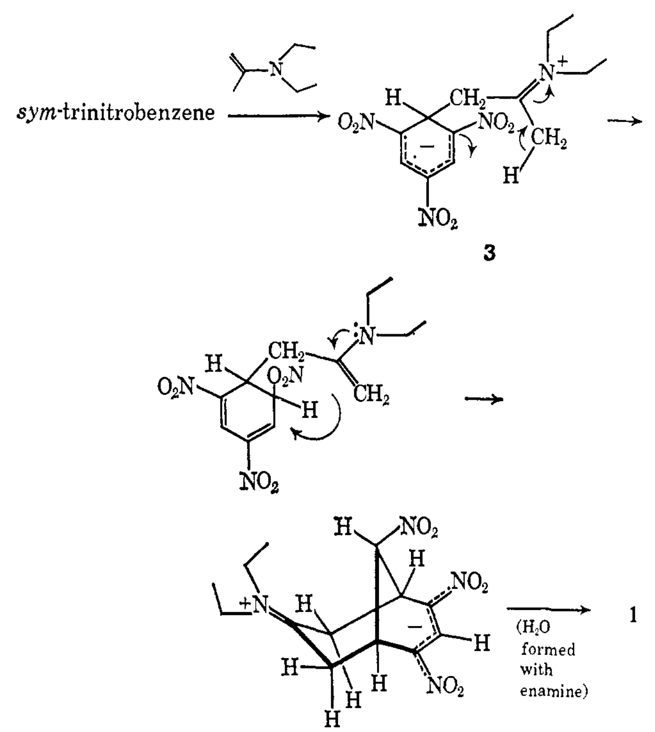

Acknowledgments. The authors wish to thank the National Aeronautics and Space Administration and the University of Vermont for an Institutional Grant in support of this research. We also wish to thank Professor M. E. Kuehne for helpful discussion and comments.

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Received February 19, 1969

Direct Observation of the Rate of Planar–Tetrahedral Equilibrium of Four-Coordinate Nickel(II) by Nuclear Magnetic Resonance. Diastereoisomeric Dihalobis(dissymmetric tertiary phosphine)nickel (II) Complexes[1]

Sir:

Dynamical planar (diamagnetic) ⇄ tetrahedral (paramagnetic) interconversions in four-coordinate nickel(II) complexes are well established. Nmr studies of a variety of nickel(II) chelate complexes have been carried out. The ligands involved include salicylaldimines,[2] aminotroponimines,[3] naphthaldimines,[4] β-ketoamines,[5] and ditertiary phosphines.[6] In all previously studied cases, the planar–tetrahedral interconversion was found to be rapid on the nmr time scale such that for a given nucleus only a single resonance was observed at a frequency which represents a weighted average over diamagnetic and isotropically shifted paramagnetic environments. For such conformational equilibria, the averaged nuclear resonance shifts from their diamagnetic positions, $\Delta\nu_i^{av}$, are given by[7]

$$\frac{\Delta\nu_i^{av}}{\nu} = -\frac{a_i}{2S}\frac{\gamma_e}{\gamma_H}\frac{g\beta S(S+1)}{3kT}N_t \qquad (1)$$

$$N_t = [\exp(\Delta G^\circ/RT) + 1]^{-1}$$

Here N_t is the mole fraction of tetrahedral species, ΔG° is the standard free-energy change for the planar ⇄ tetrahedral equilibrium, and the other symbols have their usual significance. It has been estimated that the lifetime of the stereoisomers is less than 10^{-3} or 10^{-4} sec[3,8] (only averaged resonances are observed in the pmr spectra) and greater than 10^{-13} sec (separate electronic spectra observed for the planar and tetrahedral species). Planar–tetrahedral equilibria are known for monodentate tertiary phosphine complexes of the type $Ni(PR_3)_2X_2$ where X = Cl, Br, I, and PR_3 is an alkyldiaryl- or dialkylarylphosphine;[9] however, heretofore no nmr studies of these systems have been made. The present authors recently reported[10] the pmr spectra of complexes of dissymmetric tertiary phosphines of the type $Ni(PR_1R_2R_3)_2X_2$ where X = I and $PR_1R_2R_3$ is methylphenyl-*p*-anisylphosphine. The multiplicity of pmr peaks was incorrectly (*vide infra*) attributed to a separation of resonances of the active (*dd* or *ll*) and *meso* (*dl*) diastereoisomers for the complexes synthesized from racemic phosphine. The present report deals with the X = Cl and Br analogs which, unlike the iodide, undergo a dynamical planar–tetrahedral equilibrium in solution. The unique feature of the present systems is that at low temperatures the rate of planar–tetrahedral interchange has been slowed so that separate resonances are observed for the two stereoisomers. For the first time, it is possible to measure this interconversion rate by nmr techniques.

Racemic and active, [α]D −6.5° (methanol), methylphenyl-*p*-anisylphosphine were synthesized by the method of Korpiun, *et al.*,[11] except that the reduction of phosphine oxide to phosphine was accomplished stereospecifically with hexachlorodisilane.[12] The complexes of both active and racemic phosphine were synthesized under nitrogen as described previously[10] except that a few milliliters of hot hexane was added to the ethanolic solutions before filtration. Satisfactory elemental analyses were obtained and the complexes were found to be monomeric in benzene at 37° by osmometry.

Thermodynamic Parameters for the Planar–Tetrahedral Equilibrium. At and above room temperature only a single averaged resonance is observed for each set of equivalent protons and eq 1 may be applied. Assignments were made by comparison with the well-established triphenylphosphine analogs[13] and are indicated in Figure 1. ΔG° values were obtained from the magnitudes of the isotropic shifts of the *meta* proton reso-

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[1] This research was supported by the National Science Foundation through Grant GP 6321.

[2] A. Chakravorty, J. P. Fennessey, and R. H. Holm, *Inorg. Chem.*, 4, 26 (1965).

[3] D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

[4] A. Chakravorty and R. H. Holm, *Inorg. Chem.*, 3, 1010 (1964).

[5] G. W. Everett, Jr., and R. H. Holm, *Proc. Chem. Soc.*, 238 (1964); *J. Am. Chem. Soc.*, **87**, 2177 (1965).

[6] G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.* **5**, 1968 (1966).

[7] W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, 87, 3779 (1965).

[8] M. J. O'Connor, R. E. Ernst, and R. H. Holm, *ibid.*, **90**, 4561 (1968).

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

[10] L. H. Pignolet and W. D. Horrocks, Jr., *Chem. Commun.*, 1012 (1968).

[11] O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4842 (1968).

[12] K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 2788 (1969).

[13] G. N. LaMar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).

Table I. Data for Dihalobis(methylphenyl-*p*-anisylphosphine)nickel(II) Complexes

Halide	Concn, M (solvent)	Proton[a] resonance	$\Delta\nu_i^{av}$, ppm (37°)	A_i,[b] G	$\Delta G°$ (37°), cal/mole	$\Delta H°$, cal/mole	$\Delta S°$, eu	N_t (37°)	μ_{eff} (37°), BM
Br	0.0610	*meta*-1	−9.47	0.131	−330	+312[c]	+2.08[c]	0.63	2.70
	($CDCl_3$)	*meta*-2	−7.97	0.110					
Br	0.0465	*meta*-1	−7.25					0.48	2.32
	(C_6D_6)	*meta*-2	−6.27						
Cl	0.0553	*meta*-1	−4.68	0.117	+383	+1680[d]	+4.18[d]	0.35	1.97
	($CDCl_3$)	*meta*-2	−3.77	0.094					
Cl	0.0598	*meta*-1	−2.38						
	(C_6D_6)	*meta*-2	−1.75					0.17	1.38

[a] See Figure 1. [b] Calculated as described in text. [c] From data over temperature range 13–70°. [d] From data over temperature range −10–70°.

nances of the phenyl and *p*-anisyl groups by application of eq 1 with a_i values determined from the shifts observed for the "frozen out" tetrahedral species at low temperatures. The sharper OCH_3 peak had to be used in the case of chloride owing to the small amount of tetrahedral species present. $\Delta H°$ and $\Delta S°$ values derived from a plot of $\Delta G°$ *vs.* T are shown in Table I. The estimate of N_t obtained in this manner was checked by measurement of the magnetic susceptibilities of the solutions by Evans' method.[14] N_t is given by eq 2.[7]

$$N_t = \left(\frac{\mu_{eff}}{\mu_t}\right)^2 \qquad (2)$$

where μ_t is the magnetic moment of the tetrahedral species. Agreement between the pmr and susceptibility data is obtained for μ_t = 3.3 and 3.4 BM for the chloride and bromide, respectively. These values are in good agreement with those found in the solid state for tetrahedral complexes of this type.[15] The $\Delta H°$ and $\Delta S°$ values are similar to those found for other planar-tetrahedral equilibria involving bis-chelate nickel(II) complexes.[16] The equilibrium lies considerably more toward the tetrahedral species for the bromide than for the chloride in accord with room-temperature susceptibility findings for the analogous alkyldiphenylphosphine complexes.[9]

The conformational equilibrium is solvent dependent as indicated by the N_t values for chloroform and benzene at 37° (Table I). The less polar solvent, benzene, favors the planar form. Probably for the same reason the position of equilibrium is significantly dependent on concentration, increasing concentration favoring the tetrahedral form. Molecular weight data eliminate solute association as a cause of the increasing paramagnetism with concentration.

Detection of Stereoisomers by Nmr. Rate of Interconversion. The spectra of the bromide complex at a range of temperatures are shown in Figure 1. At the highest temperatures the resonances represent an average over the planar and tetrahedral environments, while at the lowest temperatures separate resonances are observed for the planar and tetrahedral species. The resonances of the planar form are at the diamagnetic positions while those of the tetrahedral species exhibit large isotropic shifts owing to the paramagnetism. Conclusive proof of this interpretation is the fact that an integration at −58° of the shifted *meta* resonances of the tetrahedral species and the appropriate fraction (4/9) of the phenyl resonances of the diamagnetic planar species (corrected for overlap of the shifted OCH_3 peak) yields an N_t of 0.58 at this temperature, in perfect agreement with that predicted from the $\Delta H°$ and $\Delta S°$ values obtained at higher temperatures in the rapid exchange region.

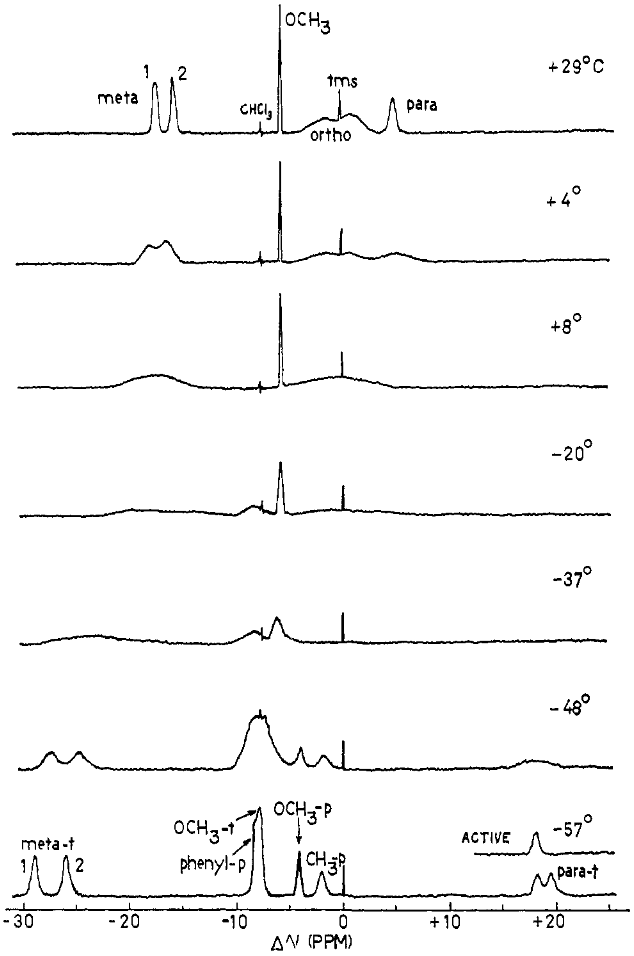

Figure 1. Pmr spectra of dibromobis(methylphenyl-*p*-anisylphosphine)nickel(II) in deuteriochloroform solution at several temperatures recorded on a Varian A-60A spectrometer. The *meta*-1 and *meta*-2 peaks refer to phenyl and *p*-anisyl protons (exact assignment unknown); p and t refer to planar and tetrahedral species, respectively.

Kinetic parameters for the conformational interchange were obtained from line broadening of the *meta* resonances of the tetrahedral species under slow ex-

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

(15) R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, 4, 1701 (1965).

(16) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *J. Am. Chem. Soc.*, 89, 6104 (1967).

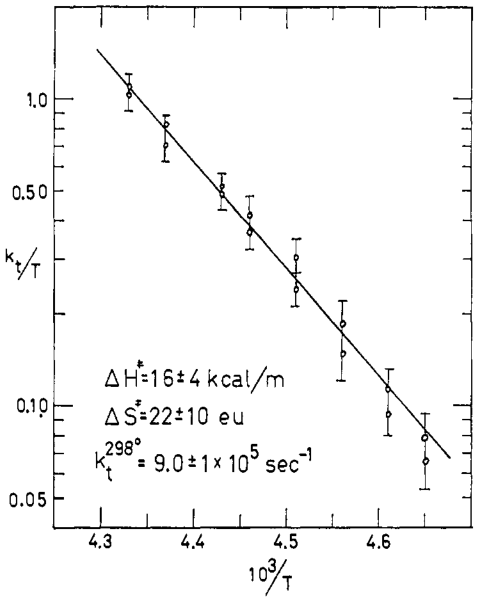

Figure 2. Plot of log (k_t/T) *vs.* $1/T$. The individual points represent line-width measurements of the *meta*-1 and *meta*-2 peaks.

change conditions[17,18] using the relation, $T_2^{-1} = T_{2t}^{-1} + \tau_t^{-1}$, where $(\pi T_2)^{-1}$ is the observed line width (at half-maximum), $(\pi T_{2t})^{-1}$ is the line width in the absence of exchange (obtained as a function of temperature in both fast and slow exchange regions), and τ_t is the average lifetime of a proton in the tetrahedral species. Figure 2 shows a plot of log (k_t/T) *vs.* $1/T$ ($k_t = 1/\tau_t$) which yields the activation parameters $\Delta H_t^{\ddagger} = 16 \pm 4$ cal/mole and $\Delta S^{\ddagger} = 22 \pm 10$ eu and an extrapolated rate constant at 25° of $k_t^{25°} = 9 \pm 1 \times 10^5$ sec^{-1}. The mean lifetime for the over-all exchange process, τ, may be derived from the relation[17] $\tau = (1 - N_t)\tau_t$. This yields an over-all average rate constant, $k = 1/\tau$, of $k^{25°} = 2.4 \pm 0.2 \times 10^6$ sec^{-1}. A similar analysis of the chloride system was impossible owing to the much smaller percentage of tetrahedral species present. An investigation of the factors which affect rates of planar–tetrahedral equilibria is in progress.

Diastereoisomeric Doubling. Catalyzed Oxidation of Phosphines to Phosphine Oxides. Recent experiments with the iodide complex have shown that the multiplicity of peaks attributed[10] to diastereoisomeric doubling (separate resonances for active and *meso* complexes) is in fact due to a mixture of bis phosphine and phosphine–phosphine oxide complexes in solution of the type $Ni(PR_1R_2R_3)(OPR_1R_2R_3)I_2$. When the iodide complexes were synthesized and solutions prepared under rigorously oxygen-free conditions, only a single set of resonances was observed. Spectra were identical for complexes made from racemic and active phosphines. Admission of air or oxygen to the solutions caused the additional set of resonances to grow in; the new peaks are phosphine proton resonances in the mixed phosphine–phosphine oxide complexes. Chemical shift differences of the order of 2 ppm at −5° are observed[10] for corresponding resonances. Additional peaks near the diamagnetic position from coordinated phosphine oxide for which isotropic shifts are small are also detectable in solution. Confirmation is provided by experiments with the nickel iodide complex of achiral *n*-butyldiphenylphosphine. Aerial oxidation of chloroform solutions of $Ni[P(C_6H_5)_2(C_4H_9)]_2I_2$ produced additional shifted peaks in exact analogy with the results for the dissymmetric phosphine complexes. Infrared spectra of mixtures of nickel iodide, triphenylphosphine, and molecular oxygen in chloroform and benzene showed the presence of significant quantities of triphenylphosphine oxide. No observable oxidation of triphenylphosphine occurred in the absence of nickel iodide under otherwise identical experimental conditions. Molecular oxygen does not affect significantly the chloride and bromide complexes of methylphenyl-*p*-anisylphosphine. Nickel iodide apparently catalyzes the oxidation of phosphines to phosphine oxides in these systems. It is possible that a nickel(0) species is responsible since these are known to be effective catalysts for such oxidations.[19]

Despite the absence of diastereoisomeric doubling in the bis(methylphenyl-*p*-anisylphosphine) complex of nickel iodide, the present results demonstrate this effect in the nickel bromide complex. Two isotropically shifted *para* proton resonances separated by 1 ppm are observed at −57° for the complex synthesized from racemic phosphine (Figure 1), while only a single *para* proton resonance is evident for the complex made from optically active phosphine. No doublings were detected for any of the other resonances. Since the doubling is observed only in the slow-exchange region, it must be attributable to a difference Δa_i in the hyperfine interaction constants for the *para* protons between the two diasterioisomers. The splitting in the present case is small, only 4% of the total isotropic shift.

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

[18] L. H. Pignolet and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **90**, 922 (1968).

[19] G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem. Intern Ed. Engl.*, **6**, 92 (1967).

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Received April 11, 1969

Hammett Correlations in Mass Spectrometry

Sir:

Following the first demonstration[1] of a correlation between intensities of ions in a mass spectrum and Hammett σ values, there has been an increasing number of studies dealing with this topic.[2] It seems now to be assumed that because of these correlations, the structures of the molecular ions undergoing fragmentation can be directly equated with the structures of the molecules before ionization and, therefore, that deductions may be drawn about the mechanisms of fragmentations. From thermochemical arguments we wish to suggest that one of the factors responsible for the correlations has major importance and has little to do with the reaction mechanism. All mass spectrometric fragmentation processes are at least two step (counting ionization as one step), and it is difficult to interpret Hammett correlations in multistep reactions. To illustrate this point we consider one of the simplest types of mass spectrometric

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[1] F. W. McLafferty, *Anal. Chem.*, **31**, 477 (1959).

[2] For leading references see M. M. Bursey, *Org. Mass Spectry.*, **1**, 31 (1968).