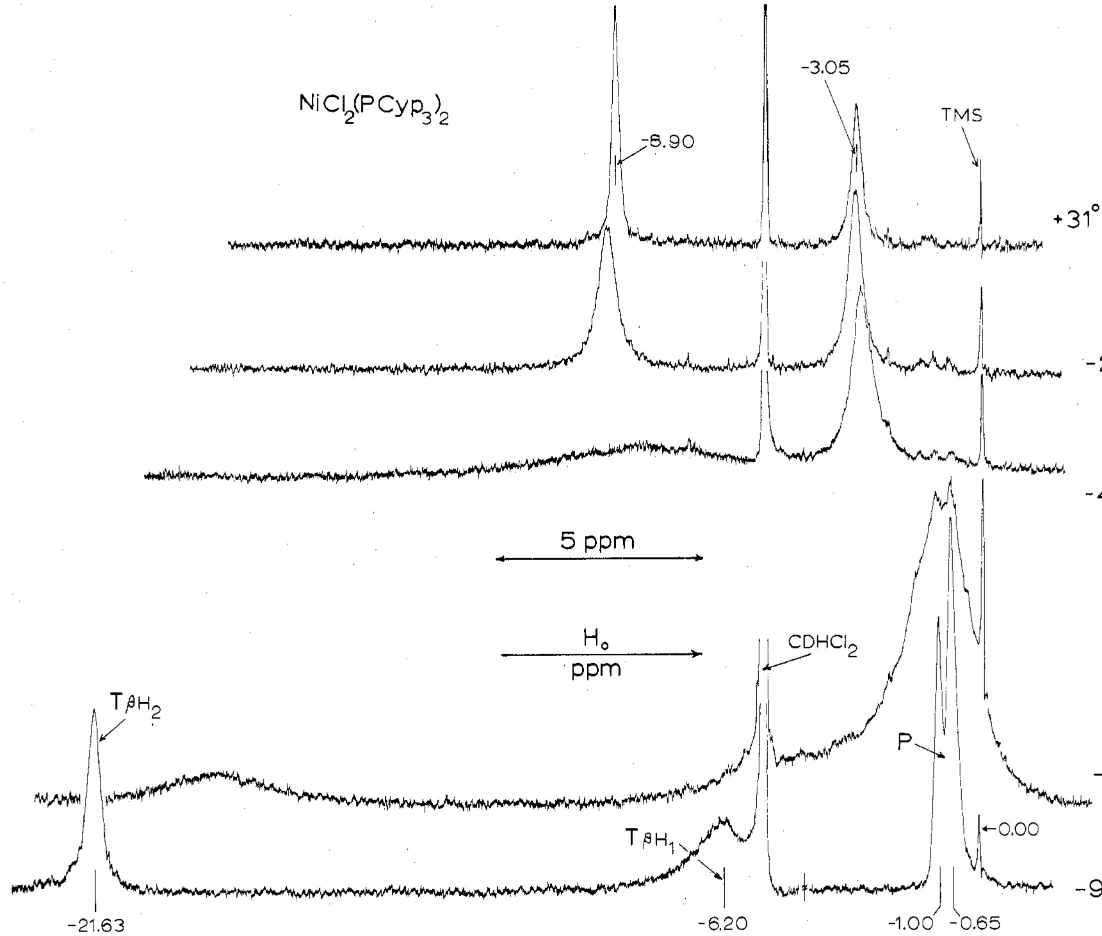

Figure 1. Pmr spectra (100 MHz) of $Ni(PCyp_3)_2Cl_2$ in CD_2Cl_2 solution illustrating coalescence of the planar, P, and tetrahedral, T, resonances. Shifts are relative to TMS internal standard.

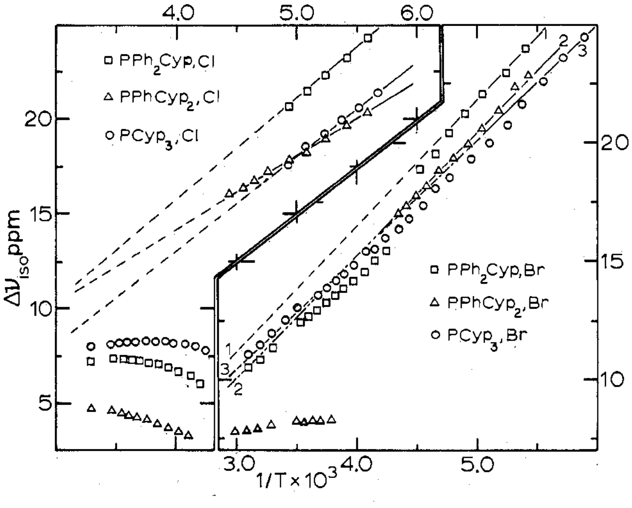

Figure 2. Curie plots for *m*-H (□ and △) or β-H_2 (○) resonance for NiL_2X_2 complexes in CD_2Cl_2 solution.

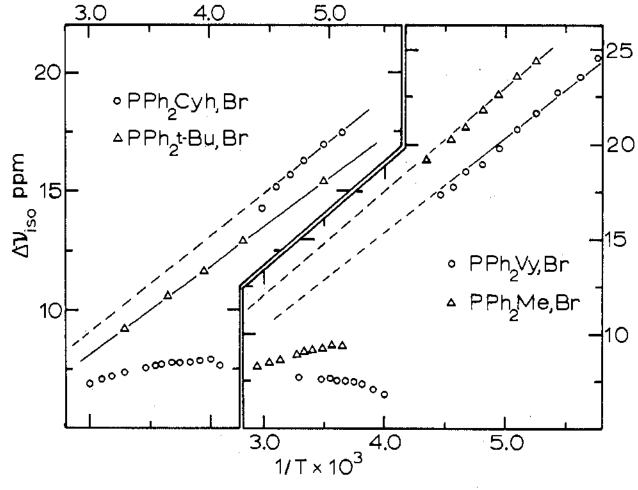

Figure 3. Curie plots for *m*-H resonance for NiL_2X_2 complexes in CD_2Cl_2 solution.

hedral resonances are only observed below *ca.* −70°. These nonzero intercepts are real and are not unexpected.[27] N_t values for all complexes exhibiting equilibrium I were determined from eq 1 at temperatures where averaged isotropic

$$N_t = \Delta\nu^{av}/\Delta\nu_t \qquad (1)$$

shifts are observed. N_t is the mole fraction of tetrahedral

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(26) Curie plots for these pseudotetrahedral complexes show definite linear behavior from +60 to −90° giving confidence to linear extrapolations from low-temperature data for complexes where $N_t < 1.0$.

(27) Non-Curie temperature dependence has been predicted for such complexes by B. R. McGarvey, *J. Amer. Chem. Soc.*, 94, 1103 (1972). In these complexes the non-Curie behavior manifests itself by yielding nonzero intercepts. Many paramagnetic complexes apparently show this behavior as recently reported by W. D. Perry and R. S. Drago, *ibid.*, 93, 2183 (1971).

Table IV. Kinetic Parameters[a,b] for NiX_2L_2 Complexes in Dichloromethane Solution

X	L	$k_t(-50°)$,[b] sec^{-1}	$k_t(25°)$, sec^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	$\Delta G^\ddagger(-50°)$,[b] kcal/mol
Cl	$PCyp_3$	4.91×10^3	1.19×10^6	9.2	0	9.16
Br	$PCyp_3$	1.11×10^3	*c*	*c*	*c*	9.81
Br	$PPhCyp_2$	3.21×10^2	1.46×10^5	10.7	+1	10.4
Br	PPh_2Cyp	4.46×10^2	1.48×10^5	9.5	−3	10.2
Br	PPh_2Cyh	1.00×10^3	9.34×10^5	9.6	−1	9.86

[a] See text for calculation of parameters. [b] Estimated error is *ca.* ±2% for $k_t(-50°)$ and $\Delta G^\ddagger(-50°)$, ±1 kcal/mol for $\Delta H^\ddagger$, and ±4 eu for $\Delta S^\ddagger$. [c] N_t too close to 1.0 for accurate measurement.

isomer at T°K, $\Delta\nu^{av}$ is the averaged isotropic shift, and $\Delta\nu_t$ is the isotropic shift of the tetrahedral isomer determined by linear extrapolation of frozen-out values as mentioned above (Figures 2 and 3). An independent method for determining N_t is by use of eq 2 in which $\mu^{av}{}_{eff}$ is the observed solution

$$N_t = (\mu^{av}{}_{eff})^2/(\mu^{t}{}_{eff})^2 \tag{2}$$

magnetic moment and $\mu^{t}{}_{eff}$ is the magnetic moment of the tetrahedral isomer determined, when possible, from solid-state susceptibility measurements (Tables I and II). If $\mu^{t}{}_{eff}$ = 3.15 BM, the average tetrahedral value observed, good agreement between these two methods is found. Free energy values, ΔG, were determined using eq 1 and 3 in which ΔG =

$$\Delta G = -RT \ln (N_t/(1 - N_t)) \tag{3}$$

$-RT \ln K_{eq}$ and $K_{eq} = N_t/(1 - N_t)$. The ΔG values were then fit by least squares to the equation $\Delta G = \Delta H - T\Delta S$. ΔH and ΔS values are presented in Table II. ΔG and N_t values are accurate to within ±30 cal/mol and ±0.02, respectively.

Kinetic Parameters. Kinetic results were obtained by monitoring the line widths at half-height, $\nu_{1/2}$ (Hz), of the *m*-H or cyclopropyl β-H_2 resonances over the entire temperature range. Standard fast- and slow-exchange approximations were used.[28,29] In the limit of fast exchange, eq 4 was used[8,28] in which T_2, T_{2t}, and T_{2s} are the transverse relaxa-

$$\frac{1}{T_2} = \frac{N_t}{T_{2t}} + \frac{N_p}{T_{2p}} + N_t^2 N_p^2 (\Delta\nu_t)^2 (\tau_t + \tau_p) \tag{4}$$

tion times for the observed averaged resonance and for the tetrahedral and planar resonances in the absence of exchange, respectively. N_p is the mole fraction of planar species, $\Delta\nu_t$ is the isotropic shift for the tetrahedral isomer, and τ_t and τ_p are preexchange lifetimes defined by eq 5 in which $k_t = (\tau_t)^{-1}$ and $k_p = (\tau_p)^{-1}$. In the limit of slow exchange, eq 6 was

$$\text{tetrahedral} \underset{k_p}{\overset{k_t}{\rightleftharpoons}} \text{planar} \tag{5}$$

used for the observed line width of the tetrahedral isomer.[7,8,28]

$$\pi(\Delta\nu_{1/2})_t = \frac{1}{T_{2t}} + \frac{1}{\tau_t} \tag{6}$$

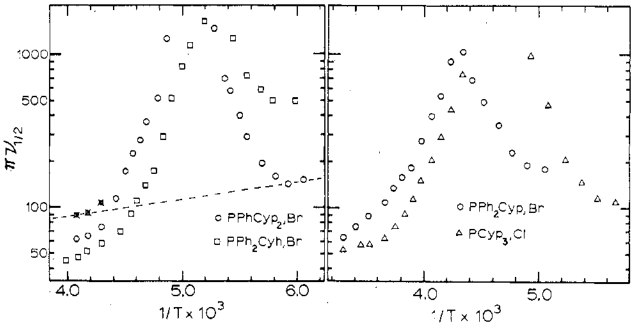

Figure 4. Log plots of π times the observed line widths *vs.* reciprocal temperature for NiL_2X_2 complexes in CD_2Cl_2 solution. Dashed line shows extrapolation used in kinetic analysis for $Ni(PPhCyp_2)_2Br_2$.

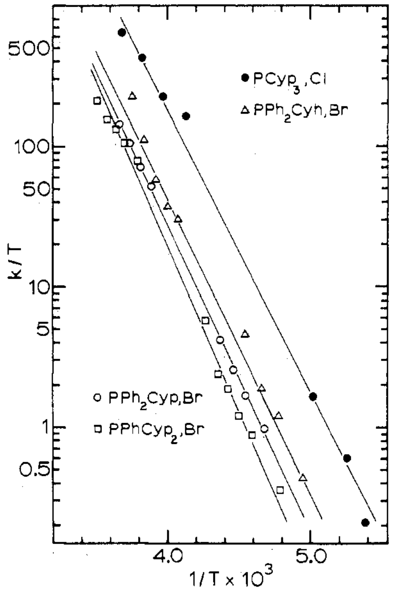

Figure 5. Log (k_t/T) *vs.* T^{-1} plot for NiL_2X_2 complexes in CD_2Cl_2 solution.

The transverse relaxation time is related to $\nu_{1/2}$ by $1/T_2 = \pi\nu_{1/2}$. T_{2t} values were determined in the region of exchange broadening by linear interpolation between the frozen-out and completely averaged regions on $\ln \pi\nu_{1/2}$ *vs.* T^{-1} plots shown in Figure 4 for $NiBr_2(PPhCyp_2)_2$. T_{2t} in the fast-exchange region was calculated by $T_{2t} = N_t T_2$. T_{2p} was assumed constant throughout the temperature range and was calculated using a 5-Hz line width for both the *m*-H and cyclopropyl β-H_2 resonances. These values were estimated from the frozen-out spectra.[30]

This analysis yields τ_t in the slow and fast-exchange regions. First-order rate constants, k_t, and activation parameters were determined from least-squares fits to $\ln (k_t/T)$ *vs.* $1/T$ plots (Figure 5) assuming the validity of eq 7

$$k_t = \frac{kT}{h} \exp\left[\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}\right] \tag{7}$$

in which $\Delta S^\ddagger$ and $\Delta H^\ddagger$ are the entropy and enthalpy changes of activation. Kinetic results are shown in Table IV. The errors in $\Delta G^\ddagger$ and k_t reported at −50° are small whereas the errors in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are significantly larger.

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

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

(30) This procedure has been used by La Mar and Sherman[8b] and was justified because the kinetic parameters are primarily affected by the N_t/T_{2t} term in eq 4.

Results and Discussion

The purpose of this study is to further our understanding of the role of steric and electronic properties of some tertiary phosphine ligands by examining their effect on structural interconversion I. We have examined a number of complexes of the type $NiX_2(PR_3)_2$ where X = Cl or Br and R is alkyl or phenyl. The phosphine ligands include trialkyl, dialkylphenyl, and alkyldiphenyl types where alkyl groups include cyclopropyl, cyclohexyl, methyl, vinyl, and *tert*-butyl. Characterization data for all complexes investigated are shown in Table I.[22] The cyclopropyl-substituted complexes are new with the exception of $NiCl_2(PCyp_3)_2$, which was reported by Shupack[20] to be the only trialkylphosphine complex exhibiting equilibrium I in solution (all others are presumably planar). We decided to study the cyclopropyl series because of this interesting result and because of the cyclopropyl group's intriguing electronic properties.[31] The cyclohexyl-substituted complexes were synthesized in order to examine the importance of ligand steric effects. During the course of our work Stone and Dori[10] reported that $NiBr_2(PCyh_3)_2$ is 32% tetrahedral. This result is in disagreement with ours (*vide infra*). The other complexes were selected for comparison to the cyclopropyl and cyclohexyl series. We have measured the thermodynamic properties of these complexes by pmr, magnetic susceptibility, and electronic spectral experiments. Tables II and III contain the magnetic and spectral data, respectively. In the last section of the paper we report the results of a kinetic study on four of these complexes. Kinetic data are shown in Table IV.

The Structural Interconversion. Pmr and Thermodynamics. The temperature dependence of the pmr shifts for $NiCl_2(PCyp_3)_2$ in CD_2Cl_2 is shown in Figure 1. Above *ca.* −55°, the resonances are averaged over the planar and tetrahedral forms whereas below *ca.* −70°, separate resonances are observed. The intermediate temperature region exhibits exchange-broadened peaks. Curie plots for the *m*-H or cyclopropyl β-H_2[32] resonances for all complexes examined are illustrated in Figures 2 and 3. The low-temperature parts of the plots clearly show linear Curie behavior for the frozen-out tetrahedral species. In general these lines have nonzero intercepts as pointed out in the treatment of data section and are shown in Table II. At higher temperatures, non-Curie temperature dependence which is characteristic of equilibrium I and given by eq 8 is observed. In this

$$\frac{\Delta\nu_i^{av}}{\nu} = -a_i \left(\frac{\gamma_e}{\gamma_n}\right)\frac{g\beta S(S+1)}{6SkT}N_t + B \qquad (8)$$

equation $\Delta\nu_i^{av}$ is the observed isotropic shift of resonance i, a_i is the electron–nucleus hyperfine coupling constant in gauss, B is a temperature-independent term shown in Table II, and N_t is the mole fraction of tetrahedral species and is defined in eq 1-3. The other symbols have their usual meanings.[4a] This behavior is observed for all complexes studied with the exception of $NiBr_2(PCyh_3)_2$ and $NiBr_2(PPh_2\text{-}t\text{-}Bu)_2$. The former complex showed no isotropic shifts at 31° which is consistent with $N_t = 0$ while the latter showed linear Curie temperature dependence from +31 to −75° which is consistent with $N_t = 1.0$.

Solution magnetic susceptibility measurements are consistent with the pmr results because moments intermediate between 0 and *ca.* 3.00 BM are found in all cases except with the above-mentioned two complexes. The solution and solid moments for $NiBr_2(PCyh_3)_2$ indicate a planar diamagnetic complex. Stone and Dori[10] have reported that $\mu_{eff} = 1.81$ BM for this complex in CH_2Cl_2 which is in disagreement with our result. We have measured this moment on numerous occasions in several thoroughly degassed solvents and have concluded that the compound slowly reacts with CH_2Cl_2 yielding paramagnetic products. The pmr spectrum at 31° in CD_2Cl_2 (freshly treated with K_2CO_3) shows the appearance of several isotropically shifted peaks which grow in with time and are quite large after *ca.* 30 min. A temperature-dependent study showed linear Curie dependence for all of these new peaks, which indicates that they are fully paramagnetic and that no configurational equilibrium is present.[33] All of the complexes studied are subject to slow solvolysis with halogenated solvents which necessitates measurements to be made quickly on fresh solutions.

The pmr and magnetic susceptibility data are only consistent with equilibrium I.[7,8] The thermodynamic results obtained from pmr measurements are shown in Table II. The magnetic data yield similar N_t values but are not presented because accurate tetrahedral solution moments are not known. The position of equilibrium I is best described by N_t or ΔG at 31° because these parameters contain the smallest experimental uncertainty. The other parameters, ΔH and ΔS, contain larger errors because they are much more sensitive to the extrapolation of isotropic shifts from frozen-out spectra. The values of ΔS are within experimental uncertainty but solvent effects can easily cause the observed variations. The ΔS values reported here are higher than those previously reported for similar compounds by *ca.* 2-3 eu because in the present study the thermodynamic parameters were calculated empirically, *i.e.*, not assuming the Curie law (see treatment of data section). Other studies assumed Curie temperature dependence.[7,8] Large variations in N_t are caused predominantly by variations in ΔH whereas small effects could result from variations in ΔS. Significant substituent effects (ΔN_t values >0.10) are therefore caused by enthalpy changes and may be best understood in terms of relative stabilization or destabilization of the planar and tetrahedral isomers. In all cases where thermodynamic parameters were measured, the planar isomer is energetically more stable than the tetrahedral. This observation is consistent with most compounds exhibiting equilibrium I.[4,7,8]

Ligand Field Spectra. Electronic spectral results are also consistent with equilibrium I. Bands assignable to the tetrahedral ($\nu_2[{}^3T_1 \rightarrow {}^3A_2]$) and planar ($\cdots d_{xy} \rightarrow \cdots d_{xy}\text{-}d_{x^2-y^2}$) isomers are observed.[7a] The transition labeled ν_1 is actually a combination band composed of both planar and tetrahedral $[{}^3T_1(F) \rightarrow {}^3T_1(P)]$ transitions. Evidence for the planar component of ν_1 is obtained by examining the extinction coefficients as a function of N_t (Table III). At low N_t, ϵ for ν_2 is small whereas ϵ for ν_1 is large. As N_t

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(31) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); C. H. Heathcock and S. R. Poulter, *J. Amer. Chem. Soc.*, **90**, 3766 (1968).

(32) The cyclopropyl β-H_2 resonance was only used for $PCyp_3$ complexes. This resonance is labeled β-H_2 in Figure 1.

(33) The variable-temperature pmr spectrum is the best instrument for demonstrating the presence of the planar–tetrahedral equilibrium because it shows the individual species causing anomalous magnetism. Stone and Dori[10] also reported a somewhat lower moment for this complex in benzene. Our experiments show diamagnetism and no isotropic shifts in toluene. We have noted that oxidation of the complex results in some phosphine oxide impurity which yields a small but measurable magnetic moment. This is presumably due to phosphine oxide coordination leading to tetrahedral stereochemistry: F. A. Cotton and D. M. L. Goodgame, *J. Amer. Chem. Soc.*, **82**, 5771 (1960).

increases, ϵ for ν_2 increases while ϵ for ν_1 slowly decreases but never below 190 l. mol^{-1} cm^{-1}. This behavior has been previously observed and is characteristic of equilibrium I. The position of ν_2 reflects the ligand field strength of the tetrahedral isomer whereas ν_1 cannot be easily interpreted because the overlapping absorptions obscure the peak positions.

Substituent Effects on Thermodynamics. The position of equilibrium I is extremely sensitive to the halide and the phosphine substituent. All studies to date including the present have shown that N_t increases in the order Cl < Br < I with constant phosphine.[6-8,10] In this study, $NiX_2(PPh_2Cyp)_2$ has $N_t = 0.56$ and 0.92 for X = Cl and Br, respectively. This trend has been interpreted as resulting from both steric and electronic effects. Space-filling models show steric crowding between phosphine ligands and the halides in trans-planar complexes. This strain is relieved in the tetrahedral isomer and hence the order in N_t depends on the size of the halide. Indeed the average P-Ni-Br angle in $NiBr_2(PPh_2Bz)_2$ is 92.7 and 108.2° for the planar and tetrahedral isomers, respectively.[9b] Electronic arguments are less clear because the ligand field strength follows the spectrochemical series (Cl > Br > I) for both isomers.

Phosphine substituents also show a marked effect on N_t. For example, in this study N_t varies from 0.0 to 0.95 for $NiBr_2L_2$ where L = $PCyh_3$ and $PCyp_3$, respectively. Steric[10] and electronic[7a] arguments have been put forth to explain trends in N_t as a function of phosphine substituent. The thermodynamic results in Table II yield proof that a trialkylphosphine and several dialkylphenylphosphine ligands can indeed exhibit equilibrium I in NiX_2L_2 type complexes. These results derive from pmr, electronic, and magnetic data. Previous reports on complexes employing these ligands were based on magnetic[10,20] measurements alone. The factors which determine this stereochemistry are discussed below.

(1) Steric Effects. The results in Table II indicate that steric effects of phosphine substituents are relatively unimportant in influencing N_t. This is clearly seen in the series of $NiBr_2L_2$ complexes where L, N_t are as follows: PPh_3, 1.0; $PCyp_3$, 0.95; $PCyh_3$, 0.0. Tricyclohexylphosphine is the largest phosphine but prefers a planar stereochemistry whereas the smaller tricyclopropylphosphine stabilizes the tetrahedral. Steric arguments would predict the opposite effect because the larger, more bulky phosphine would destabilize the crowded planar isomer. Steric effects are evident, however, as shown in the series of $NiBr_2(PPh_2R)_2$ complexes where R, N_t are as follows: CH_3, 0.64; C_2H_5, 0.67;[8b] n-C_4H_9, 0.70;[8b] t-C_4H_9, 1.00. The steric influence of the t-C_4H_9 substituent greatly destabilizes the planar isomer whereas the n-alkyl groups have only a small effect. The pmr of the t-C_4H_9 complex shows splittings of methyl and phenyl meta resonances at 31° which result from hindered rotation of P-C bonds which demonstrates steric strain in the tetrahedral isomer. The strain in the planar isomer is expected to be great enough to prevent its formation. These arguments show that steric factors are only important in affecting N_t in extreme cases.

An interesting trend in ν_2 (Table III) as a function of phosphine substituent sheds more light on ligand steric effects. In the cyclohexyl series with X = Br [L, ν_2 (cm^{-1}) = PPh_3, 10,980; PPh_2Cyh, 11,360; $PPhCyh_2$, 11,120] the ligand field strength should follow the trend in ligand basicity (*vide infra*) which explains the increase from PPh_3 to PPh_2Cyh. The subsequent decrease in ligand field strength on going to $PPhCyh_2$ can only be explained by steric lengthening of the Ni-P bond. This observation has been noticed by others.[10] In the cyclopropyl series where steric strain is minimized the following trend is observed with X = Br: L, ν_2 (cm^{-1}) = PPh_3, 10,980; PPh_2Cyp, 11,520; $PPhCyp_2$, 11,560; $PCyp_3$, 11,840. Here we see the expected correlation with ligand basicity. Further evidence for steric weakening of the ligand field is seen in the series with X = Br and L = PPh_2R: R, ν_2 (cm^{-1}) = CH_3, 11,680; C_2H_5, 11,360; n-C_4H_9, 11,420; t-C_4H_9, 10,800.[34] These phosphines have similar electronic properties but different steric requirements. These steric effects should be even more important in the planar isomers but the planar transition cannot be independently observed (*vide supra*).

(2) Electronic Effects. Electronic arguments are clearly needed to explain why $NiBr_2(PCyh_3)_2$ is planar and $NiBr_2(PCyp_3)_2$ is greater than 95% tetrahedral. Indeed, electronic arguments have often been used to explain why triarylphosphines always cause tetrahedral stereochemistry, while replacement of aryl with alkyl groups stabilizes the planar (or destabilizes the tetrahedral).[6,9a,10,20] These arguments usually take the form that effects which weaken the ligand field tend to stabilize the tetrahedral form relative to the planar form. Such arguments are vague because it is not clear to which isomer the ligand field strength refers. It has recently been shown that phenyl para substituents, which are electron withdrawing, decrease ν_2 but increase ν_1(planar).[7a] These same electron-withdrawing groups were found to stabilize the planar isomer relative to the tetrahedral.[7a] These observations contradict earlier explanations. In the present work the tetrahedral ligand field strength in $NiBr_2(PCyp_3)_2$ is the strongest we have observed, yet $N_t >$ 0.95. Clearly, electronic effects are not as simple as have been argued.

The relative σ-donor strength of phosphine ligands can be determined by measurements of basicity. Streuli[35] has determined numerous pK_a values of substituted phosphines and Denney and Gross have recently measured the pK_a of $PCyp_3$.[36] Pertinent results are as follows for L, pK_a: PPh_3, 2.73; $PPhMe_2$, 6.49; $PCyp_3$, 7.60; P-i-Bu_3, 7.97; PMe_3, 8.65; $PCyh_3$, 9.70. These data illustrate that PPh_3 is a much weaker base than any trialkylphosphines. The low ligand field strength in $NiBr_2(PPh_3)_2$ clearly results from this weak σ-donor property. However, this cannot be the only factor which causes high N_t because $PCyp_3$ which has a basicity similar to other trialkylphosphines produces very large ligand fields and yields high values of N_t. The electronic interaction which causes high N_t values must involve a π interaction among phosphorus, nickel, and substituents.

Convincing evidence for π interaction in an inductive sense has been reported.[7a] Thermodynamic and electronic data were measured for $NiX_2(PMe(aryl)_2)_2$ type complexes where phenyl para substituents were varied over a wide range of Hammett σ_p values. A linear correlation between ΔG and $\Sigma\sigma_p$ was found such that the more electron-withdrawing para substituents (high $\Sigma\sigma_p$) caused high ΔG values (low N_t). A corresponding trend was observed with ν_2(tetrahedral) and ν_1(planar). Groups which caused high N_t

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[34] Table III and ref 9a.

[35] C. A. Streuli, *Anal. Chem.*, 32, 985 (1960); W. A. Henderson, Jr., and C. A. Streuli, *J. Amer. Chem. Soc.*, 82, 5791 (1960).

[36] D. B. Denney and F. J. Gross, *J. Org. Chem.*, 32, 2445 (1967).

values resulted in high ν_2 and low ν_1. Linear correlations of this type were found. These results were interpreted in terms of ligand field stabilization energy (LFSE). The decrease in ν_1(planar) with increasing electron-withdrawing ability was interpreted as a π-bonding interaction (see Figure 7 of ref 7a). This argument cannot account for the differences in PPh_3, $PCyp_3$, and $PCyh_3$.

Phenyl and cyclopropyl groups have π-symmetry orbitals which can conjugate to the phosphorus 3d orbitals. The cyclohexyl group cannot participate in this type of interaction. There are numerous results which support π-bonding and conjugative effects produced by the cyclopropyl group.[31,37,38] This conjugative interaction will decrease the ligand field splitting in the planar isomer in the following way. Overlap of the π-symmetry orbitals of the phenyl or cyclopropyl group with the 3d orbitals of phosphorus will reduce the π-acceptor capacity of the phosphorus atom. This will reduce the nickel $d_{xy} - d_{x^2-y^2}$ separation by destabilizing the π-symmetry d_{xy} orbital.[39] The $d_{x^2-y^2}$ orbital has σ symmetry and will not be affected by this interaction. The ligand field splitting in the tetrahedral isomer will not show this large π effect because the t_2 and e orbitals both have π symmetry and will be similarly affected.[40] Thus, these groups will reduce the LFSE of the planar isomer relative to the tetrahedral. The planar transition, ν_1, cannot be accurately measured in these complexes because of interference from the $^3T_1 \rightarrow {}^3T_1(P)$ tetrahedral transition. Stone and Dori[10] have examined a series of planar thiocyanate complexes of the type $Ni(NCS)_2L_2$ in which ν_1(planar) decreases in the order $PCyh_3 > PPhCyh_2 > PPh_2Cyh > PPh_3$. The above arguments provide evidence for π interaction between cyclopropyl and phosphorus and between phosphorus and nickel.

The vinyl group is also expected to π bond with the phosphorus and thereby destabilize the planar isomer. The low N_t value presumably results because PPh_2Vy produces a weaker tetrahedral ligand field than PPh_2Cyp (ν_2 in Table III). Therefore the LFSE of the tetrahedral isomer is also lowered resulting in the observed N_t. This illustrates that the relative N_t values for these complexes are a sensitive function of competitive electronic effects in both isomers.

Substituent Effects on Kinetic Parameters. Kinetic parameters for five complexes are reported in Table IV. $\Delta S^\ddagger$ values are all small and $\Delta H^\ddagger$ values reflect the trends in rate constant. The parameters are similar to those reported by La Mar and Sherman[8b] for analogous complexes. The most accurate parameters for comparison are $\Delta G^\ddagger(-50°)$ or $k_t^{-50°}$ because these values were determined in the region of line broadening and are not subject to extrapolation errors. The halide dependence, Cl faster than Br, is consistent with other investigations.[7,8] The dependence on phosphine substituent is less obvious and, as concluded by others,[7a,8b] uninterpretable. The results for $PCyp_3$ and $PPhCyp_2$ ligands are the first reported for trialkyl- and aryldialkylphosphines. However, these ligands cause no unusual kinetic effects.

La Mar and Sherman[8b] reported a second-order kinetic acceleration of the rate of planar-tetrahedral interconversion for $NiBr_2(PPh_2Me)_2$ with added phosphine ligand. We have performed similar experiments with $NiBr_2(PPh_2Cyh)_2$ and excess PPh_2Cyh with completely different results. In this case, as much as 0.28 molar excess ligand failed to perturb the kinetics of interconversion. The free ligand appeared in the pmr spectrum at its unshifted diamagnetic position even at +80°. In the case of PPh_2Me, as little as 0.0003 M excess phosphine significantly accelerated the rate. This kinetic acceleration presumably results from a ligand exchange process because the added ligand resonances are averaged with the planar and tetrahedral resonances.[41] La Mar and Sherman[8b] pointed out that PPh_2Me must exchange with its tetrahedral complex faster than PPh_3 with $NiBr_2(PPh_3)_2$. Ligand-exchange kinetics of the latter have been measured and are second order in added phosphine.[42] Our results show that PPh_2Cyh ligand exchange is even slower. This must result from steric hindrance caused by the bulkier PPh_2Cyh ligand which would slow down second-order ligand exchange. Tolman[43] has shown that steric factors are more important than electronic factors in determining the thermodynamics and kinetics of ligand exchange in NiL_4 type complexes. The relative sizes of tertiary phosphine ligands can be estimated from their steric cones defined by Tolman.[43] This order is $PCyh_3 > PPh_3 > PMe_3$ which supports our observations.

Registry No. *sp*-$NiCl_2(PCyp_3)_2$, 36673-22-0; *sp*-$NiCl_2(PPhCyp_2)_2$, 36673-24-2; *sp*-$NiCl_2(PPh_2Cyp)_2$, 36655-08-0; *sp*-$NiBr_2(PPhCyp_2)_2$, 36673-25-3; *sp*-$NiBr_2(PCyh_3)_2$, 36673-26-4; *sp*-$NiBr_2(PPhCyh_2)_2$, 36673-27-5; *sp*-$NiBr_2(PPh_2Cyh)_2$, 36673-28-6; *sp*-$NiBr_2(PPh_2Vy)_2$, 36673-29-7; *sp*-$NiBr_2(PPh_2Me)_2$, 28582-49-2; *td*-$NiCl_2(PCyp_3)_2$, 36673-23-1; *td*-$NiCl_2(PPhCyp_2)_2$, 36673-31-1; *td*-$NiCl_2(PPh_2Cyp)_2$, 36655-09-1; *td*-$NiBr_2(PCyp_3)_2$, 36673-32-2; *td*-$NiBr_2(PPhCyp_2)_2$, 36688-77-4; *td*-$NiBr_2(PPh_2Cyp)_2$, 36655-10-4; *td*-$NiBr_2(PPh_2Cyh)_2$, 36655-11-5; *td*-$NiBr_2(PPh_2Vy)_2$, 36673-33-3; *td*-$NiBr_2(PPh_2\text{-}t\text{-}Bu)_2$, 36673-34-4; *td*-$NiBr_2(PPh_2Me)_2$, 36673-35-5; *td*-$NiBr_2(PPh_3)_2$, 36673-36-6.

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(37) M. J. Jorgenson and T. Leung, *J. Amer. Chem. Soc.*, 90, 3769 (1968); G. Dauben and G. H. Berezin, *ibid.*, 89, 3449 (1967).

(38) F. A. Van Catledge, submitted for publication.

(39) This argument is essentially the one put forth by Venanzi to explain why the replacement of alkyl groups by phenyl groups in $Ni(PR_3)_2X_2$ complexes weakens the planar crystal field energy (see Figure 5 of C. R. C. Cousmaker, M. H. Hutchinson, J. R. Mellor, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 2705 (1961)). The observations of Pignolet, Horrocks, and Holm[7a] are also consistent with this description. Inductive π perturbations will further vary the LFSE of the planar and tetrahedral isomers according to Figure 7 of ref 7a and arguments therein.

(40) La Mar has shown that π bonding is unimportant in tetrahedral dihalobis(tertiary phosphine)nickel(II) complexes: G. N. La Mar, E. O. Sherman, and G. A. Fuchs, *J. Coord. Chem.*, 1, 289 (1971).

(41) We have noticed that added PPh_2Me not only accelerates the rate of the planar-tetrahedral interconversion but also changes the equilibrium constant. The added phosphine favors formation of the planar isomer requiring $k_{t\rightarrow p}$ to be increased over $k_{p\rightarrow t}$. This implies that the role of added phosphine is to produce a five-coordinate transition state primarily from the tetrahedral isomer which would rapidly convert into the planar and tetrahedral isomers. The net result, provided ligand exchange is faster than the planar-tetrahedral interconversion, would be to accelerate the interconversion and shift the equilibrium toward the planar form.

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

(43) C. A. Tolman, *J. Amer. Chem. Soc.*, 92, 2956 (1970).