Thermodynamics and Kinetics of the Planar–Tetrahedral Interconversion of Dihalobis(diarylmethylphosphine)nickel(II) Complexes

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Abstract: A series of 26 dihalobis(tertiary phosphine)nickel(II) complexes of the general type $Ni[(p\text{-}ZC_6H_4)(p\text{-}Z'C_6H_4)MeP]_2X_2$ ($X = Cl^-, Br^-$, and I^-) has been prepared and the existence of a planar $\rightleftharpoons$ tetrahedral structural equilibrium in chloroform solution demonstrated by a combination of magnetic, spectral, and proton resonance measurements. The unique feature of a number of chloride and bromide complexes is the temperature dependence of their rates of structural interconversion. Within the temperature range of *ca.* −70–50° it has been possible to obtain in certain cases both the frozen-out and completely averaged pmr spectra, permitting the quantitative measurement of the kinetic and thermodynamic quantities associated with the isomerization reaction by line-broadening and contact-shift methods, respectively. Complete thermodynamic data have been obtained for 21 complexes and structural trends in series of constant halide and constant phosphine determined. At parity of phosphine the relative stability of the tetrahedral form increases in the order $Cl < Br < I$. In the three constant halide series the stereochemical populations have been found to be remarkably sensitive to the electronic properties of Z and Z′, and in each a linear free energy relationship has been found with the Hammett substituent constants $\Sigma\sigma_p$. Relative ligand field stabilization energies of planar and tetrahedral isomers, inferred from spectral measurements on equilibrium mixtures in the chloride and bromide series, are nearly linearly related to the proportions of the isomers independently measured by pmr. This correlation provides the basis of the interpretation of stereochemical trends in the halide series. Rate constants and activation parameters for the tetrahedral $\rightleftharpoons$ planar conversion of four complexes have been evaluated; the former vary from *ca.* 10^2–10^3 sec^{-1} at −50° to *ca.* 10^5–10^6 sec^{-1} at 25°. The limited data available indicate that for complexes with constant phosphine ligands, the rates of structural change increase in the order $Br < Cl < I$.

The configurational equilibrium 1 is now well established for a wide variety of bischelate nickel(II) complexes in noncoordinating solvents.[3] Thermodynamic parameters characterizing the structural change and spin density distributions in the paramagnetic, tetrahedral isomers are in most cases readily evaluated from an analysis of the isotropic hyperfine contact shifts of ligand protons.[4] In contrast to the considerable body of thermodynamic data collected for the structural conversion, the dynamics of this process remain unspecified except for the estimation of the probable range of lifetimes for the stereoisomers. All bischelate nickel(II) complexes involved in equilibrium 1 manifest nmr signals whose chemical shifts are averaged over both isomers at temperatures as low as *ca.* −60°, whereas both forms are detectable in the electronic spectra of equilibrium mixtures. These results have led to the conclusion that the upper limit of the lifetime of each isomer is *ca.* 10^{-4}–10^{-5} sec and the lower limit is *ca.* 10^{-13} sec.[5–7]

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

Equilibrium 1 is not restricted to bischelate species and has been demonstrated with various degrees of completeness for dihalobis(tertiary phosphine)-[8–12] and dihaloditertiary phosphine–nickel(II) complexes[13,14] in solution. Appreciable population of both isomers of complexes in the first group under ordinary conditions is confined to species of the type $Ni(Ar_2RP)_2X_2$ ($X = Cl^-, Br^-, I^-$), derived from diarylalkylphosphines. In some cases both stereoisomers of a given complex have been isolated,[15] while in at least one other case, *viz.*, $Ni[Ph_2(PhCH_2)P]_2Br_2$,[16] both may be incorporated in the same unit cell. Complexes of the type $Ni(R_3P)_2X_2$,[8,17–20] with the apparent exception of dichlorobis(tricyclopropylphosphine) nickel(II),[11] and $Ni(ArR_2P)_2$-

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X_2[8,10] are planar and diamagnetic in the solid and solution phases. $Ni(Ar_3P)_2X_2$ complexes are paramagnetic and tetrahedral in the solid state,[21-23] and in solution exist completely, or nearly completely,[9] in the tetrahedral form as deduced from ligand field spectra,[9,22] dipole moments,[9,21] and pmr data.[24,25]

Very recently it has been discovered that the structural interconversion of a number of $Ni(Ar_2RP)_2X_2$ complexes, specifically $Ni[(p\text{-}MeOC_6H_4)PhMeP]_2Br_2$[12] and $Ni(Ph_2MeP)_2X_2$,[26] can be frozen out in chloroform, dichloromethane, or toluene solutions at temperatures below *ca.* −20°. Further, the dynamics of the process are such that it has been possible to obtain within an accessible temperature interval both the frozen-out and completely averaged pmr spectra, with the consequence that the kinetic and thermodynamic properties of the structural change can be quantitatively measured by line-broadening and contact-shift methods, respectively. This report contains the results of an investigation of the thermodynamics and kinetics of the planar–tetrahedral structural conversion of complexes of the type $Ni[(p\text{-}ZC_6H_4)(p\text{-}Z'C_6H_4)MeP]_2X_2$. Availability of mono- and disubstituted diarylmethylphosphines has permitted variation of the substituents Z and Z′ over a meaningful range of resonance and inductive effects, thereby facilitating the first detailed examination of the electronic factors operative in the structural equilibrium of $Ni(Ar_2RP)_2X_2$ complexes.

Table I. Characterization Data for $Ni[(p\text{-}ZC_6H_4)(p\text{-}Z'C_6H_4)MeP]_2X_2$ Complexes[a]

X	Z	Z′	Mp, °C[b,c]	% calcd C	% calcd H	% found C	% found H
Cl	H	H	143–145	58.91	4.95	59.23	4.98
	H	Cl	152–154	52.14	4.04	51.83	4.19
	H	Me	117–120	60.25	5.42	60.32	5.54
	H	OMe	120–122	57.10	5.13	56.76	5.33
	H	NMe_2	133–136	57.36	6.09	57.08	5.94
	H	CF_3	110–113	50.49	3.63	50.77	3.50
	Cl	Cl	169–174	47.47	3.37	47.30	3.23
	Me	Me	160–163	61.37	5.85	61.01	5.93
	OMe	OMe	142–144	55.42	5.27	55.18	5.29
Br	H	H	164–167	50.45	4.23	50.27	3.97
	H	Cl	147–149	45.40	3.52	45.28	3.67
	H	Me	139–142	51.97	4.67	52.00	4.72
	H	OMe	150–153	49.61	4.46	49.42	4.74
	H	NMe_2	152–157	51.70	5.48	51.96	5.89
	Cl	Cl	165 (dec)	41.27	2.93	41.41	2.75
	Me	Me	156–158	53.37	5.08	53.43	5.36
	OMe	OMe	160–162	48.75	4.64	48.98	4.80
I	H	H	160–165	43.80	3.68	43.77	3.56
	H	Cl	120–123	39.94	3.09	39.68	3.04
	H	Me	122–125	45.38	4.08	45.43	3.92
	H	NMe_2	148–150	44.88	4.77	44.53	4.56
	H	CF_3	72–74	39.61	2.85	39.78	3.01
	Cl	Cl	147–150	36.71	2.61	36.44	2.57
	Me	Me	143 (dec)	46.60	4.46	46.34	4.38

[a] Data refer where appropriate to complexes prepared from racemic phosphines. [b] Uncorrected. [c] Solids may contain mixtures of planar and tetrahedral isomers.

Experimental Section

Preparation of Compounds. (a) Phosphines. The oxides of the *para*-substituted phosphines, $(p\text{-}ZC_6H_4)(p\text{-}Z'C_6H_4)MePO$, were either synthesized by the method of Korpiun, *et al.*,[27] or received from Dr. J. P. Casey.[28] The reduction of the phosphine oxides to phosphines was achieved with hexachlorodisilane.[29] Methyldiphenylphosphine was purchased from the Strem Chemical Co. All of the phosphine oxides and phosphines were characterized by their pmr spectra. The phosphines were stored under nitrogen at 0°.

(b) Complexes. The complexes were synthesized by mixing hot ethanolic solutions of the appropriate phosphine and hydrated nickel halide under nitrogen. In cases where precipitation did not occur on cooling to room temperature, hot, degassed *n*-hexane was added. The solid product was filtered under nitrogen and thoroughly washed with *n*-hexane. The *p*-perfluoromethylphenylphosphines were soluble in *n*-hexane, requiring the substitution of *n*-pentane. The solid complexes were used without further purification because satisfactory elemental analyses were obtained. Characterization data for the complexes are given in Table I. The solid complexes are air-stable. They vary in color, the chlorides, bromides, and iodides in most cases being red, green, and brown, respectively. In solution, the complexes slowly oxidize, the apparent ease of oxidation being I > Br > Cl. During this process the original colors of the solutions change to a light green, which is followed by formation of a cloudy solution and the separation of a white, water-soluble solid, which has not been characterized. Two complexes, $Ni[(p\text{-}CF_3C_6H_4)_2MeP]_2Br_2$ and $Ni[(p\text{-}MeOC_6H_4)_2MeP]_2I_2$, have been reported in Tables II and III without satisfactory elemental analyses. The solutions of these complexes were filtered and used without further purification.

Proton Magnetic Resonance Spectra. The pmr spectra used for the thermodynamic measurements and for characterizations were recorded on a Varian A-60 or A-60-A instrument equipped with a variable-temperature probe. All line width measurements were made on a Varian HA-100 spectrometer operated in the HR mode. All spectra were calibrated by the conventional sideband technique and the resonances were measured to within ±1 cps. All samples were dissolved in degassed deuteriochloroform or benzene-d_6, *ca.* 2% in TMS used as internal reference. The nmr tubes were sealed under nitrogen and the spectra were recorded within several hours as slow decomposition occurred after *ca.* 5 hr.

Magnetic Susceptibility Measurements. The solution moments were determined by the nmr method[30] in deuteriochloroform or benzene-d_6 which contained ~5% v/v TMS, and were 0.07–0.09 *M* in complex. Data are given in Table II. Moments of solids at room temperature were measured by the Gouy method using aqueous nickel chloride solution as the calibrant. The following results were obtained for $Ni(Ph_2MeP)_2X_2$ at 22.0°. $X = I^-$: $\chi_{corr}^M = 4216 \times 10^{-6}$ cgs units, $\mu_{eff} = 3.17$ BM; $X = Br^-$: $\chi_{corr}^M = 4337 \times 10^{-6}$ cgs units, $\mu_{eff} = 3.22$ BM.

Electronic Spectra. Electronic spectra were recorded on a Cary Model 14 spectrophotometer using 10^{-2}–10^{-3} *M* solutions. The samples were weighed into quartz vacuum cells and pumped free of oxygen before diluting to volume with degassed chloroform under nitrogen. This procedure was essential to prevent oxidation of the dissolved complex mentioned above. Data and representative spectra are presented in Table III and Figures 4 and 5.

Molecular Weight Determination. Measurements were made with a Mechrolab Model 302 osmometer at 37° using benzene solutions *ca.* 0.06 *M* in complex. Benzil and triphenylphosphine were used as calibrants.

Calcd for $Ni[(p\text{-}MeOC_6H_4)PhMeP]_2Cl_2$: mol wt, 586. Found: 593. Calcd for $Ni[(p\text{-}MeOC_6H_4)PhMeP]_2Br_2$: mol wt, 678. Found: 656.

Results and Discussion

This investigation has been directed toward an elucidation of the thermodynamics and kinetics of

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Table II. Magnetic and Thermodynamic Data[a] for Ni[(p-ZC_6H_4)(p-$Z'C_6H_4$)MeP]$_2X_2$ Complexes in Chloroform Solution

X	Z	Z′	$\mu_{eff}^{303°}$, BM	$\Delta\nu_m^{303°}$, ppm	ΔH, cal/mol	ΔS, eu	$\Delta G^{298°}$, cal/mol	$N_t^{298°}$	Temp range, °K
Cl	H	H	1.77	−3.67	1640	3.70	+537	0.29	255–325
	H	Cl	1.41	−1.92	2140	4.31	+854	0.19	255–325
	H	Me	1.81	−3.86	1830	4.49	+486	0.31	260–327
	H	OMe	1.97	−4.68	1730	4.63	+355	0.36	273–343
	H	NMe_2	2.25	−4.80	1410	4.68	+12	0.50	268–332
	H	CF_3	1.13	−1.18			∼+1100[b]	∼0.13[b]	
	Cl	Cl		−0.90			∼+1200[c]	∼0.10[c]	
	Me	Me	1.92	−4.18	1820	4.86	+374	0.35	266–323
	OMe	OMe	2.05	−4.68	1380	3.76	+264	0.39	265–332
Br	H	H	2.48	−8.21	638	2.85	−212	0.59	283–332
	H	Cl	2.16	−5.58	1150	3.31	+163	0.43	277–333
	H	Me	2.63	−8.79	497	3.09	−423	0.68	282–331
	H	OMe	2.70	−8.20	383	3.00	−512	0.70	286–343
	H	NMe_2	2.92	−8.47	136	3.55	−921	0.83	268–332
	Cl	Cl	1.51	−3.14	1860	3.73	+747	0.22	265–329
	Me	Me	2.68	−9.19	492	3.19	−459	0.69	283–332
	OMe	OMe	2.83	−9.32	6.3	2.38	−704	0.77	265–332
	CF_3	CF_3		−1.20			∼+1200[c]	∼0.10[c]	
I	H	H	2.70	−9.32	179	2.60	−597	0.73	237–323
	H	Cl	2.35	−6.82	869	3.29	−111	0.55	244–323
	H	Me	2.75	−10.0	296	3.21	−661	0.75	232–315
	H	NMe_2	3.02	−12.4			−1310[b]	0.92[b]	
	H	CF_3	1.96	−4.88	1500	3.92	+330	0.36	226–303
	Cl	Cl	1.93	−4.28	1530	4.00	+335	0.36	223–318
	Me	Me	2.88	−10.2	5.2	3.19	−946	0.83	237–313
	OMe	OMe		−10.3			−1000[c]	0.84[c]	

[a] Data refer to mixtures of diastereoisomers where appropriate. [b] Determined at 303° from measurements of μ_{eff} and use of μ_t values cited in text. [c] Approximate values, determined from measurement of contact shift and average value of coupling constants in series of disubstituted complexes (X = Cl, av a_m = +0.107 G; X = Br, av a_m = +0.117 G; X = I, av a_m = +0.115 G).

Table III. Ligand Field Spectral Data for Ni[(p-ZC_6H_4)(p-$Z'C_6H_4$)MeP]$_2X_2$ Complexes in Chloroform Solution

X	Z	Z′	$N_t^{298°}$	ν_1[a] (ϵ[b])	ν_2[c] (ϵ[b])	ν_3[c] (ϵ[b])
Cl	H	NMe_2	0.50	5,500 (20)	11,960 (91)	*d*
	OMe	OMe	0.39	5,500 (19)	11,910 (73)	*d*
	H	OMe	0.36	5,500 (18)	11,890 (93)	*d*
	Me	Me	0.35	*e*	11,870 (60)	20,250 (530)
	H	Me	0.31	5,500 (14)	11,850 (60)	20,300 (530)
	H	H	0.29	5,500 (15)	11,790 (59)	20,420 (550)
	H	Cl	0.19	5,500 (6.4)	11,710 (33)	20,520 (610)
	H	CF_3[f]	0.13	*e*	11,620	20,730
	Cl	Cl	0.10	5,500 (4.0)	11,680 (15)	20,700 (660)
Br	H	NMe_2	0.83	5,200 (31)	11,860 (190)	*d*
	H	OMe	0.70	5,200 (47)	11,820 (290)	18,620 (sh)
	Me	Me	0.69	5,200 (34)	11,800 (180)	18,620 (190)
	H	Me	0.68	5,200 (36)	11,710 (250)	18,690 (342)
	H	H	0.59	5,200 (31)	11,690 (180)	18,780 (290)
	H	Cl	0.43	5,200 (23)	11,590 (140)	19,050 (410)
	Cl	Cl	0.22	5,200 (15)	11,510 (65)	19,350 (410)
	CF_3	CF_3[f]	0.10	*e*	11,350	19,550
I	Me	Me	0.83	4,800 (50)	11,140 (420)	*d*
	H	H	0.73	4,800 (39)	11,030 (360)	*d*
	Cl	Cl	0.36	4,800 (26)	10,820 (220)	*d*

[a] ±150 cm^{-1}. [b] l. mol^{-1} cm^{-1}. [c] ±40 cm^{-1}. [d] Obscured by rapidly rising absorption extending to ultraviolet region; maximum could not be located accurately. [e] Insufficient sample. [f] Impure sample.

the planar–tetrahedral structural interconversion of complexes of the type Ni[(p-ZC_6H_4)(p-$Z'C_6H_4$)MeP]$_2$-X_2, X = Cl^-, Br^-, I^-, in chloroform solution. Particular emphasis has been placed on the effects of variation of the substituents Z and Z′ and of halide on the position of equilibrium 1 and, to a considerably lesser extent, on the rate of structural change. Because of their location, variation of the phosphine substituents should have no significant, purely steric effect on the relative stabilities of planar and tetrahedral isomers of a given species, thus allowing measurement of electronic effects on the thermodynamic and kinetic properties of the structural isomerization reaction. Some 26 complexes have been prepared and investigated. For 21 of these complete thermodynamic data characterizing equilibrium 1 have been obtained and are discussed first. Kinetic measurements were made on four systems and results obtained are considered in the final section. Characterized complexes are listed in Table I; of these, only the members of the Ni(Ph_2MeP)$_2X_2$ series have been reported previously by other investigators.[15]

Establishment of the Planar–Tetrahedral Equilibrium. The configurational equilibrium has been established by measurement of magnetic moments, ligand field spectra, and isotropic pmr shifts in chloroform solu-

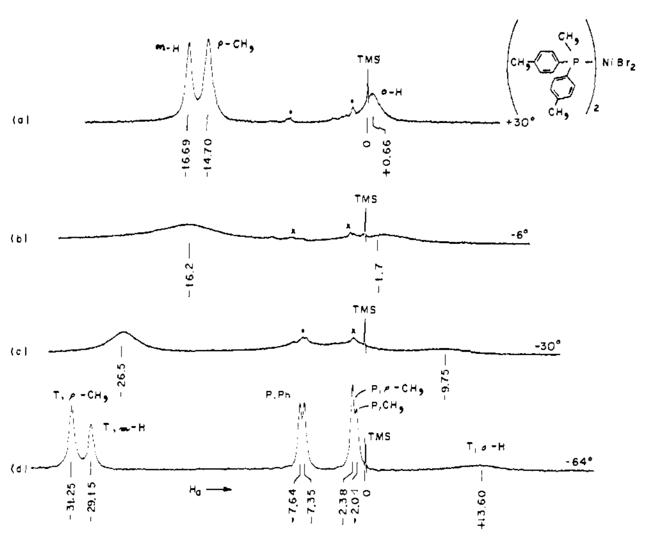

Figure 1. Pmr spectra (100 MHz) of $Ni[(p\text{-tol})_2MeP]_2Br_2$ in $CDCl_3$ solution illustrating completely averaged (a), intermediate (b, c), and frozen-out (d) cases. X indicates an impurity which is probably phosphine oxide. P, planar; T, tetrahedral.

tion. Solution magnetic moments at 30°, given in Table II, fall below the usual range of 3.1–3.4 BM[31] for tetrahedral dihalobis(tertiary phosphine)nickel(II) complexes.[6–11,15] Isotropic shifts of complexes, where checked, have the non-Curie temperature dependencies required by equilibrium 1 in those temperature ranges where the structural interconversion is fast on the pmr time scale. The ligand field spectra reveal in most cases bands assignable to both planar and tetrahedral species whose relative intensities are qualitatively consistent with the proportions of the two isomers determined by the contact shift method (*vide infra*). The spectra are considered in more detail in a subsequent section; spectral data are set out in Table III. Two representative complexes, $Ni[(p\text{-}MeOC_6H_4)PhMeP]_2X_2$, $X = Cl^-$ and Br^-, were determined to be monomeric in benzene solution. These results are consistent only with the existence of a planar–tetrahedral equilibrium, indicating that the present group of $Ni(Ar_2MeP)_2X_2$ complexes constitutes a further set of examples of dihalobis(diarylalkylphosphine)nickel(II) species[8–10] which exhibit this equilibrium in solution.

The temperature dependencies of the pmr spectra for two typical complexes are shown in Figures 1 and 2. At relatively high temperatures in the range of measurement, signals averaged over the two stereoisomers are observed. As the temperature is lowered all observable signals broaden markedly and eventually separate into two sets of sharp, usually distinct peaks. One set, occurring in the diamagnetic region of the free phosphine, is due to the planar isomer, and the other, containing signals markedly shifted from the diamagnetic region, arises from the tetrahedral isomer. This behavior signifies passage from the temperature region of fast structural interchange on the pmr time scale through a range of intermediate rates, and finally to the completely frozen-out equilibrium mixture of isomers. The latter situation could be reached with a number of complexes of the chloride and bromide series, but none of the iodide systems could be completely frozen out down to −70°. Signal assignments for the planar forms were readily made from the spectra of the appropriate phosphines. Those for the tetrahedral isomers were obtained by comparison with the spectra of $Ni(Ph_3P)_2X_2$ and $Ni(p\text{-}tol_3P)_2X_2$ complexes[24,25,32] and by integration. The only signal not consistently detected in the averaged and frozen-out spectra was that of the phosphine methyl group, which is expected to be strongly shifted and severely broadened in the tetrahedral form due to its proximity to the paramagnetic metal ion.[33] In the frozen-out temperature region the isotropic shifts of the *m*-H signals of the phenyl groups showed excellent Curie dependence in plots of shifts *vs.* $1/T$, which extrapolated through zero shift at infinite temperature.

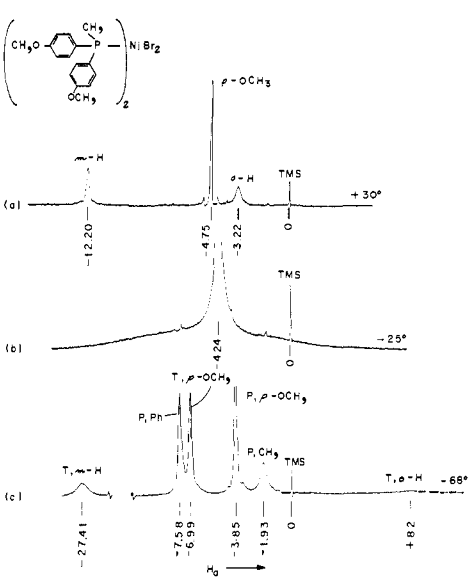

Figure 2. Pmr spectra (100 MHz) of $Ni[(p\text{-}MeOC_6H_4)_2MeP]_2Cl_2$ in $CDCl_3$ solution illustrating completely averaged (a), intermediate (b), and frozen-out (c) cases. P, planar; T, tetrahedral.

Thermodynamics of the Structural Conversion. Thermodynamic quantities were determined in most cases from measurement of the solution magnetic moments at 30° and the temperature dependencies of the isotropic shifts of the *m*-H signals in the region of rapid structural interconversion. Previous studies[24,25] of the pmr spectra of tetrahedral $Ni(Ar_3P)_2X_2$ complexes have provided reasonable evidence that isotropic shifts of phenyl protons and methyl groups arise predominantly, if not exclusively, from contact interactions resulting from π delocalization of spin in the phenyl rings. Similar observations were made in this work. Isotropic shifts of *ortho*, *meta*, and *para* protons alternate in sign with the *meta* shifts being negative. Replacement of *p*-H with methyl produced a negative shift, consistent with the opposite signs of Q_{CH} and Q_{CCH_3}.[24,25] Hence, the temperature dependence of a *m*-H shift is given by eq 2, in which $\Delta\nu_m^{av}$ is the measured contact shift of the averaged *m*-H

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[31] Note that the range of moments (2.92–3.07 BM) of solid $Ni(Ph_3P)_2X_2$ complexes reported by Venanzi[21] is apparently too low. Subsequent measurements indicate a range of 3.27–3.41 BM.[22]

[32] L. H. Pignolet and W. DeW. Horrocks, Jr., *J. Amer. Chem. Soc.*, 90, 922 (1968).

[33] This signal was observed as a broadened feature at −11.8 ppm from TMS in the averaged (30°) spectrum of $Ni[(p\text{-}ClC_6H_4)_2MeP]_2Cl_2$, which is 10% tetrahedral (*cf.* Table II). The isotropic shift $\Delta\nu$ of this signal in the tetrahedral isomer is estimated to be −99 ppm from the relation $\Delta\nu = \Delta\nu^{av}/N_t$, in which $\Delta\nu^{av}$ is the observed shift minus that (−1.92 ppm *vs.* TMS) of the planar form (*cf.* eq 2).

resonance obtained using −7.50 ppm as the resonance position in all planar isomers, a_m the electron–nuclear

$$\frac{\Delta\nu_m^{\text{av}}}{\nu} = -a_m\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g\beta S(S+1)}{6SkT}N_t \qquad (2)$$

hyperfine coupling constant in gauss, and N_t the mole fraction of tetrahedral form. The other symbols have their usual meanings.[4] Values of N_t were determined from magnetic moments using eq 3, in which μ_t is the

$$N_t = \mu_{\text{obsd}}^2/\mu_t^2 = [\exp(\Delta G/RT) + 1]^{-1} \qquad (3)$$

limiting mnment of the tetrahedral form and μ_{obsd} the measured moment of the equilibrium mixture. $\Delta G = -RT \ln K_{\text{eq}}$ and $K_{\text{eq}} = N_t/(1 - N_t)$. Values of a_m were obtained from measurements of $\Delta\nu_m^{\text{av}}$ and N_t at 30°. The temperature dependence of ΔG was then evaluated from measurements of contact shifts within a range defined by the onset of slow structural interconversion at the low temperature end and thermal decomposition at the high temperature end. The ΔG data were fit by least squares to the equation $\Delta G = \Delta H - T\Delta S$. The complete set of thermodynamic data is presented in Table II. In obtaining these results the values of μ_t were assumed to be constant in a given halide series. The following values were employed:[34] 3.18 ($X = Cl^-$), 3.22 ($X = Br^-$), 3.17 BM ($X = I^-$). Errors in ΔG and N_t are estimated as ±100 cal/mol and ±0.04, assuming an error of ±0.10 BM in the magnetic moment measurements. Because of their lack of analytical purity or because they represented cases obviously near the extremes of stereochemical population within a given halide series, complete thermodynamic data for five complexes in Table II were not determined.

Stereochemical Trends. The series of chloride, bromide, and iodide complexes investigated contain nine, nine, and eight members, respectively. Although these series are not exact duplicates of one another, they do contain four members with common phosphine ligands whose complete sets of thermodynamic values were determined, and possess an otherwise sufficiently close correspondence to permit definition of the two basic stereochemical trends now considered.

(1) Series with Constant Phosphines. Seven comparisons of $N_t^{298°}$ values are available for the three halide series and several additional ones can be made for two of the series. In every case the order of increasing N_t is $Cl < Br < I$; ΔH values, where available, show the opposite trend. The trend in N_t values is consistent with that observed for other–$Ni(Ar_2RP)_2X_2$[8,10,15] and for dihaloditertiary phosphine–Ni(II) complexes.[13,14] It presumably results from the steric requirements of the halides. Metal chelate space-filling models clearly reveal a greater degree of steric crowding in *trans*-planar iodides than in the analogous bromides and chlorides.

(2) Series with Constant Halides. It has already been pointed out that in such a series the order of increasing stability of the tetrahedral isomer is $R_3P \sim ArR_2P < Ar_2RP < Ar_3P$.[8–10,15] In previous work the stability trends within the general class of $Ni(Ar_2RP)_2X_2$ complexes have not been well established, and the few results available have been derived from changes in the alkyl group[10] and are not quantitative. In this investigation use of the phosphines $(p\text{-}ZC_6H_4)(p\text{-}Z'C_6H_4)MeP$ has permitted the examination of two groups of complexes, those containing monosubstituted ($Z \neq Z' = H$) and disubstituted ($Z = Z'$) diphenylmethylphosphines. The substituents Z and Z′ have been varied over a significant span of differing inductive and resonance properties.

Stereochemical trends are not usually as pronounced in the constant halide as in the constant phosphine series. The effects of varying one *para* substituent are, however, readily observed. In the bromide series, for example, alteration of Z from Cl to NMe_2 ($Z' = H$) nearly doubles the percentage of tetrahedral form at 30°. Variation of the substituents in the disubstituted group from CF_3 to OMe produces a sevenfold increase in the proportion of tetrahedral isomer. From an inspection of the data in Table II, it is clear that in each halide series the stereochemical population is strikingly sensitive to changes in Z and Z′. Further, the data reveal that groups which are normally electron releasing when in *para*-substituted phenyl derivatives have a decided tendency to populate the tetrahedral form, whereas electron-withdrawing groups have the opposite effect. In order to correlate substituent properties with this stereochemical trend in each halide series, the relation between $\Delta G^{298°}$ and the appropriate Hammett substituent constants,[35] which are sensitive to both resonance and inductive effects,[36] has been investigated. The results are shown in Figure 3. A linear free energy relationship exists for the three halide series containing monosubstituted phosphines. The corresponding eq 4–6 were obtained by a least-squares treatment. A similar correlation also exists for the disubstituted phosphine complexes, but these were not included in the least-squares treatment because of the fewer number of examples and their

$$X = Cl^- \qquad \Delta G^{298°} = 0.944\Sigma\sigma_p + 0.598\ \text{(kcal/mol)} \qquad (4)$$

$$X = Br^- \qquad \Delta G^{298°} = 1.28\Sigma\sigma_p - 0.173\ \text{(kcal/mol)} \qquad (5)$$

$$X = I^- \qquad \Delta G^{298°} = 1.42\Sigma\sigma_p - 0.473\ \text{(kcal/mol)} \qquad (6)$$

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[34] The values for the bromide and iodide series were taken from our measurements on solid $Ni(Ph_2Me)_2X_2$ complexes, and are somewhat lower than the moments reported by Hayter and Humiec.[15] The analogous chloride complex is diamagnetic as a solid. Consequently, the μ_t value for the chloride series has been taken as an average of those for solid $Ni[Ph_2(n\text{-}C_5H_{11})P]_2Cl_2$ and $Ni[Ph_2(PhCH_2)P]_2Cl_2$.[10,15] Although a more desirable procedure might have been to obtain moments of each of the complexes under study which crystallized in the tetrahedral form, the formation of diamagnetic solids in many cases and the small amounts of material usually available rendered this approach impractical. The assumption implicit in the use of the above μ_t values is that the moments will not be significantly dependent upon the nature of the diarylalkylphosphine, especially not upon changes in phenyl *para* substituents, in a series with constant halide ligand. For several cases in which the structural change could be completely frozen out, a check on this assumption was made. Values of a_m were determined directly from the contact shift $\Delta\nu_m$ of the tetrahedral isomer using eq 2 with $\Delta\nu_m^{\text{av}} = \Delta\nu_m$ and $N_t = 1$. This procedure eliminates the use of μ_t. In each case the thermodynamic quantities obtained in this way agreed to within experimental error of those reported in Table II. This alternate procedure was not used throughout because the frozen-out limit could not be attained for a majority of the complexes, and, as a consequence, it was considered more meaningful to evaluate the thermodynamic data by an internally consistent method.

[35] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 87.

[36] R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **79**, 1045 (1957).

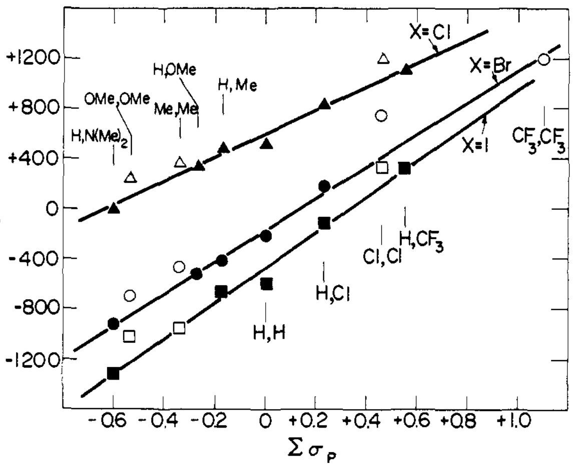

Figure 3. Correlation of standard free energy changes for the planar-tetrahedral structural conversion of Ni[(p-ZC$_6$H$_4$)(p-Z'-C$_6$H$_4$)MeP]$_2$X$_2$ in chloroform solution with Hammett σ_p constants. Solid points (monosubstituted complexes) have been fit to the least-squares lines shown. Open points refer to disubstituted complexes.

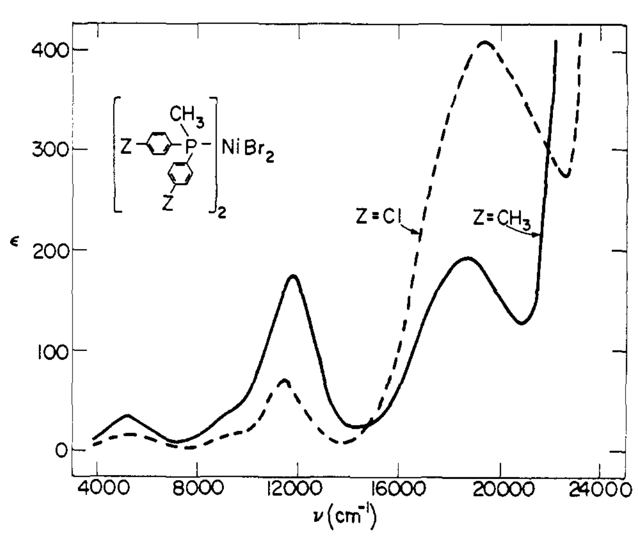

Figure 4. Ligand field spectra of Ni[(p-ClC$_6$H$_4$)$_2$MeP]$_2$Br$_2$ and Ni[(p-tol)$_2$MeP]$_2$Br$_2$ in chloroform solution at 25°.

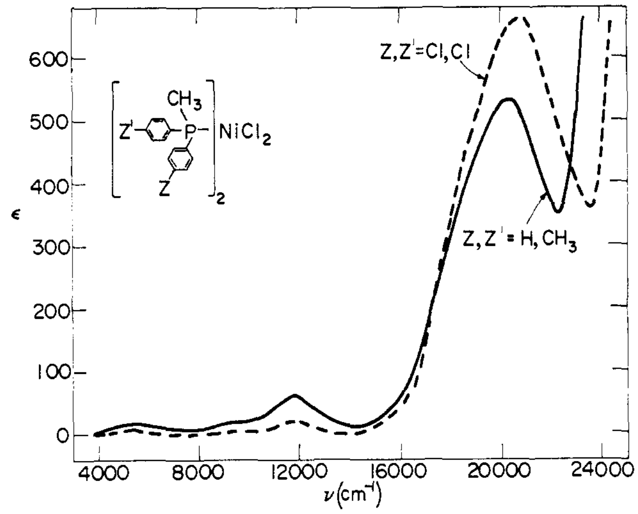

Figure 5. Ligand-field spectra of Ni[(p-ClC$_6$H$_4$)$_2$MeP]$_2$Cl$_2$ and Ni[(p-tol)PhMeP]$_2$Cl$_2$ in chloroform solution at 25°.

somewhat larger deviations from linear relationships. This apparently successful correlation of equilibrium position with $\Sigma\sigma_p$ implies that the electronic effects are a combination of inductive and resonance contributions, with the latter presumably being transmitted to the phosphorus from the phenyl rings by weak interactions of the 3d-pπ type. A poor correlation was found with $\Sigma\sigma_I$, the Taft inductive parameters.[36,37]

Solvent Effects. The position of equilibrium 1 is expected to be considerably solvent dependent because of the large difference in dipole moments[8-10,21] between the *trans*-planar (*ca.* 0–2 D) and the tetrahedral (*ca.* 6–8 D) forms. This point has been investigated for two representative complexes, Ni[(p-MeOC$_6$H$_4$)-PhMeP]$_2$X$_2$ (X = Cl$^-$, Br$^-$) in benzene solution at 30°. The following results have been obtained: X = Cl$^-$, 1.38 BM, N_t = 0.19; X = Br$^-$, 2.32 BM, N_t = 0.52. These values are significantly lower than those measured in chloroform solution (*cf.* Table II), and reflect the expected shift of the equilibrium toward the less polar planar form in the solvent with the lower dielectric constant.

Ligand Field Spectra. Typical spectra of four equilibrium solutions containing rather different proportions of the two stereoisomers are shown in Figures 4 and 5. Features in the 5,000- and 12,000-cm^{-1} regions are assigned in idealized T$_d$ symmetry as $\nu_1[^3T_1 \rightarrow {}^3T_2]$ and $\nu_2[^3T_1 \rightarrow {}^3A_2]$, respectively, by comparison with the spectra of the analogous triphenylphosphine complexes[22,38] and by the trend of increasing extinction coefficient with increasing N_t revealed by the data in Table III. The remaining band at *ca.* 20,000 cm^{-1} is a composite of tetrahedral $\nu_3[^3T_1 \rightarrow {}^3T_1(P)]$ and the lowest energy spin-allowed transition of the *trans* planar isomer (presumably $^1A_g(\ldots d_{xy}^2) \rightarrow {}^1B_{1g}(\ldots d_{xy}d_{x^2-y^2})$). The assignment of tetrahedral ν_3 was made by a fit of ν_1 and ν_2 to the Liehr–Ballhausen nomograph[39] for the d^8 case in T$_d$ symmetry. The existence of the planar band is made evident by comparison with the spectra of trialkylphosphine complexes, whose first d–d band is found in the 17,000–22,000-cm^{-1} range,[8,17-19] and by the trend of increasing extinction coefficient with decreasing N_t. Hereafter, this combination band will be referred to as ν_3 for convenience. One or two very weak features are also observed in the 8,000–11,000-cm^{-1} region. These have been noted earlier in the solid state spectra of Ni(Ph$_3$P)$_2$X$_2$ and assigned as components of ν_1 arising from the actual symmetry of the complex or spin-forbidden transitions.[38] The collection of spectral data is given in Table III. Addition of excess phosphine resulted in no significant changes in band maxima or intensities.

The most significant property of the ligand field spectra is the existence of well-defined trends in the energies of ν_2 and the planar component of ν_3 as the substituents Z, Z', and therewith the relative amounts

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(37) The only other apparent correlation of ligand electronic properties as assessed by substituent constants with any thermodynamic property of equilibrium 1 is the linear relationship between ΔH and $\Sigma\sigma_I$ for a series of bis(N,N'-di-*para*-substituted phenylaminotroponiminato)-nickel(II) complexes.[5]

(38) D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, 4, 139 (1965).

(39) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (New York), 2, 134 (1959).

of the isomers, are varied in constant halide series. The pertinent observations are summarized in Figure 6, which reveals a nearly linear relationship between the energies of these features and the mole fractions of the tetrahedral isomers. A similar relationship presumably also exists in the iodide series but overlying charge transfer absorptions extending into the visible prevented measurement of ν_3. The ν_1 bands were observed as quite broad features relative to ν_2 and, while they provide a direct measure of the ligand field splitting parameter Δ_t and reflect the expected decrease in this quantity (I < Br < Cl) in various constant phosphine comparisons, they are relatively insensitive in energy to changes in phosphine ligands. The Liehr–Ballhausen calculations indicate that in the relevant range of Δ_t (4800–5500 cm^{-1}) the energies of ν_2 and ν_1 should vary monotonically. Consequently, ν_2 is equally as good a measure of ligand field strengths as is ν_1, and has the further advantage of not being split by such lower symmetry components of the field as may be operative in the present group of complexes.

The ν_3 combination bands provide a measure of the frequency trend of the planar d-d absorptions in a constant halide series for the following reasons. First, as noted above, the extinction coefficients increase as N_t decreases. Second, the trend in ν_3 energies with N_t is *opposite* to that of ν_2 in the chloride series where the equilibrium favors the planar isomer. This trend is also apparent in the bromide series. The Liehr–Ballhausen calculations indicate that tetrahedral ν_3 and ν_2 energies also should vary monotonically with Δ_t. This requires that the observed opposite trend in ν_3 must arise from the presence of another band whose effect is to move the maxima of the composite feature in the reverse direction expected if ν_3 were solely a property of the tetrahedral isomers. In nearly all cases the two components of ν_3 were not resolved. However, the spectrum of Ni[(p-$CF_3C_6H_4$)$_2$MeP]$_2$Br$_2$ (N_t ~0.10) revealed tetrahedral ν_3 as a very weak low energy shoulder on the much more intense planar band. The energy order of these two features is that expected (*cf.* Figure 6) if the energies of tetrahedral ν_3 and ν_2 roughly parallel each other.

Interpretation of Stereochemical Trends in Constant Halide Series. The most striking and significant observation in this study is the remarkably sensitive dependence of the position of equilibrium 1 to variation of Z and Z′ in the three halide series. The correlations among stereochemical populations, substituent electronic effects, and ligand field transition energies which are evident in Figures 3 and 6 and from the data in Tables II and III form the basis for our interpretation of stereochemical trends in the three series.

It is first noted that the basicities of tertiary phosphines have been linearly correlated with the Taft constants $\Sigma\sigma_I$.[40] It is reasonable to extend this correlation such that *within* the group of phosphines (p-ZC_6H_4)(p-Z′C_6H_4)MeP the differential basicities will be reflected by variations in $\Sigma\sigma_p$. On this basis the more electron-releasing substituents would be expected to be stronger σ-bonding ligands in both the planar and tetrahedral isomers and effect the larger ligand field splittings. The trends in ν_2 energies in the chloride and bromide series, while spanning only 280 and 510 cm^{-1}, respectively, are unquestionably real and are in the anticipated direction. The ν_3 trends are somewhat larger but are in the opposite direction, *viz.*, the more electron-releasing groups produce the *smaller* splittings. However, this observation is not without precedent in planer d^8 complexes,[18,41,42] as the data in Table IV reveal. In each of the four comparative pairs, the phosphine ligands with the more electronegative substituents produce the larger ligand field splittings.

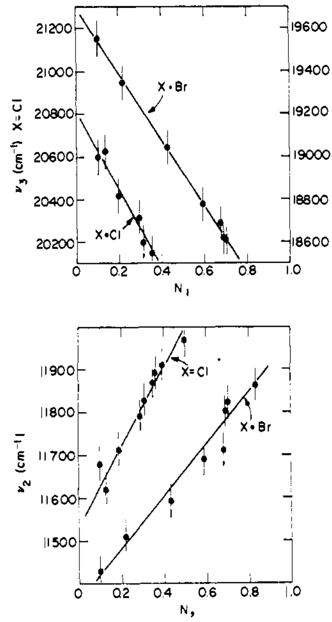

Figure 6. Relationships between ν_2 and ν_3 and the mole fraction of tetrahedral form in chloroform at 30° for two series of Ni[(p-ZC_6H_4)(p-Z′C_6H_4)MeP]$_2$X$_2$ complexes.

Table IV. Lowest Energy d–d Bands in Some *trans* Planar d^8 Complexes

Complex	λ_{max}, cm^{-1}	Ref
Ni(Me_3P)$_2$Cl$_2$	18,800	18
Ni(Me_2PCF_3)$_2$Cl$_2$	20,900	18
Ni(Me_3P)$_2$Br$_2$	18,500	18
Ni(Me_2PCF_3)$_2$Br$_2$	20,500	18
Ni(Ph_3P)$_2$(CN)$_2$	27,000	41
Ni(Ph_2POEt)$_2$(CN)$_2$	29,400	41
Pt(PPr_3)(pip)Cl$_2$	32,600	42
Pt[P(OMe)$_3$](pip)Cl$_2$	33,400	42

The energy trends of the lowest energy spin-allowed transitions of the planar isomers in Table III and of the complexes in Table IV are interpreted by reference to the simple MO diagram in Figure 7. The relatively high-lying phosphorus 3d orbitals of effective π symmetry are considered to mix weakly but primarily with d_{xy}, which is slightly antibonding in the absence of this interaction. This mixing should, in an approximate sense, vary inversely as the energy separation of the interacting orbitals, resulting in an increase in the one-electron $\sigma^*(d_{x^2-y^2})$–$\pi^*(d_{xy})$ separation as the 3dπ orbital energy is lowered by substitution of pro-

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(40) W. A. Henderson, Jr., and C. A. Streuli, *J. Amer. Chem. Soc.*, **82**, 5791 (1960).

(41) B. B. Chastain, E. A. Rick, R. I. Pruett, and H. B. Gray, *ibid.*, **90**, 3994 (1968).

(42) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 1047 (1959).

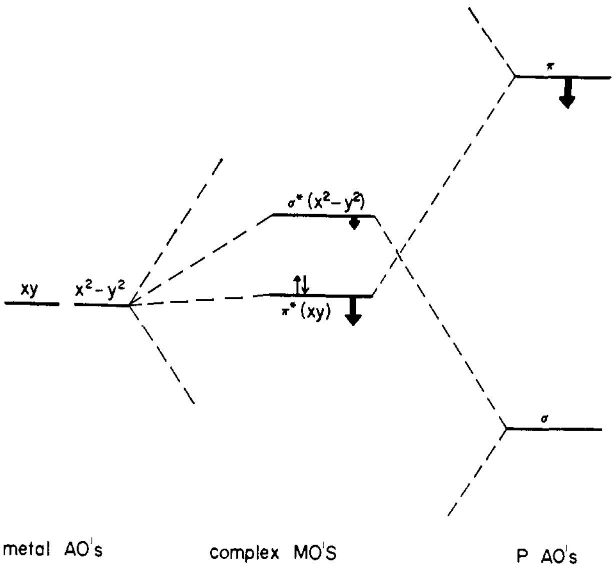

Figure 7. Partial MO diagram for planar d^8 bis(phosphine) complexes. Arrows indicate the qualitative changes in the orbital energies upon increasing the electron-withdrawing properties of the phosphine substituents.

gressively more electron-withdrawing groups.[43] This argument is equivalent to that put forth by Chatt, *et al.*,[44] to explain why the first d–d transition energy is larger in phosphine than in amine complexes of platinum(II).

The energy quantities associated with the planar–tetrahedral isomerization reaction have been considered in some detail elsewhere.[45] In assessing the source of relative isomer stabilities in a series of complexes of the same metal ion with very similar ligand structures, relative ligand field stabilization energies (LFSE's) should represent a significant portion of the stability differences provided entropy changes are essentially constant. This situation is approached here inasmuch as in the chloride, bromide, and iodide series the maximum differences in ΔS are 1.2, 1.4, and 1.4 eu, respectively. The correlations in Figure 6 provide convincing evidence that electronic energy differences, embodied in ΔH, are dominant in determining the position of equilibrium 1. The energies of ν_2 and, correspondingly, the LFSE's of the tetrahedral isomers ($^4/_5\ \Delta_t$ in the one-electron approximation) increase as N_t increases. The reverse trend holds for ν_3, implying that the LFSE's of the planar isomers increase[46] as N_t decreases. Therefore, it is proposed that at least in the chloride and bromide series the dependence of stereochemical population upon Z and Z′ arises from differences in the LFSE's of the two isomers. It is observed that these quantities vary in *opposite* directions in the two series. Finally, it is pointed out that because the total spread of available ΔG and ΔH values in any halide series never exceeds *ca.* 2 kcal/mol, the understanding of stereochemical trends necessitates the interpretation of relatively small energy differences. While other factors may contribute to these differences, the correlation between independently measured trends in LFSE and N_t values constitutes the best available interpretation.

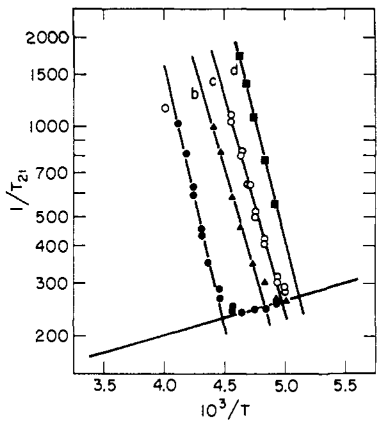

Figure 8. Temperature dependence of $(T_{2t})^{-1}$ for the *meta* phenyl resonance in $CDCl_3$ solution at 100 MHz for (a) Ni[(*p*-$MeOC_6H_4)_2$-$MeP]_2Br_2$, (b) Ni[(*p*-$ClC_6H_4)_2MeP]_2Br_2$, (c) $Ni(Ph_2MeP)_2Br_2$, and (d) Ni[(*p*-$MeOC_6H_4)_2MeP]_2Cl_2$.

Kinetics of the Structural Change. Kinetic results were obtained by analysis of measured line widths at half-height, $\Delta\nu_{1/2}$ (cps), of the contact-shifted *m*-H signal of the tetrahedral species in the limit of slow exchange. The effective transverse relaxation time, $1/T_{2t}$, was calculated using the relationship $1/T_{2t} = \pi\Delta\nu_{1/2}$. The transverse relaxation time in the absence of exchange, $1/T_{2t}'$, is related to $1/T_{2t}$ and τ_t, the average lifetime of the tetrahedral species, by eq 7.[47] This

$$1/T_{2t} = 1/T_{2t}' + 1/\tau_t \qquad (7)$$

equation is valid under conditions of slow exchange where $\tau_t\Delta\omega_t \gg 1$ ($\Delta\omega_t$ is the contact shift in radians/sec) and assumes a Lorentzian line shape. These conditions were satisfied. The analysis yielded τ_t at various temperatures. The first-order rate constant for tetrahedral $\xrightarrow{k_t}$ planar is given by eq 8, in which

$$k_t = \frac{1}{\tau_t} = \frac{kT}{h}\exp\left[\frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}\right] \qquad (8)$$

$\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the entropy and enthalpy changes of activation, respectively. Kinetic parameters were obtained from a plot of log (k_t/T) *vs.* $1/T$.

The experimental data are shown in a plot of log $(1/T_{2t})$ *vs.* $1/T$ in Figure 8. The solid line at the bottom represents the temperature variation of $1/T_{2t}'$ and was obtained by extrapolation of line width data obtained in the absence of exchange. This line was assumed for all systems even though the interconversion of com-

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(43) This entirely qualitative argument is not subject to any definite experimental proof and it is recognized that convincing evidence for the existence of metal–phosphorus $d\pi$ bonding in planar d^8 systems is at present lacking (*cf.* L. M. Venanzi, *Chem. Brit.*, 4, 162 (1968)). Another explanation has been offered for the trend in ligand field strengths of Ph_3P, $Ph_2P(OR)$, and $PhP(OR)_2$.[41] The π-bonding model is preferred here inasmuch as it most simply rationalizes the opposite trends of ligand field strengths in the planar and tetrahedral isomers in constant halide series. If these trends were controlled by metal–ligand σ interactions, they would be expected to parallel each other.

(44) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

(45) G. W. Everett, Jr., and R. H. Holm, *Inorg. Chem.*, 7, 776 (1968).

(46) This statement is based on the assumption that the energies of other MO's principally metal 3d in character are not altered such as to produce a net decrease in LFSE even though ν_3 increases. The only ligand field band observable in the planar form is that assigned as $\pi^*(d_{xy}) \rightarrow \sigma^*(d_{x^2-y^2})$ (Figure 7).

(47) 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, pp 221-223; C. S. Johnson, Jr., *Advan. Magn. Resonance*, **1**, 33 (1965).

Table V. Kinetic Parameters[a] for Structural Conversion of Ni[$(p\text{-}ZC_6H_4)_2MeP]_2X_2$ Complexes[b] in Chloroform Solution

Complex Z, X	$k_t(-50°) \pm 0.5$[c], sec^{-1}	$k_t(25°) \pm 1.0$, sec^{-1}	$\Delta H^\ddagger \pm 4$, kcal/mol	$\Delta S^\ddagger \pm 10$, eu
H, Br	1.1×10^3	8.5×10^5	11	6
Cl, Br	5.2×10^2	3.8×10^5	11	4
OMe, Br	6.8×10^1	1.4×10^5	13	9
OMe, Cl	3.3×10^3	1.6×10^6	10	5

[a] Parameters obtained from a least-squares fit to plot of log k_t/T *vs.* $1/T$ and using the relationship $k_t = \frac{kT}{h}\exp\left[\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}\right]$.

[b] Complex concentrations are ~0.1 *M*. [c] k_t is the first-order rate constant for the reverse reaction in $P \underset{k_t}{\overset{k_p}{\rightleftharpoons}} T$.

plexes c and d in the figure could not be completely slowed down due to prior freezing of their solutions. This assumption is a reasonable one because transverse relaxation times are expected to be nearly equal for such similar complexes.[48] The calculated τ_t values from eq 7 are insensitive to small changes in $1/T_{2t}'$ due to the rapidly rising behavior of $1/T_{2t}$ when exchange broadening becomes important. The rate constants and kinetic parameters determined from a least-squares fit of eq 8 are set out in Table V.[49]

The principal purpose of the kinetic study has been to demonstrate that the structural interconversion of the present group of $Ni(Ar_2MeP)_2X_2$ complexes, in sharp contrast to all known bischelate Ni(II) systems involved in this process, can be demonstrably slowed down or completely frozen out in chloroform solution at temperatures down to *ca.* $-70°$ as a lower limit. Consequently, a comprehensive study of all of the complexes in Table II has not been performed. From the limited data at hand the order of increasing frequency of structural interchange at parity of phosphine is Br < Cl < I. In no case could an iodide system be frozen out. From this unexpected rate order, which has also been found by LaMar in dichloromethane solutions,[26] it appears that the factors determining the kinetics are complex and involve a combination of steric and electronic effects. Attempts to measure kinetics on several other systems were thwarted by overlapping signals, low concentrations of tetrahedral isomers, and freezing of solutions before reaching the slow exchange region. A full evaluation of kinetic trends must await additional results obtained in solvents of different dielectric constants and lower freezing points.

Acknowledgments. This research was supported by research grants NSF GP-7576X (M. I. T.) and GP-6321 (Princeton University). L. H. P. is the recipient of a National Institutes of Health Postdoctoral Fellowship for 1969–1970. We are indebted to Dr. G. N. LaMar for communication of results prior to publication and for a number of useful discussions.

(48) The line assumed here for log $(1/T_t')$ *vs.* $1/T$ is similar to that reported for the analogous triphenylphosphine complexes.[32]

(49) The activation parameters in Table V were determined over a small temperature range (typically 30°) and, therefore, are subject to large experimental error. Other methods of kinetic analysis, *e.g.*, use of fast exchange approximations which would extend the temperature range, were not employed due to uncertainties in determining the temperature dependencies of the widths of the planar *m*-H resonances. The experimental errors given in Table V were estimated by assuming an error of ±1 cps in $\Delta\nu_{1/2}$ and ±1° in T and plotting plus and minus extremes of log (k_t/T) *vs.* $1/T$.

Thermodynamic Interpretation of Chemical Shifts in Core-Electron Binding Energies

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Abstract: By making several approximations, it is possible to calculate, from available thermodynamic data, a "thermochemical energy" corresponding to the core-electron binding energy for an atom in a compound. For a given element, such calculated "thermochemical energies" are linearly related to experimental binding energies. Thus it is possible to estimate thermodynamic data from binding energies, and *vice versa*. The principal approximation made in these calculations is that atomic cores which have the same charge are chemically equivalent. The relatively small shifts in core-electron binding energy observed for an atom in a particular cation or anion in a series of salts are explicable in terms of lattice energy considerations.

Atomic core-electron binding energies for solid compounds can be measured by X-ray photoelectron spectroscopy with a precision of ±0.2 eV and, for a given element, have been shown to change as much as 15 eV with changes in chemical environment.[1] The binding energies correlate with the oxidation states of

(1) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmar, S.-E. Karlsson, I. Lindgren,