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NMR Studies of Nickel Hydrides: The Intramolecular Rearrangement of the Hydridotris(tri-*p*-tolyl phosphite)nickel(II) Ion

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Abstract: The reaction of tetrakis(tri-*p*-tolyl phosphite)nickel(0) with strong acids has been investigated by using ^{1}H, ^{31}P, and ^{2}H NMR spectroscopy. The results differ from those previously obtained for similar reactions with other Ni(0) phosphites in that both five- and four-coordinate Ni hydrides are formed in concentrations sufficient for spectroscopic studies. The latter complexes are thought to be the active species in a number of reactions catalyzed by Ni(0) phosphites. Their presence has been inferred from kinetic considerations but they have not previously been detected directly. The four-coordinated hydride is a fluxional molecule at the temperatures of the NMR experiments. It is shown that under the conditions of these experiments the exchange process is exclusively intramolecular in nature. This allows a very simple method to be used for the analysis of the NMR data. Activation parameters for the exchange process are reported and compared with literature data for related intramolecular and intermolecular reactions. The large negative entropy of activation and small enthalpy of activation are interpreted in terms of ion pairing in the transition state. NMR evidence for the structures of the other products resulting from the reactions of acids with both the metal complexes and the free phosphite ligands is presented. The interplay of steric and electronic factors which determines the relative stabilities of the four- and five-coordinated hydrides is discussed.

Hydrides can often be obtained by the protonation of complexes containing metals in low oxidation states.[1] An example is provided by the reaction of strong acids with Ni(0) tetraphosphites.[2,3] This reaction leads to five-coordinated hydrides which have been characterized by NMR and other physical techniques.[2,3] The chemistry of one such complex, tetrakis(triethyl phosphite)nickel hydride, has been examined in some detail in a series of elegant investigations by Tolman.[4-7] This complex acts as a catalyst for the coupling of 1,3-butadiene and ethylene and for the isomerization of 1-butene. Tolman was able to elucidate the mechanisms of these catalytic reactions and to use them as models for the understanding of a wide variety of reactions catalyzed by organometallic compounds. A key intermediate in the proposed reaction schemes is the four-coordinated tris(triethyl phosphite)nickel hydride cation. Convincing kinetic evidence for this complex was obtained but it was not present in high enough concentrations to be detected spectroscopically. An analogous four-coordinated hydride containing phosphine rather than phosphite ligands was studied by English, Meakin, and Jesson.[8-10] This complex was shown to have a square-planar geometry but to be fluxional with rapid exchange between ligands cis and trans to the hydride. Quantitative analysis of the NMR data was complicated by the occurrence of concurrent intermolecular ligand exchange processes. The phosphine complexes also have catalytic activity but are generally less effective than the phosphites.[7] Five-coordinated trigonal bipyramidal hydride complexes of nickel are also fluxional but all of the examples examined thus far have rates too rapid for detailed NMR studies.

In light of the above literature reports, it seemed worthwhile to examine the hydrides formed by a range of nickel tetraphosphites. The objectives were (1) to find a system in which the four-coordinated complex is present in sufficient concentration to allow NMR studies, (2) to find conditions such that the intramolecular exchange process could be studied without interference from intermolecular reactions, and (3) if possible, to obtain rates and activation parameters for the rearrangements of both the four- and the five-coordinated complexes. At present such data are not available for either geometry. Comparison with the activation parameters reported for phosphite complexes with other metals would be of interest. The complex tetrakis(tri-*p*-tolyl phosphite)nickel(0) proved suitable for attaining most of the above objectives and the present paper reports a study of the reaction of this compound with strong acids.

Experimental Section

Tetrakis(tri-*p*-tolyl phosphite)nickel(0) was prepared by a method which closely followed that given by Levison and Robinson[11] for the preparation of the corresponding phenyl compound. Preparation of the hydride solutions was carried out in a drybox under an atmosphere of dry nitrogen. Typically 0.1–0.2 g of Ni[P(O-*p*-tolyl)$_3$]$_4$ was placed in a 30-mL beaker cooled to dry ice temperature. A total of 3–4 g of CD_2Cl_2 was added, followed by a measured amount of trifluoroacetic or concentrated sulfuric acid from a syringe. Any excess ligand required was also added at this point. The beaker was removed from the dry ice and allowed to warm until the Ni complex dissolved. At this stage the solution has an orange-red color. On recooling in dry ice, there is separation into two layers. The upper organic layer contains the nickel hydrides and this solution was pipetted into NMR tubes which were stored at dry ice temperature. The solutions are stable for up to 24 h under these conditions. Other Co and Ni hydrides were prepared by literature methods.[12] Phosphite ligands were purchased from BDH and Kodak Chemicals and used without further purification.

NMR spectra were obtained on Bruker WM-250 and WM-400 spectrometers. Proton spectra were measured in CD_2Cl_2 solution with Me_4Si as an internal calibrant. ^{31}P spectra, obtained at 101.2 and 161.9 MHz, were referenced to an external sample of 85% H_3PO_4. Deuterium spectra were obtained on the WM-250 instrument at 38.4 MHz with the solvent CD_2Cl_2 acting as an internal calibrant.

Results

The addition of either trifluoroacetic or sulfuric acid to a solution of tetrakis(tri-*p*-tolyl phosphite)nickel(0) in deuterated methylene chloride or deuterated toluene leads to the appearance of new lines in the ^{1}H NMR spectrum. Resonances to high field of Me_4Si are observed and this is diagnostic for metal hydride formation. The choice of acid does not affect the chemical shifts observed for the hydrides but the best resolved ^{31}P spectra were obtained with sulfuric acid and CD_2Cl_2 and unless stated otherwise the results described below refer to this combination. The spectra

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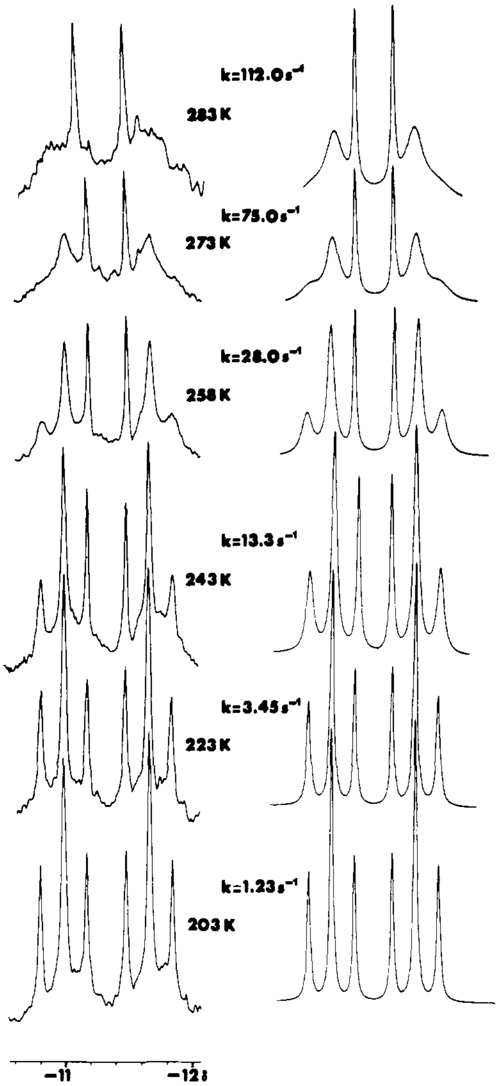

Figure 1. Variable-temperature 250-MHz ^1H NMR spectra of NiP_3H^+. The right-hand spectra are simulated by using the rate constants of Table I.

are, however, dependent on both the temperature and the concentration of added acid. The thermal stability of the hydride solutions is limited and it was not possible to obtain spectra above 15 °C. The freezing point of the solutions (around −80 °C) imposes a lower limit of the temperature measurements. With the initial addition of acid a quintet with chemical shift −13.2 ppm and coupling constant 32 Hz is observed. This is in excellent agreement with the chemical shift of −13.2 ppm and coupling constant of 33 ± 2 Hz reported by Tolman[7] for the pentacoordinate NiP_4H^+ species. The appearance of this resonance is accompanied by a new resonance in the region 2.27–2.33 ppm assigned to the methyl groups of the pentacoordinate hydride and by changes in the aromatic region around 7.1 ppm.

Further reactions occur with the addition of excess acid. A new hydride resonance, of a type not previously reported for nickel phosphite complexes, is observed at −11 ppm. At room temperature the spin coupling pattern of this resonance is complex but at low temperatures it simplifies to a doublet of triplets. The doublet spacing corresponds to a coupling constant of 174 Hz and the triplet spacing to a coupling of 48 Hz. The temperature dependence is illustrated by the spectra of Figure 1. This resonance will be assigned to the four-coordinated nickel hydride, NiP_3H^+. The large coupling constant corresponds to coupling to the trans P, and the small J to coupling to the cis P's. Concurrently, additional resonances appear in 2.35–2.37 ppm region, assigned to the methyl groups of the four-coordinated hydride, and in the aromatic region. Examination of the spectra reveals two further lines which comprise a doublet centered at 7.3 ppm with a large coupling constant which varies from 764 Hz at 268 °C to 776 Hz at 193 °C. Continued addition of acid leads to a decrease in the intensity of the lines ascribed to the five-coordinate hydride and an increase in those of the four-coordinate hdyride. There are corresponding changes in the low field part of the spectrum.

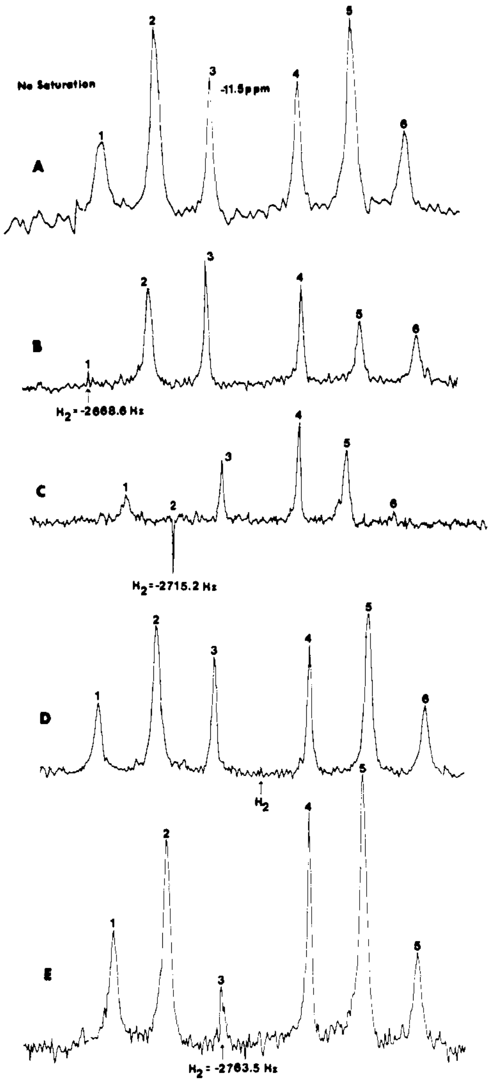

Figure 2. Double-resonance spin-saturation-transfer experiment on the ^1H hydride resonance of NiP_3H^+. The second radio frequency H_2 is applied in the positions indicated in B–E. All spectra at 253 K.

The analysis of the spectra attributed to the four-coordinated hydride will be discussed in detail below. From Figure 1 it is apparent that the low-temperature spectrum corresponds to that expected for a square-planar complexes. The complications in the spectra at higher temperatures must be ascribed to the onset of an exchange process but it is clear that the rapid exchange limit has not been reached at the highest temperature shown. Thermal decomposition prevents extension of the measurements to higher temperature. Two additional experiments have been carried out to further elucidate the interpretation of these spectra. Figure 2 shows the results of a double-resonance, spin-saturation-transfer, experiment carried out at −80 °C. In this experiment the individual lines in the multiplet are irradiated to test for the transfer for magnetization to other spin states. There are six lines in the multiplet. It is apparent from the spectra shown in Figure 2 that irradiation of line 1 decreases the intensity of line 5 more than the intensity of any other line in the spectrum. Irradiation of line 5 has a similar effect on line 1. Lines 2 and 6 are similarly related. Lines 3 and 4 are only slightly affected in the double-resonance experiment and it may be noted from Figure 1 that these two lines remain sharp over the complete temperature range. The mech-

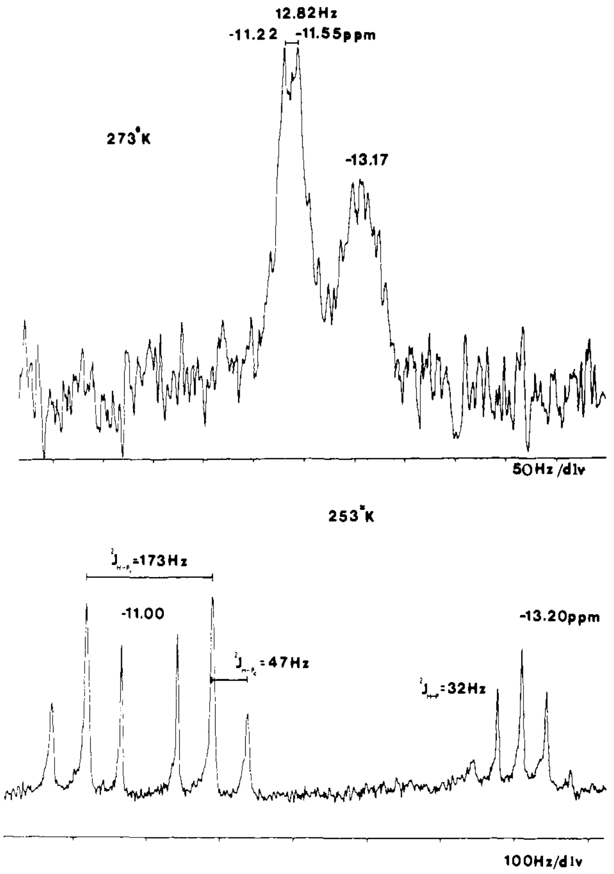

Figure 3. The upper picture is of the ^{2}H spectrum in the hydride region showing resonances at δ −13.2, from the 5-coordinate hydride NiP_4H^+, and at δ −11.4 from the 4-coordinate hydride NiP_3H^+. In the fast-exchange limit the latter hydride should give a quartet with a 4-Hz spacing (calculated from the ^{1}H spectrum shown in the lower photograph). Somewhat below this limit, the outer lines, with a spacing of 12 Hz, are expected to be sharp and the inner lines should be broad. This situation corresponds to the 273 K spectrum and is confirmed by computer simulation.

anistic significance of these observations will be discussed below. The second experiment involved the use of deuterated sulfuric acid and observation of the ^{2}H spectrum. Since the splittings of Figure 1 are caused by proton–phosphorus spin coupling, they will be reduced by a factor of approximately 6 if the proton is replaced by a deuteron, since this is the ratio of the magnetic moments of the two nuclei. It follows that the deuteride spectrum will reach its fast-exchange limit at a lower temperature than the hydride spectrum. Hopefully this will occur at a temperature below the decomposition temperature of the complex. Figure 3 shows the results of this experiment. The reduction in the spin–spin coupling constants has led to some difficulty in attaining good resolution in the experimentally more difficult ^{2}H spectrum and it does not appear that the fast-exchange limit has been quite reached, but the qualitative difference between this spectrum and the proton spectrum at the same temperature is clear.

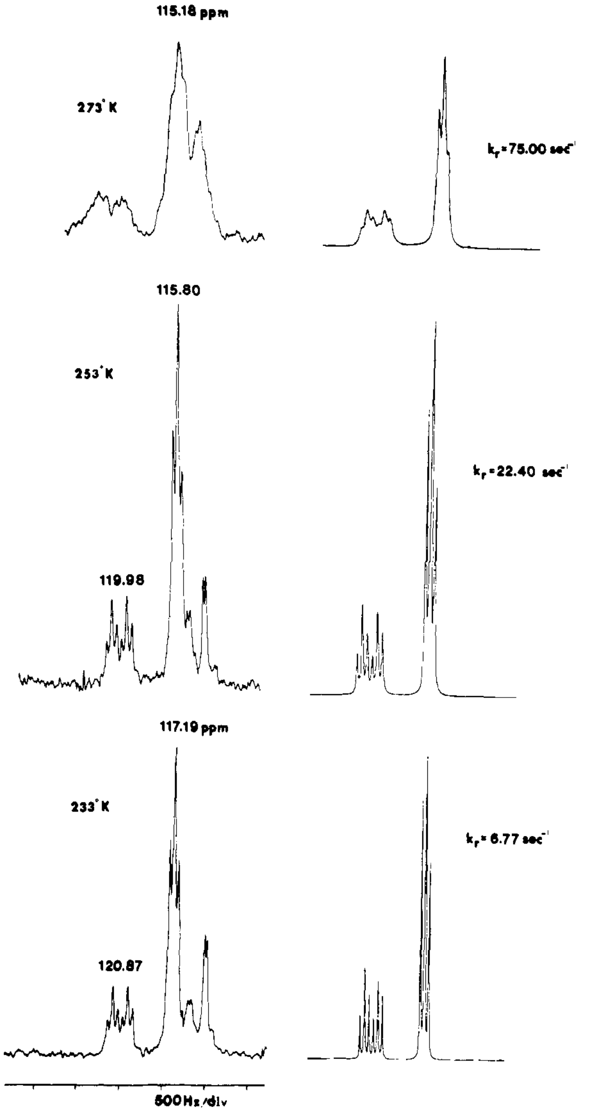

Figure 4. Temperature dependence of the ^{31}P spectrum in the 110–120 ppm region. The right-hand spectra are computer simulations using the activation parameters derived for NiP_3H^+ from the proton spectrum. The resonances around 110 ppm arise from the five-coordinated hydride and are not included in the simulations.

The NMR experiments described above have been complemented by ^{31}P NMR experiments. The free ligand ^{31}P resonance is observed at 128.6 ppm from 85% phosphoric acid (lit.[3] 127.7 ppm). Solutions of NiP_4 (P = tri-*p*-tolyl phosphite) give a single line at 134.1 ppm (lit.[3] 130.4). On adding acid to a solution of the free ligand in deuterated methylene chloride, the free ligand resonance completely disappears after a small amount of acid has been added. This observation that no free ligand remains in the presence of excess acid is important. New resonances appear in the form of a doublet (J = 760 Hz) at 5.1 ppm and a singlet at −16.0 ppm. On adding acid to solutions of NiP_4, a number of new lines are observed. Initially, a doublet (J = 28 Hz) appears at 113.5 ppm at 233 K. With proton decoupling this becomes a singlet. It must be assigned to NiP_4H^+. With the addition of more acid, two multiplets, intensity ratio 1:2, appear at 120 and 117 ppm. At low temperature, the 120 ppm resonance appears as a doublet of triplets. This is consistent with assignment to the P trans to H in square-planar NiP_3H^+ with J(PH) = 174 Hz and J(PP) = 57.5 Hz. The 117 ppm resonance appears to be a triplet with a coupling of around 50 Hz. Proton decoupling reduces this to a doublet with approximately the same coupling. These observations are consistent with the assignment of this resonance to the cis P's of NiP_3H^+. the expected doublet of doublets appears as a triplet because of the similarity of J(PP) and J(PH). The values of J(PP) and J(PH) are consistent with those obtained from the proton spectra. Raising the temperature leads to broadening and increasing complexity in this spectrum. The temperature dependence is shown in Figure 4. Addition of excess ligand to a solution containing the nickel hydrides leads to an increase in the intensity of the resonance assigned to NiP_4H^+ and a decrease in those assigned to NiP_3H^+. The spin–spin coupling structure of the NiP_3H^+ resonances is also lost, indicating rapid intermolecular ligand exchange. In addition to the resonances discussed above, an additional weak line in the low-field part of the spectrum is observed at 144.5 ppm.

Concurrent with the spectral changes described above additional lines appear in the high-field part of the ^{31}P spectrum. Initially, a strong doublet at 4.9 ppm (J = 778 Hz) and a weak singlet at

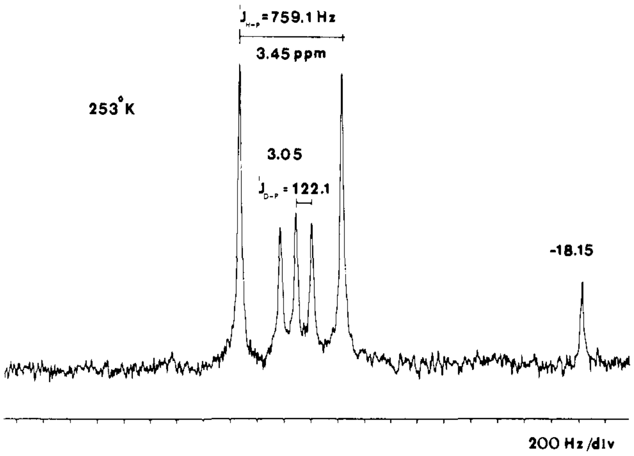

Figure 5. High-field part of the ^{31}P spectra obtained from the reaction of NiP_4 with partly deuterated sulfuric acid.

−18 ppm are observed. A decoupling experiment demonstrates that the doublet arises from phosphorus–proton coupling. This is confirmed by examining the reaction with partly deuterated sulfuric acid. The spectrum from this experiment is shown in Figure 5. The central triplet with $J = 120$ Hz (approximately one-sixth of J(PH) clearly arises from the deuterated compound. These large coupling constants indicate that these products contain H directly bonded to P. Addition of more acid leads to the appearance of a second doublet with chemical shift 12.1 ppm and coupling constant 873 Hz.

We have examined the NMR spectra of a number of other phosphite complexes looking for evidence for four-coordinated hydrides. In agreement with the earlier reports[2,3] the triethyl phosphite system gives only a five-coordinated hydride. There are obviously a number of rapid exchange processes occurring. In the ^{31}P spectrum the chemical shift of NiP_4H^+ and the spin–spin coupling constant of the high-field resonance are both very temperature dependent. The isopropyl phosphite derivative has also been prepared. It is only stable below −40 °C and shows a broad resonance in the proton spectrum at −13.8 ppm. This resonance shows signs of a triplet structure with J around 37 Hz and is almost certainly the pentacoordinate hydride poorly resolved. The triphenyl phosphite complex behaves similarly to the tri-*p*-tolyl phosphite compound. The hydrides formed with this ligand are, however, significantly less stable at higher temperatures than the *p*-tolyl phosphite complexes. The NMR spectra are also somewhat less well resolved. For these reasons the *p*-tolyl complexes were selected for detailed study. The Co complexes $HCoP_4$, where P = triphenyl phosphite and triethyl phosphite, have also been examined but no evidence for phosphite dissociation was found.

Discussion

A. Rearrangement Reaction of the Four-Coordinate Hydride. The multiplet observed at −11 ppm in the ^{1}H NMR spectrum is assigned to NiP_3H^+. At low temperature, the six-line pattern apparent in Figure 1 is consistent with a square-planar arrangement of ligands about the Ni atom. The hydride proton is coupled to the single trans P with a large coupling constant and to the two cis P's with a smaller coupling constant. The changes in the spectrum which occur on raising the temperature are attributed to fluxionality in the molecule leading to interchange of the cis and trans phosphorus ligands. Jesson and Meakin[7-9] have considered the interpretation of this type of temperature-dependent spectrum in some detail by using permutation theory to systematize the possible modes of intramolecular exchange. Unfortunately, the four-coordinate Ni phosphine complex to which they applied this theory did not give spectra which could be fitted in a completely satisfactory manner. The low-temperature limit spectrum could not be fitted accurately to an AB_2X model and two other rate processes, one an intermolecular ligand exchange, and another thought to involve a hydride-bridged species, become important at higher temperatures.

There is a reason to believe that the present molecule does not suffer from these disadvantages. Intermolecular exchange requires the presence of free ligand. No free ligand resonance is observed in the ^{31}P NMR spectra. Further, it was shown in an independent experiment that in the presence of excess acid free ligand is completely converted to other species. The retention of spin coupling in the high-temperature ^{2}H spectrum confirms the absence of intermolecular exchange. The spectra can in fact be analyzed by using a much simpler treatment than the density matrix/permutation theory approach adopted by Jesson and Meakin. This latter approach requires extensive computation, and the physical interpretation of the results is not always obvious. We prefer the formalism commonly applied to the interpretation of rate effects in ESR spectroscopy.[13]

In the present case the single proton is coupled to three phosphorus atoms, two of which are equivalent in the slow-exchange limit. Eight nuclear wave functions are generated by appropriate combinations of the three phosphorus spins. We label the phosphorus trans to the hydride as atom 1 and the cis phosphorus atoms 2 and 3. There are a number of possible mechanisms for exchanging the cis and trans phosphorus atoms. For example, rotation of phosphorus P_1 and P_2 by 180° about an axis bisecting the P_3–hydride edge of the square plane interchanges P_1 and P_2 and accomplishes the isomerization. In this case a tetrahedral intermediate or transition state is involved. Other possible mechanisms can be envisaged, but regardless of the detailed pathway the effect of the rearrangement on the nuclear spin wave functions is to exchange the P_1 and P_2 wave functions, e.g., $\alpha\beta\alpha \rightarrow \beta\alpha\alpha$. Here the ordering of the α's and β's is that of the P nuclei. The six lines in the slow-exchange hydride spectrum can be labeled with the appropriate P wave functions. Since phosphorus atoms 2 and 3 are equivalent, $\alpha\alpha\beta = \alpha\beta\alpha$ and $\beta\alpha\beta = \beta\beta\alpha$ and these pairs of wave functions are associated with the central lines of the triplets with intensity 2. The exact assignments depends on the signs of the spin–spin coupling constants. We note that if the two coupling constants have the same sign $\alpha\alpha\alpha$ and $\beta\beta\beta$ will be the outside lines of the two triplets, but if the coupling constants have different signs these two wave functions will be associated with the inside lines of the triplets. It is also clear that the two wave functions $\alpha\alpha\alpha$ and $\beta\beta\beta$ are unaffected by any permutation of the phosphorus spins and that the spectral lines associated with these wave functions must therefore be unaffected by the exchange process. Inspection of Figure 1 shows that the inside lines of the triplets satisfy this condition. The two coupling constants therefore have opposite signs. This is anticipated from consideration of the variation of two bond P–H coupling constants with the H–M–P angle.[14] If it is assumed that J(trans) is positive and J(cis) negative, as indicated by theory,[14] the lines may be labeled, from low field to high field, $\beta\alpha\alpha$, ($\beta\alpha\beta$, $\beta\beta\alpha$), $\beta\beta\beta$, $\alpha\alpha\alpha$ ($\alpha\beta\alpha$, $\alpha\alpha\beta$), $\alpha\beta\beta$. If J(cis) is positive and J(trans) is negative, the assignments are completely reversed but the conclusions stated below are unaffected. If the lines in the low-temperature spectrum are labeled 1–6 from low field to high field, inspection of the results given above for the effect of rearrangement on the nuclear spin wave functions leads to the conclusions that lines 3 and 4 are not affected by the exchange process and that lines 1 and 6 will broaden twice as fast as lines 2 and 5. It is easy to demonstrate that any rearrangement process which interchanges the trans ligand with a cis ligand leads to identical predictions with regard to the NMR spectrum. A tetrahedral intermediate is not necessary to obtain the above results and in fact the NMR spectra provide no information on the detailed mechanism of the rearrangement other than that it is an intramolecular rather than an intermolecular process.

The above considerations show that raising the temperature from the slow-exchange limit should not broaden the inside lines of the triplets and should broaden the outside lines twice as rapidly as the central lines. The spectra shown in Figure 1 are consistent

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Table I. Observed Rates of Isomerization

temp, K	k_r, s^{-1}	calcd^a k_r, s^{-1}	temp, K	k_r, s^{-1}	calcd^a k_r, s^{-1}
188	0.80	0.15	253	22.40	23.94
198	0.96	0.41	258	28.00	32.30
203	1.23	0.64	263	43.65	41.97
208	1.29	0.99	268	49.00	54.55
218	2.23	2.23	273	75.00	70.89
223	3.45	3.34	278	91.00	88.93
233	6.77	6.77	283	112.00	115.47
243	13.30	12.75	288	150.00	144.77
248	18.50	17.80			

^{a}Calculated from activation parameters in text.

with these predictions. Confirmation of the correctness of the model is provided by the double-resonance spectra of Figure 2. It is predicted that irradiation of line 1 will affect line 5 and vice versa and irradiation of line 2 will suppress line 2 and vice versa but other combinations will not occur. The experimental results are again in agreement with predictions. Quantitative analysis is straightforward. Since only the pairs of lines 1 and 5 and 2 and 6 are exchanging and the frequency separations and intensities of the two pairs of lines are identical, it is in effect only a simple two-site exchange problem which can be treated by using the standard formulae. Further, since the central lines are unaffected by the exchange, they provide a calibration to allow for variation of the nonexchange broadened line width with temperature. Figure 1 also shows a set of calculated spectra for comparison with the experimental results. The calculated spectra were obtained by using the computer program DNMR 3.[15]

Figure 4 shows the ^{31}P spectra of the four-coordinated hydride. At low temperature the anticipated spectrum is observed—a doublet of triplets for the P trans to H and a doublet of doublets for the two P's cis to the H. The temperature dependence cannot be treated quite so simply as that of the proton spectrum. Considerations along the lines of those given above show that all the lines in the spectrum are affected by the exchange process. The activation parameters obtained from the proton spectra, together with the chemical shift difference and J(PP) obtained from the low-temperature ^{31}P spectrum, have been used to calculate the spectra shown in Figure 4. The agreement between observed and calculated spectra is good. The first-order rate constants obtained at different temperatures are given in Table I and may be used to calculate an enthalpy and an entropy of activation using the Eyring equation

$$k = (KT/h)\exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT)$$

A plot of ln (k/T) vs. $1/T$ is linear with a correlation coefficient of 0.9984 and yields the activation parameters $\Delta H^{\ddagger} = 7.3$ kcal/M and $\Delta S^{\ddagger} = -24.6$ eu. The present data cover a relatively wide temperature range, and the simple nature of the spectra has allowed a rather precise fit of the first-order rate constants. Nevertheless, there are still problems in deriving accurate activation parameters from NMR data as has been discussed by Binsch.[15b] We have estimated the probable errors in these parameters by examining the fit of other straight lines to the data with different values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. On the basis of these considerations, we estimate the error in $\Delta H^{\ddagger}$ as ± 2 kcal/M and that in $\Delta S^{\ddagger}$ as ±3 cal deg^{-1} M^{-1}. In Table II some literature data on the activation parameters of rearrangement reactions of 4-, 5-, and 6-coordinated hydride complexes and on the rates of square planar/tetrahedral isomerizations of Ni complexes have been collected.[16-25] It is usually considered that five, seven, and higher coordinated complexes are stereochemically labile and that octahedral and four-coordinated square planar complexes are stereochemically inert. This belief can be rationalized on the basis of the smaller ligand field stabilization energies of the trigonal prismatic and tetrahedral geometries which are the likely intermediates in the isomerization processes. The present value of 7.1 kcal/mol for the enthalpy of activation for a square-planar isomerization is not in line with these expectations. It is, however, not dissimilar to the values reported for the rearrangements of five- and six-coordinated transition-metal hydrides. The large negative value for the entropy of activation is also anomalous. It is interesting to note that most of the known examples of stereochemically labile octahedral and square-planar complexes contain hydride ligands. The only exception of which we are aware is the recent observation of facile intramolecular ligand exchange in a Pt complex containing very bulky ligands.[25]

Table II. Activation Parameters for Metal Complex Reactions

	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	ref
isomerization $H_2Fe[P(OC_2H_5)_3]_4$	13.7	−8.8	22
isomerization $HRh[P(OC_2H_5)_3]_4$	5.2	−11.9	16
isomerization $HNi[P(OC_7H_7)_3]_3^+$	7.3	−24.6	this work
isomerization $HNi[P(C_2H_5)_3]_3^+$	9.6	−7.9	9
isomerization $(PPh_3)_2Pt(HgGePh_3)GePh_3$	14.2	+6.3	25
isomerization $Ni[P(OCH_2)_3CC_2H_5]_5^{2+}$	8.2	−0.5	18
isomerization $Fe[P(OC_2H_5)_3]_5^{2+}$	9.9	−7.1	19
ligand exchange $HPd[P(C_2H_5)_3]_3^+$	1.9	−27.8	9
ligand exchange $HPt[P(C_2H_5)_3]_3^+$	2.4	−28.5	9
planar/tetrahedral $[C_2H_5P(C_6H_5)_2]_2NiBr_2$	9.0	−4.7	23
planar/tetrahedral $[C_2H_5P(C_6H_5)_2]_2NiCl_2$	9.0	−1.0	23
planar/tetrahedral $Ni[(C_6H_5)_2CH_3P]_2Br_2$	11	+6	24

The data of Table II show that a six-coordinated Fe(II) phosphite hydride has an enthalpy of activation for rearrangement of 13.7 kcal/mol and an entropy of −8.8 eu. The corresponding values for five-coordinated Rh(1) compound are 5.18 kcal/mol and −11.9 eu. The only values available for a four-coordinated hydride complex are for $HNi(P(C_2H_5)_3)^{3+}$ for which English et al.[9] report $\Delta H^{\ddagger}$ as 9.6 kcal/mol and $\Delta S^{\ddagger}$ as −7.9 eu, but they also note complications in the fitting of the NMR spectra. For rearrangements of five-coordinated phosphites the $\Delta H^{\ddagger}$'s are in the range 8–10 kcal/mol and the $\Delta S^{\ddagger}$'s from −7.1 to +6.5 eu. The single example[25] of stereochemical nonrigidity in a non-hydride square complex give a relatively high $\Delta H^{\ddagger}$ (14.2) and a positive $\Delta S^{\ddagger}$. Rates for the tetrahedral to square-planar isomerization of Ni(II) phosphine halides yield $\Delta H^{\ddagger}$ around 7–13 kcal/mol and $\Delta S^{\ddagger}$–5 to +6 eu. Simple considerations would suggest that the $\Delta S^{\ddagger}$ value for an intramolecular rearrangement should be close to 0 and values from +7 to −7 are usually considered consistent with a unimolecular rearrangement mechanism. The large negative value (−24.6) found in the present instance is much more suggestive of a bimolecular substitution mechanism as is illustrated

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by the values of −28.5 and −27.8 quoted in Table II for square-planar Pd and Pt hydride substitutions. We note that there is a tendency for hydride rearrangements to show negative $\Delta S^{\ddagger}$'s and Meakin et al.[16] did indeed remark that the value of −11.9 quoted above for the Rh complex "is larger than might be expected for a simple intramolecular rearrangement". The NMR spectra make it clear that we are indeed dealing with an intramolecular process since the phosphorus–hydrogen coupling constants as not lost as would be the case for intermolecular exchange. The direct implication of the large negative entropy of activation is that the transition state for the process, presumably a ligand arrangement close to tetrahedral, is more highly ordered than the square-planar ground state. In cases where both the square-planar and tetrahedral states are accessible to study there is usually a positive difference in entropy between the two states.[24,25] This has been attributed to interactions of donor solvent molecules at axial positions of the square-planar complex. Methylene chloride is a poor donor and the large bulk of the phosphite ligands prevents axial coordination in the present case. We suggest that the likely reason for the negative entropy difference is the existence of a more tightly bound ion pair in the tetrahedral configuration. Ion pairing in the nonpolar solvent methylene chloride would certainly be anticipated. A probable structure for such an ion pair would involve hydrogen bonding to the hydride ligand. A model indicates that steric crowding in the square-planar complex results in the phenyl groups shielding the hydride ligand from the bisulfate counterion. Since there is no other obvious point of interaction, the complex is probably present in solution as a loose solvent separated ion pair. The fact that the hydride chemical shifts are invariant with anion is consistent with this model. The steric crowding is relieved in the tetrahedral geometry and a model indicates that direct hydrogen bonding interaction between the hydride and the anion is plausible. Hydrogen-bonding interactions between metal complexes and second-sphere ligands are well documented.[26] In terms of the entropy change, complexing of the anion by hydrogen bonding is equivalent to the addition of another ligand. The formation of a strong hydrogen bond in the transition state also accounts for the low enthalpy of activation of the rearrangement. Only hydrides can form ion pairs of this type. Such a mechanism therefore accounts for the unusual stereochemical lability of square-planar and octahedral complexes containing this ligand. It has been argued[27] that the intramolecular isomerism of a square-planar complex is a thermally "forbidden" (but photochemically allowed) reaction and requires the participation of a fifth ligand or, in the present case, a counterion, if it is to proceed rapidly. There is no requirement of this nature for tetrahedral to square-planar transitions and all the reported $\Delta H^{\ddagger}$'s are in the range for unimolecular reactions.[23,24] The only other reported nonrigid square-planar complex[25] shows a small positive entropy of activation for the rearrangement process. This complex has very bulky ligands probably leading to distortion from square-planar geometry in the ground state and, as the authors suggest, to rearrangement through a digonal twist.

B. The Five-Coordinated Hydride. The quintet in the ^{1}H spectrum at −13.2 ppm is assigned to a five-coordinated complex NiP_4H^+. The corresponding doublet is observed in the ^{31}P spectrum at 113.5 ppm. The apparent equivalence of the four phosphorus atoms could indicate a square-pyramidal complex with an apical hydride ligand. A more probable explanation is rapid rearrangement of a trigonal-bipyramidal complex. The present results provide some support for the latter view. There is a marked broadening of the hydride resonance at low temperature. Comparison with other lines in the spectrum shows that this is not simply the result of increased solvent viscosity at lower temperatures. We were, however, unable to approach the slow-exchange limit at an accessible temperature with any of the five-coordinated hydrides that we have examined. The calculation of activation parameters is therefore highly inaccurate and we can do no more than place a limit of <5 kcal on the activation energy for rearrangement.

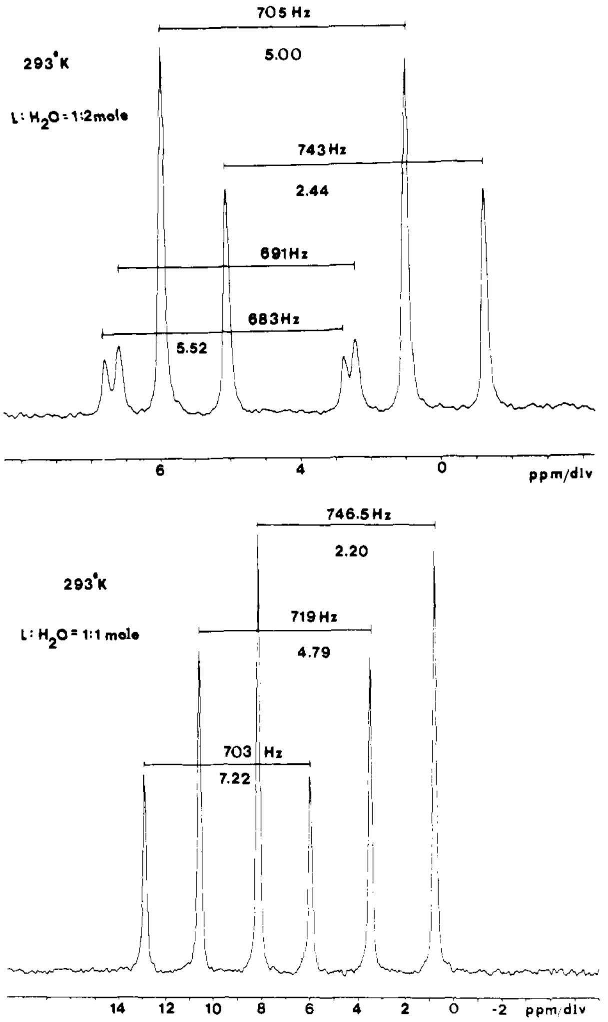

Figure 6. ^{31}P NMR spectra obtained from the reaction of tri-*p*-tolyl phosphite with water.

C. Mechanism of the Reaction of Ni(0) Phosphide Complexes with Acids. The ^{31}P NMR spectra described above show that the reaction of Ni(0) phosphites with acids is quite complex. Clearly the first two steps are

$$NiP_4 + H^+ \rightleftarrows HNiP_4^+ \quad (1)$$

$$HNiP_4^+ \rightleftarrows HNiP_3^+ + P \quad (2)$$

It was shown by Tolman that oxidation of the Ni hydride only occurs with the four-coordinated complex and may be written

$$HNiP_3^+ + H^+ \rightarrow Ni^{2+} + H_2 + 3P \quad (3)$$

Reactions 2 and 3 both produce free phosphite ligand and this can then react with any excess acid. The principal product of the reaction of tri-*p*-tolyl phosphite in methylene chloride with acid has a ^{31}P chemical shift of 5.1 ppm and a PH coupling constant of 760 Hz. The PH proton appears in the ^{1}H spectrum at 7.3 ppm. This product can be identified with some confidence as di-*p*-tolyl phosphonite formed by the reaction

$$P(O\text{-}p\text{-tolyl})_3 + H_2O \rightarrow HP(O)(O\text{-}p\text{-tolyl})_2 + HO\text{-}p\text{-tolyl} \quad (4)$$

The chemical shift and coupling constant agree closely with those reported for the corresponding phenyl compound.[29] Both the chemical shift and coupling constant vary with acid concentration and with temperature. These effects have been ascribed

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to equilibria with O-protonated species. The formation of this compound requires reaction with water rather than with acid. That this is indeed the reactant was demonstrated by adding water to the phosphite in methylene-d_2 chloride. The ^{31}P spectra obtained from this experiment are shown in Figure 6. The three doublets with coupling constants 747, 719, and 703 Hz are readily assigned to $HP(O)(O\text{-}p\text{-tolyl})_2$, HP(O)(OH)(O-tolyl), and $HP(O)(OH)_2$ by comparison with spectra in the literature.[14,15] Note the decrease in coupling constant as the *p*-tolyl groups are replaced. On adding acid to the Ni complex, the compound $HP(O)(p\text{-tolyl})_2$ is obtained and at higher acid concentrations a further doublet, chemical shift 12.1 ppm and coupling constant 873 Hz, is also observed. This is assigned to $HP(p\text{-tolyl})_3^+$ on the basis of the similarity of the NMR parameters to those of the corresponding phenyl compound,[15] i.e.

$$P(O\text{-}p\text{-tolyl}) + H^+ \rightleftarrows HP(O\text{-}p\text{-tolyl})_3^+ \qquad (5)$$

In all of these solutions a ^{31}P line is observed at −18 ppm. This is identical with the reported chemical shift of triphenyl phosphate[32] and is therefore assigned to $OP(O\text{-}p\text{-tolyl})_3$. The only remaining unassigned line is at 144.5 ppm.

D. The Relative Stabilities of the Four- and Five-Coordinated Hydrides. It is of interest to compare the geometries of the Ni hydrides formed with the ligands triethylphosphine, triethyl phosphite, and tri-*p*-tolyl phosphite. English, Meakin, and Jesson[9] found that the equilibrium leading to the formation of five-coordinated complex from the square-planar triethyl phosphine compound and triethylphosphine ligand strongly favored the higher coordination number complex. Tolman,[4] was unable to detect the four-coordinated complex in the system with triethyl phosphite as the ligand and concluded that the dissociation constant of the five-coordinated compound was very small. The present results show that for the *p*-tolyl phosphite ligand the square-planar molecule is relatively more stable and both geometries can be detected in the same solution. A combination of steric and electronic factors suffice to account for these observations. Tolman[33] has rationalized the steric factors affecting the stabilities of metal complexes in terms of the cone angles subtended by different ligands at the metal ion. He gives values of 132°, 109°, and 121° for the triethylphosphine, triethyl phosphite, and triphenyl phosphite ligands, respectively. We assume that the tri-*p*-tolyl phosphite will be sterically very similar to the phenyl analogue. Thus the reduced stability of the five-coordinated *p*-tolyl phosphite complex relative to the four-coordinated compound compared to the corresponding ethyl phosphite compounds can be rationalized on steric grounds. Electronic factors also play a role. Thus, Meakin et al.[9] found that the five-coordinated Pd and Pt complexes were much less stable than their Ni analogues in spite of the more favorable steric factor. It has been suggested[34] that the geometries of Ni(II) complexes are in part determined by a "competition involving energy gained by forming more or stronger bonds vs. energy lost through interelectronic repulsion between bonding electrons". In the present case steric factors would suggest that the triethylphosphine ligand would have a smaller tendency to form a five-coordinated compound that the tri-*p*-tolyl phosphite ligand. Clearly this steric disadvantage is offset by the electronic advantage provided by the more strongly bonding phosphine. Tolman[33] has also provided a measure of the relative donor abilities of different phosphine and phosphite ligands by measuring the carbonyl stretching frequencies of $Ni(CO)_3L$ complexes. These results indicate that triethylphosphine is the best donor of the three ligands and tri-*p*-tolyl phosphite the worst.

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