

to these s and p orbitals in preference to d orbitals favor the five-coordinate structure, the tendency toward fivefold coordination should decrease in the order $(\text{CH}_3)_3\text{P} > (\text{C}_6\text{H}_5)_2\text{POCH}_3 > \text{CH}_3\text{P}(\text{OCH}_3)_2 > \text{P}(\text{OCH}_3)_3$, according to σ -bonding arguments.^{5,8}

The stability of the $\text{NiL}_3(\text{CN})_2$ complexes toward the corresponding $\text{NiL}_2(\text{CN})_2$ complexes decreases in the order $(\text{CH}_3)_2\text{POCH}_3 \sim \text{CH}_3\text{P}(\text{OCH}_3)_2 > \text{P}(\text{OCH}_3)_3 > (\text{CH}_3)_3\text{P}$ (Table III). This does not reflect the order predicted by either π -acceptor or σ -donor arguments alone but suggests that the stability of five-coordinate $\text{NiL}_3(\text{CN})_2$ complexes is determined by a combination of these two effects.⁸

The proposed stability of the NiL_5^{2+} complexes relative to the corresponding NiL_4^{2+} complexes decreases in the order predicted by π -bonding arguments alone: $\text{P}(\text{OCH}_3)_3 > \text{CH}_3\text{P}(\text{OCH}_3)_2 > (\text{CH}_3)_2\text{POCH}_3 > (\text{CH}_3)_3\text{P}$. However, in this case ligand steric effects may be important. Cone angles of $(\text{CH}_3)_3\text{P}$ and $\text{P}(\text{OCH}_3)_3$ are 118 and 107°, respectively.⁹ In $\text{NiL}_3(\text{CN})_2$ trigonal-bipyramidal complexes each phosphine has an available ligand cone angle of nearly 120° and steric interactions should not be important. In NiL_5^{2+} complexes, however, the ligands are considerably more crowded, and steric effects could dominate the dissociation to NiL_4^{2+} .

Registry No. $\text{Ni}[(\text{CH}_3)_2\text{POCH}_3]_3(\text{CN})_2$, 55299-05-3; $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{POCH}_3]_2(\text{CN})_2$, 55299-04-2; $\text{Ni}[(\text{CH}_3)_2\text{POCH}_3]_3(\text{CN})_2$, 55299-03-1; $\text{Ni}[(\text{CH}_3)_2\text{POCH}_3]_2(\text{CN})_2$, 55299-02-0; $\text{Ni}[(\text{CH}_3)_3\text{P}]_3(\text{CN})_2$, 54515-54-7; $\text{Ni}[(\text{CH}_3)_3\text{P}]_2(\text{CN})_2$, 38889-86-0; $[\text{Ni}[(\text{C}_6\text{H}_5)_2\text{POCH}_3]_2]_3(\text{ClO}_4)_2$, 55299-01-9; $[\text{Ni}[(\text{CH}_3)_2\text{POCH}_3]_3]_3(\text{ClO}_4)_2$, 55298-99-2; $[\text{Ni}[(\text{CH}_3)_3\text{P}]_4]_3(\text{BF}_4)_2$, 55298-97-0; $\text{Ni}[\text{P}(\text{OCH}_3)_3]_3(\text{CN})_2$, 21007-23-8; $\text{Ni}[\text{P}(\text{OCH}_3)_3]_2(\text{CN})_2$, 55299-08-6; $[\text{Ni}[\text{P}(\text{OCH}_3)_3]_3]_3(\text{ClO}_4)_2$, 55009-50-2.

References and Notes

- (1) To whom correspondence should be addressed at the Department of Chemistry, State University of New York, College at Potsdam, Potsdam, N.Y. 13676.

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Contribution from the Department of Chemistry,
Michigan State University, East Lansing, Michigan 48823

Proton Magnetic Resonance Temperature Studies of Four- and Five-Coordinate Transition Metal Complexes with Tertiary Phosphorus Ligands

E. J. LUKOSIUS and K. J. COSKRAN*¹

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The temperature dependence of the proton NMR spectra is reported for the complexes $\text{NiL}_3(\text{CN})_2$ ($\text{L} = (\text{CH}_3)_3\text{P}$, $(\text{CH}_3)_2\text{POCH}_3$, $\text{CH}_3\text{P}(\text{OCH}_3)_2$, $\text{P}(\text{OCH}_3)_3$), $\text{Ni}[(\text{CH}_3)_3\text{P}]_2(\text{CN})_2$, $[\text{Ni}[\text{P}(\text{OCH}_3)_3]_3]_3(\text{ClO}_4)_2$, $[\text{Co}[\text{P}(\text{OCH}_3)_3]_3]_3\text{ClO}_4$, $[\text{Rh}[\text{P}(\text{OCH}_3)_3]_3]_3\text{B}(\text{C}_6\text{H}_5)_4$, and $[\text{Ni}[(\text{CH}_3)_2\text{POCH}_3]_3]_3(\text{ClO}_4)_2$. Each of these five-coordinate complexes is in equilibrium in solution with a four-coordinate complex and free ligand, with a ligand-exchange rate which can be varied with temperature. The proton NMR spectra are similar for all complexes: a doublet at fast exchange rates, a sharp singlet at intermediate rates, and a multiplet at slow exchange rates. The doublets are simply $^{31}\text{P}-^1\text{H}$ coupling; however, the coupling constants and chemical shifts are an average of complexed and free ligand in solution. Decoupling of phosphorus and hydrogen nuclei at intermediate exchange rates is believed due to a spin-exchange mechanism for which strong $^{31}\text{P}-^{31}\text{P}$ coupling is necessary. Multiplets at slow exchange rates are due to $^{31}\text{P}-^{31}\text{P}$ coupling. J_{PCH} is found to be of opposite sign in complexed and free ligand, while J_{POCH} has the same sign. Qualitative rates of ligand exchange follow the order $(\text{CH}_3)_3\text{P} > \text{P}(\text{OCH}_3)_3 > \text{CH}_3\text{P}(\text{OCH}_3)_2 > (\text{CH}_3)_2\text{POCH}_3$. In the metal complexes of the type ML_5^{n+} , where $\text{L} = \text{P}(\text{OCH}_3)_3$, the rate follows the order $\text{Co}^+ > \text{Rh}^+ > \text{Ni}^{2+}$.

Introduction

In the previous paper² we reported on some five-coordinate complexes of the types $\text{NiL}_3(\text{CN})_2$ and $(\text{NiL}_5)(\text{ClO}_4)_2$ where L is a tertiary phosphorus ligand. These complexes were shown by absorption spectral studies to dissociate in solution, and equilibria like $\text{NiL}_3(\text{CN})_2 \rightleftharpoons \text{NiL}_2(\text{CN})_2 + \text{L}$ and NiL_5^{2+}

$\rightleftharpoons \text{NiL}_4^{2+} + \text{L}$ were proposed.

The equilibria cause intermolecular ligand exchange, and we have now undertaken the study of the temperature-dependent proton NMR spectra. The complexes studied are $\text{NiL}_3(\text{CN})_2$ ($\text{L} = (\text{CH}_3)_3\text{P}$, $(\text{CH}_3)_2\text{POCH}_3$, $\text{CH}_3\text{P}(\text{OCH}_3)_2$, $\text{P}(\text{OCH}_3)_3$), $(\text{NiL}_5)(\text{ClO}_4)_2$ ($\text{L} = \text{CH}_3\text{P}(\text{OCH}_3)_2$, $\text{P}(\text{OCH}_3)_3$),

(RhL₅)B(C₆H₅)₄ and (CoL₅)ClO₄ (L = P(OCH₃)₃), and, last, the lone four-coordinate complex Ni[(CH₃)₃P]₂(CN)₂. The rhodium and cobalt complexes also dissociate in solution, as shown by absorption spectral studies.

The proton NMR spectra were recorded over a wide temperature range for each complex to obtain both fast and slow exchange rates.

Experimental Section

Transition Metal Complexes. The complexes [Ni[P(OCH₃)₃]₃](ClO₄)₂,³ [Co[P(OCH₃)₃]₃](ClO₄)₂,³ and [Rh[P(OCH₃)₃]₃](B(C₆H₅)₄)⁴ were prepared according to previously described methods. The complexes NiL₃(CN)₂ (L = (CH₃)₃P, (CH₃)₂POCH₃, CH₃P(OCH₃)₂, P(OCH₃)₃) and Ni[(CH₃)₃P]₂(CN)₂ were prepared as reported in the previous paper.²

Physical Measurements. The proton NMR spectra were recorded on a Varian Model A56/60D analytical spectrometer, equipped with a Varian Model V-6040 variable-temperature controller. Low temperatures were determined by measuring the chemical shift difference for methanol, while ethylene glycol was used for high temperatures. All of the spectra were recorded in CH₂Cl₂ solutions except the high-temperature spectrum of [Rh[P(OCH₃)₃]₃](B(C₆H₅)₄) which was recorded in CH₃CN; both solvents were dried over CaH₂ before use. The high-temperature spectra were taken in thick-walled NMR tubes which were sealed under an atmosphere of N₂. Chemical shifts were measured by using the solvents as references (CH₂Cl₂, δ 5.30 ppm; CH₃CN, δ 2.00 ppm).⁵ Magnetic susceptibilities were determined by Evans' NMR method⁶ in CH₂Cl₂ solutions. Ultraviolet-visible spectra were recorded on a Unicam Model SP-800B spectrophotometer using CH₂Cl₂ solvent. Samples were prepared under nitrogen in ground-glass stoppered cells so as to minimize concentration changes while the spectra were recorded at various temperatures. The samples could be run at different temperatures (±0.1°) using a thermostated bath of methanol-water, attached to the spectrophotometer.

Results and Discussion

Three classes of complexes were studied: the four-coordinate complex, Ni[(CH₃)₃P]₂(CN)₂, the five-coordinate complexes, NiL₃(CN)₂, and the five-coordinate complexes, ML₅ⁿ⁺ (Mⁿ⁺ = Ni²⁺, Co⁺, Rh⁺). The temperature-dependent proton NMR spectra obtained for all of these complexes are similar over their individual temperature ranges. For each complex there are three distinct spectral features that occur at specific temperatures. These spectral features are doublet (high-temperature spectrum), sharp singlet (intermediate-temperature spectrum), and multiplet (low-temperature spectrum). The three classes of complexes will be discussed in turn.

Ni[(CH₃)₃P]₂(CN)₂. The temperature-dependent proton NMR spectrum is shown in Figure 1. At ambient probe temperature (~38°) the spectrum is a sharp singlet at δ 1.52 ppm. If the solution is cooled, this singlet broadens and collapses and finally at -56° a three-line pattern is observed. Alternatively, if the solution is heated above ambient temperature, the resonance broadens and finally forms a sharp doublet at 97° with a coupling constant of about 10 Hz; the chemical shift is slightly downfield from the singlet.

The general features of these spectra are like those obtained for some trans square-planar Pd(II)⁷ and Rh(I)⁸ complexes of methylphosphine. In those systems the room-temperature spectra of the pure complexes were virtually coupled triplets. With successive additions of ligand the triplets collapsed, forming singlets and, finally, doublets at high ratios of added ligand to complex. An intermolecular process of ligand exchange was proposed. We similarly propose that a process of intermolecular ligand exchange is occurring for Ni[(CH₃)₃P]₂(CN)₂. However, there is one important difference in the nickel system in that no excess ligand was added. This might suggest that this four-coordinate nickel complex is dissociatively unstable with respect to free ligand and a lower

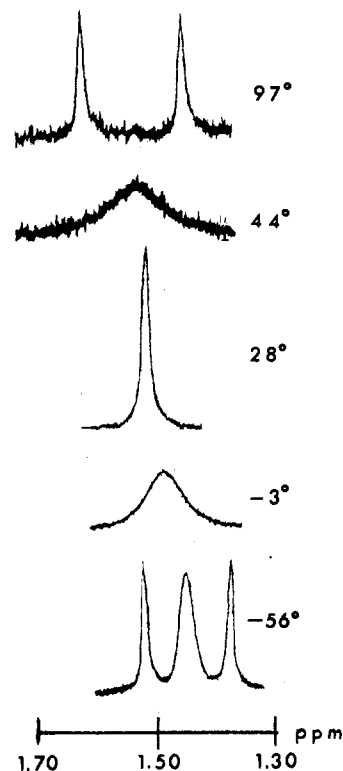


Figure 1. ¹H NMR spectra of Ni[(CH₃)₃P]₂(CN)₂ in CH₂Cl₂.

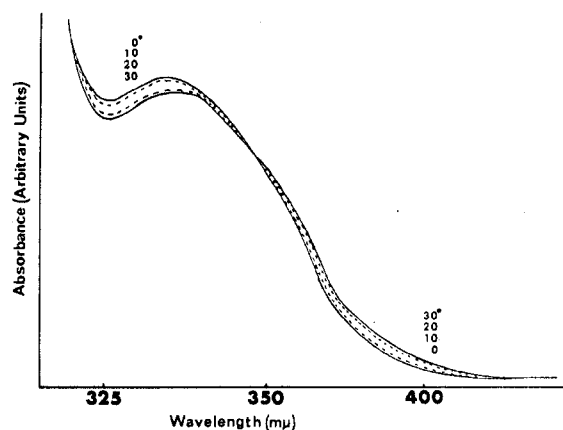


Figure 2. Effect of temperature on the ultraviolet-visible spectrum of Ni[(CH₃)₃P]₂(CN)₂ in CH₂Cl₂.

coordinated species: NiL₂(CN)₂ ⇌ NiL(CN)₂ + L. The absorption spectrum of Ni[(CH₃)₃P]₂(CN)₂ (Figure 2) supports this suggestion in that an isobestic point at 345 mμ is produced when the temperature is varied. The three-coordinate nickel complex in the above equilibrium can be classed as a 14-electron complex (d⁸ metal ion and three two-electron donor ligands). Such systems are not common.⁹ One might speculate, however, that the three-coordinate complex dimerizes through cyanide bridging forming L(CN)Ni(CN)₂Ni(CN)L. In this complex there would be a square-planar arrangement about each four-coordinate Ni atom and bridging cyanide groups.¹⁰

It is also possible that the intermolecular ligand exchange occurs by an associative mechanism: NiL₂(CN)₂ + L ⇌ NiL₃(CN)₂. It is known that Ni[(CH₃)₃P]₂(CN)₂ will associate with ligand to form a five-coordinate complex.² If the rate of ligand exchange is very fast, only a small amount of ligand need be absorbed on the four-coordinate complex during isolation in order to give the observed ¹H NMR spectra. A characteristic isobestic point occurs at 335 mμ in the ab-

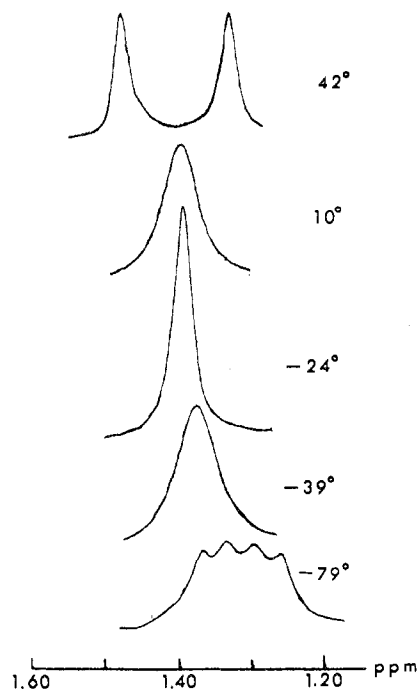


Figure 3. ^1H NMR spectra of $\text{Ni}[(\text{CH}_3)_3\text{P}]_2(\text{CN})_2$ in CH_2Cl_2 .

sorption spectrum of the four-coordinate–five-coordinate equilibrium.² If successive amounts of ligand are added to a solution of the four-coordinate complex, this isosbestic point is observed. The apparent isosbestic point at $345\text{ m}\mu$ could be caused by vibronic effects and inasmuch as the concentration of free ligand and five-coordinate complex would simply be too low in solutions of the four-coordinate complex, the $335\text{-m}\mu$ isosbestic point would not be observed.

Other equilibria that may be considered to be present in this solution do not account for the observed ^1H NMR and absorption spectra. For example, the complex $\text{Ni}[\text{P}(\text{OCH}_3)_3]_2(\text{CN})_2$ has been proposed to dimerize through cyanide bridging.¹¹ A similar monomer–dimer equilibrium for $\text{Ni}[(\text{CH}_3)_3\text{P}]_2(\text{CN})_2$ would not involve ligand exchange and thus could not explain the ^1H NMR spectra.

Numerous examples of trans square-planar d^8 metal complexes¹² of organophosphorus ligands have exhibited proton NMR spectra similar to the triplet spectrum observed for $\text{Ni}[(\text{CH}_3)_3\text{P}]_2(\text{CN})_2$ at -65° . This is an example of an $\text{X}_n\text{AA}'\text{X}'_n$ type spectrum where X is H and A is P of one ligand, X' and A' are the H and P of the second ligand, and $n = 9$. The separation of two outer lines of the triplet equals $|J_{\text{AX}} + J_{\text{AX}}|$ and the central line, which varies in intensity from complex to complex, can be qualitatively used as a measure of $J_{\text{AA}'}$;^{13,14} the more intense the central line, the larger $J_{\text{AA}'}$. Therefore, the triplet spectrum for this trans square-planar nickel complex with an intense central resonance means that the two ^{31}P nuclei are strongly coupled to each other through the metal. For a complex exhibiting ligand exchange this coupling could only occur under the limiting conditions of very slow ligand exchange.

$\text{NiL}_3(\text{CN})_2$ Complexes. The five-coordinate dicyanide complexes of $(\text{CH}_3)_x\text{P}(\text{OCH}_3)_{3-x}$ ($x = 0-3$), which are probably trigonal bipyramidal with trans apical cyanides,^{2,11} exhibit temperature-dependent spectra very similar to that of the four-coordinate complex $\text{Ni}[(\text{CH}_3)_3\text{P}]_2(\text{CN})_2$ (see Figure 3). For these complexes, however, the low-temperature multiplet is a poorly resolved quartet. For the complexes of $\text{CH}_3\text{P}(\text{OCH}_3)_2$ and $(\text{CH}_3)_2\text{POCH}_3$, two resonances are observed for the two types of ligand protons in each complex. Therefore, two doublets and two singlets are observed for each complex as the temperature of the solution is lowered; however,

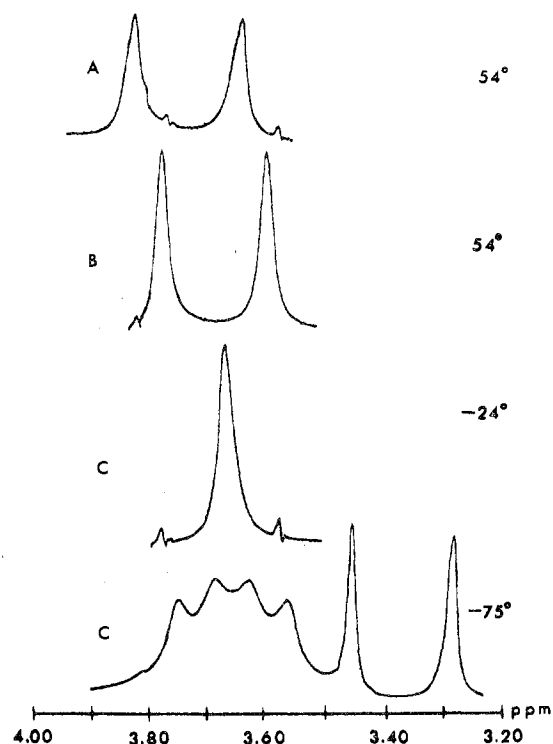


Figure 4. ^1H NMR spectra of (A) $\text{Ni}[\text{P}(\text{OCH}_3)_3]_3(\text{CN})_2$ in CH_2Cl_2 , (B) solution A with added $\text{P}(\text{OCH}_3)_3$, (C) solution B when cooled.

only for the OCH_3 protons is the quartet splitting observed while for the CH_3 protons only a broad singlet is recorded. The failure to resolve a quartet is surprising, because the OCH_3 proton splitting is observed in the same ligand, and, furthermore, the CH_3 proton splitting is readily observed in the five-coordinate $(\text{CH}_3)_3\text{P}$ complex (see Figure 3).

To account for these temperature-dependent spectra we again propose a process of intermolecular ligand exchange which is consistent with the postulate² that all of these complexes are dissociatively unstable according to the equilibrium $\text{NiL}_3(\text{CN})_2 \rightleftharpoons \text{NiL}_2(\text{CN})_2 + \text{L}$. The poorly resolved quartet observed at low temperatures represents a spectrum of the type $\text{AA}'\text{A}''\text{X}_n\text{X}'_n\text{X}''_n$. This assignment is based primarily on the similarities in the overall spectral changes for these five-coordinate complexes and the previously mentioned four-coordinate complex. In the latter case, the triplet spectrum due to ligand–ligand interaction through the metal is well understood,¹³ and we believe that under similar limiting conditions of slow exchange, coupling through the metal between the three ligands in the equatorial plane does take place for these trigonal-bipyramidal complexes and gives rise to the quartet spectrum.

A simple experiment to demonstrate the intermolecular nature of the exchange process is shown in Figure 4. If $\text{P}(\text{OCH}_3)_3$ is added to $\text{Ni}[\text{P}(\text{OCH}_3)_3]_3(\text{CN})_2$ at 54° , only one doublet is observed slightly upfield from the original doublet for the complex only. If this solution is cooled, the doublet collapses, a sharp singlet forms, and eventually a quartet forms, similar to a solution of pure complex, but in addition, a doublet due to the added $\text{P}(\text{OCH}_3)_3$ appears.¹⁵ Therefore, under conditions of fast and intermediate exchange rates the observed spectra are representative of a weighted average of all species in solution. The process is reversible as one doublet appears if the above solution is warmed to 54° .

Further support for the proposal that the doublet spectrum in these complexes represents an average of all species in solution comes from the experiment which is summarized in Figure 5. As successive amounts of $(\text{CH}_3)_3\text{P}$ are added to

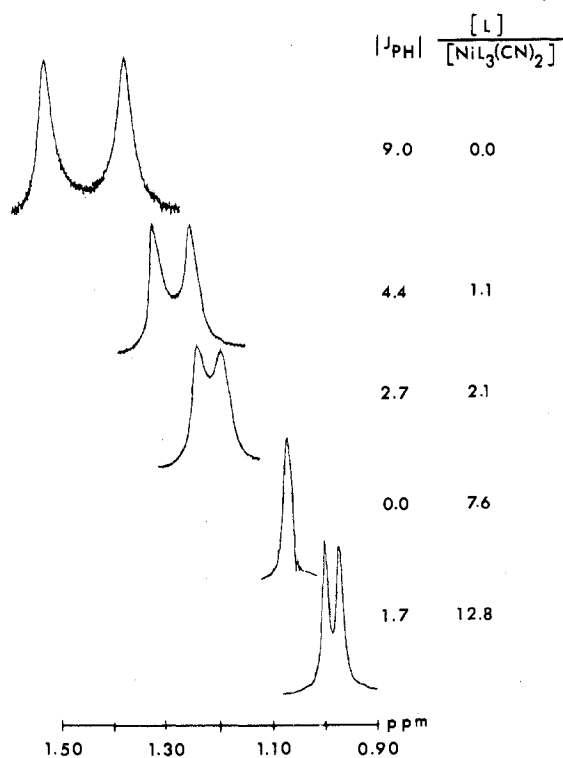


Figure 5. ^1H NMR spectra of $\text{Ni}[(\text{CH}_3)_3\text{P}]_3(\text{CN})_2$ in CH_2Cl_2 with successive additions of $(\text{CH}_3)_3\text{P}$. The molar ratio of added ligand to dissolved complex is given by $[L]/[\text{NiL}_3(\text{CN})_2]$.

$\text{Ni}[(\text{CH}_3)_3\text{P}]_3(\text{CN})_2$ at 42° , the separation of the doublet is observed to decrease, pass through zero, and form a new doublet with physical constants very much like those of pure $(\text{CH}_3)_3\text{P}$. Therefore, under these conditions of fast ligand exchange, coupling between ligands through the metal has been removed and a doublet results which is simply J_{PCH} but whose coupling constant and chemical shift are strongly influenced by the metal ion complex. The addition of free ligand heavily

weights the solution in favor of uncomplexed ligand and the spectrum indicates this by the changes in chemical shift and J_{PCH} . An interesting point to note is that at a mole ratio of added ligand to complex of approximately 7.6:1, the coupling passes through zero. Thus, free and complexed ligands have coupling constants of opposite signs. Similar observations have been made for other methylphosphine complexes,^{16,17} and it is probable that J_{PCH} for the complexed ligand is negative since a positive sign has been proposed¹⁸ for free $(\text{CH}_3)_3\text{P}$.

This same type of experiment was also performed by successive addition of small amounts of $\text{Ni}[(\text{CH}_3)_3\text{P}]_2(\text{CN})_2$. This causes a change in chemical shift and J_{PCH} , to the values of the four-coordinate complex at room temperature (δ 1.52 ppm and $J_{\text{PCH}} = 0.0$ Hz). The ^1H NMR spectrum of a solution which contains both four- and five-coordinate complexes exhibits an overlapping triplet and quartet at low temperatures.

If $\text{CH}_3\text{P}(\text{OCH}_3)_2$ is added to a solution of $\text{Ni}[\text{CH}_3\text{P}(\text{OCH}_3)_2]_3(\text{CN})_2$ (Figure 6), the doublet for the OCH_3 proton shifts upfield, but there is essentially no change in the coupling constant. The CH_3 protons similarly shift upfield, but the coupling constant passes through zero. Therefore, J_{POCH} does not change sign on going from free to complexed forms, but J_{PCH} does. This same result is observed for complexes of $\text{P}(\text{OCH}_3)_3$ and $(\text{CH}_3)_2\text{POCH}_3$. Since J_{POCH} has been predicted to be positive in the free ligands,^{18,19} it is also positive in these complexes. However, J_{PCH} appears to be negative in the complexed form, since it is positive in the free ligands.¹⁸

The sharp singlet which is observed at intermediate temperatures and which is representative of an intermediate rate of ligand exchange indicates that the phosphorus and hydrogen nuclei are decoupled. The temperatures at which the singlets for each complex reach a maximum intensity are listed in Table I. The mechanism for this decoupling cannot be due to an averaging of coupling constants of opposite signs because at the singlet temperatures the concentration of free ligand is very small, and, moreover, J_{POCH} has the same sign in both free and complexed forms. Paramagnetic relaxation effects²⁰⁻²² similarly cannot be responsible, since we have measured the

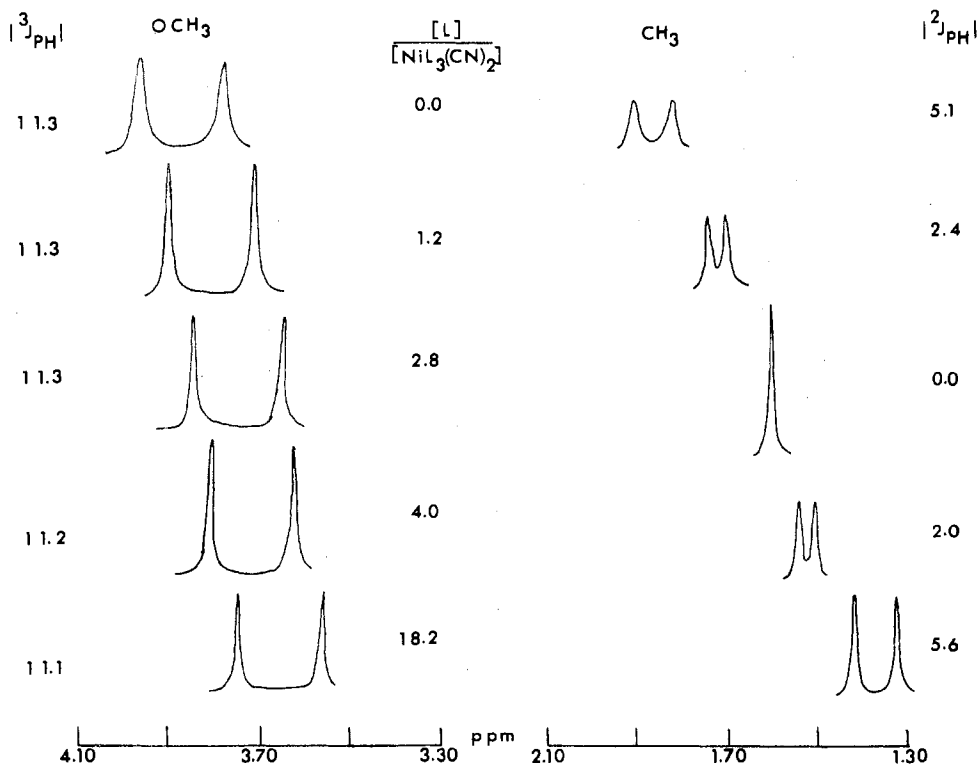


Figure 6. ^1H NMR spectra of $\text{Ni}[\text{CH}_3\text{P}(\text{OCH}_3)_2]_3(\text{CN})_2$ with successive additions of $\text{CH}_3\text{P}(\text{OCH}_3)_2$.

Table I. Temperatures of Singlet Maxima and Magnetic Susceptibility Data

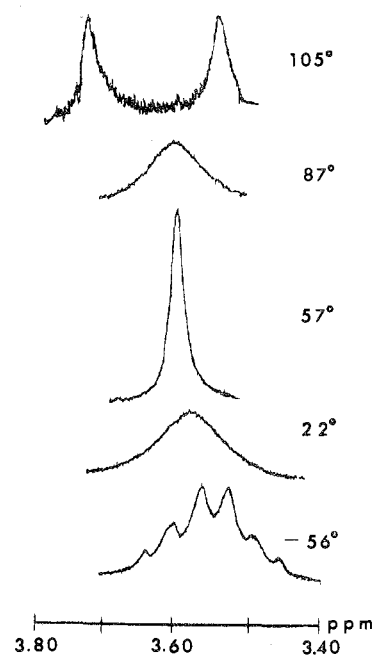
Complex	$T, ^\circ\text{C}$		$10^6 \chi_M,^a$ cgsu	$10^6 \chi_M^{\text{cor}},^b$ cgsu
	CH_3	CH_3O		
$\text{Ni}[(\text{CH}_3)_3\text{P}]_2(\text{CN})_2$	28		22	202
$\text{Ni}[(\text{CH}_3)_3\text{P}]_3(\text{CN})_2$	-24		~0	251
$\text{Ni}[(\text{CH}_3)_2\text{POCH}_3]_3(\text{CN})_2$	25	16	24	289
$\text{Ni}[\text{CH}_3\text{P}(\text{OCH}_3)_2]_3(\text{CN})_2$	-5	1	13	291
$\text{Ni}[\text{P}(\text{OCH}_3)_3]_3(\text{CN})_2$		-17	3.4	296
$\{\text{Ni}[\text{P}(\text{OCH}_3)_3]_3\}(\text{ClO}_4)_2$		>77	32	531
$\{\text{Ni}[\text{CH}_3\text{P}(\text{OCH}_3)_2]_3\}(\text{ClO}_4)_2$	>72	>72	24	500
$\{\text{Rh}[\text{P}(\text{OCH}_3)_3]_3\}(\text{ClO}_4)_2$		57	170	645
$\{\text{Co}[\text{P}(\text{OCH}_3)_3]_3\}(\text{ClO}_4)_2$		~10 ^d	1549	2016

^a Magnetic susceptibility at the corresponding maximum singlet temperature. For complexes with both methyl and methoxy groups, a temperature intermediate between the two singlet temperatures was used. ^b Magnetic susceptibility corrected for diamagnetism: see I. M. Kolthoff and P. J. Elving, *Treatise Anal. Chem.*, 4, 1778 (1963). ^c Trace paramagnetic Co(II) impurities were present in this complex. ^d Only a very broad singlet was formed for this complex.

magnetic susceptibility of all samples at the temperatures where the singlets are at a maximum and have found the solutions are essentially diamagnetic. The magnetic susceptibilities were measured by Evans' NMR method;⁶ the corrected susceptibilities for the four- and five-coordinate dicyanide complexes are recorded in Table I. Some of these corrected susceptibilities are quite large, but they are within the range of diamagnetic behavior.²³

Therefore, by analogy with the Pd(II) and Rh(I) complexes, the decoupling mechanism must be similar in kind to that proposed by Fackler et al.^{7,24} In an elegant fashion, these authors showed that the phosphorus-hydrogen decoupling could arise from spin exchange of the strongly coupled phosphorus atoms under conditions of chemical exchange. The similarities between the Pd(II) and Rh(I) systems and the complexes studied in this work are obvious, for indeed, strong ³¹P-³¹P coupling across the metal ion is apparent from the virtually coupled spectra.

Some more qualitative comments may be made, however, concerning the decoupling mechanism. In the slow exchange limit the exchange time, τ_e , is very long and $\tau_e \gg 1/J_{PP}$. Hence, the virtually coupled spectra are observed for these complexes whose features are dependent upon J_{PP} , J_{PH} , and J_{PH} . As the temperature is increased and the exchange time decreases, τ_e approaches $1/J_{PP}$ and the large J_{PP} provides a decoupling mechanism for J_{PH} . The rapid intermolecular chemical exchange of one ligand has the effect of averaging the spin states at the site of phosphorus atom exchange that the remaining phosphorus atoms (momentarily bonded to the metal) "see". This spin flipping causes the spin-lattice relaxation rate of the remaining phosphorus atoms to increase which in turn causes the P-H coupling to be averaged out. It is apparent then that a large J_{PP} value is necessary for this mechanism. If J_{PP} were very small, τ_e would exceed $1/J_{PP}$ at relatively slow exchange rates, and the induced relaxation rates sufficient for decoupling would never be realized. If the rate of exchange is increased beyond the point where the singlet appears, eventually τ_e is $< 1/J_{PP}$, and the "resident" ligand does not "see" the exchanging ligand. Hence the decoupling mechanism is lost, the spectrum appears as if there were no ³¹P-³¹P coupling or at least very weak coupling, and the fast exchange spectrum is a simple doublet of separation J_{PH} which

Figure 7. ¹H NMR spectra of $[\text{Rh}[\text{P}(\text{OCH}_3)_3]_3]\text{B}(\text{C}_6\text{H}_5)_4$.

is a weighted average of complexed and uncomplexed ligand in solution.

It is interesting to note that in the complexes of $(\text{CH}_3)_2\text{POCH}_3$ and $\text{CH}_3\text{P}(\text{OCH}_3)_2$ the singlet maxima for the methyl and the methoxy protons occur at different temperatures for each ligand (see Table I). This difference is understandable since J_{PCH} and J_{POCH} for each ligand have different values.

ML₅ⁿ⁺ Complexes. The proton NMR spectra of these complexes are also temperature dependent and the general features of the spectra are similar to the previous two classes of complexes discussed. Figure 7 shows the spectra of $\text{Rh}[\text{P}(\text{OCH}_3)_3]_3^{5+}$. Again, a high-temperature doublet, an intermediate temperature singlet, and a low-temperature multiplet are observed; however, in this case the multiplet is a well-resolved six-line resonance. The corresponding Ni(II) and Co(I) complexes of $\text{P}(\text{OCH}_3)_3$ show very similar spectra; however, the nickel complex decomposes at approximately 90°, when the spectrum is a broad singlet. Therefore, no high-temperature doublet is observed. In addition, the Co(I) complex exhibited only a very broad singlet intermediate between the doublet and sextet. This may be due to the trace paramagnetic Co(II) impurities which were identified by ESR and which may be present from unreacted starting material. Also, like $\text{Ni}[\text{CH}_3\text{P}(\text{OCH}_3)_2]_3(\text{CN})_2$, the complex $\text{Ni}[\text{CH}_3\text{P}(\text{OCH}_3)_2]_3^{2+}$ exhibits two resonances for the two types of protons, and again only the OCH_3 protons exhibit the low-temperature splitting pattern while the CH_3 resonance is a broad singlet.

Absorption spectra studies reported in the previous paper² on the Ni(II) complexes demonstrated their instability in solution with respect to free ligand and a lower coordinated species. Similar experiments on the rhodium and cobalt complexes in this work and elsewhere²⁵ have shown their dissociative instability, and we have observed isosbestic points in the absorption spectra as the temperature is varied. For the rhodium complex the isosbestic points occur at 280 and 336 m μ and for the cobalt complex at 341 and 402 m μ . Furthermore, the corresponding four-coordinate complexes of rhodium, RhL_4^+ , have been isolated for $\text{L} = \text{P}(\text{OCH}_3)_3$ and other similar ligands,²⁵ though not those of Ni(II) and Co(I). No doubt an equilibrium of the form $\text{ML}_5^{n+} \rightleftharpoons \text{ML}_4^{n+} + \text{L}$ is present in solutions of all of these complexes. In the case where $\text{M} = \text{Rh}$, this equilibrium has already been proposed

in order to account for the ligand equivalence indicated by the singlet in the ^1H NMR spectrum at 38° for $\{\text{Rh}[\text{P}(\text{OCH}_3)_3]_3\text{B}(\text{C}_6\text{H}_5)_4\}$.²⁵ This observation is consistent with the work reported here since a singlet was observed in the proton NMR spectrum at approximately 38° (Figure 7).

The symmetrical six-line multiplet which is nearly a 1:5:10:10:5:1 spectrum represents the strong ^{31}P - ^{31}P coupling through the metal in these trigonal-bipyramidal complexes. It may be considered as an $\text{AA}'\text{A}''\text{A}'''\text{X}_n\text{X}'_n\text{X}''_n\text{X}'''_n$ type of spectrum (rapid intramolecular exchange make all the phosphorus nuclei equivalent). The separation of the two outer lines ($J_{\text{AX}} + J_{\text{AX}'} + J_{\text{AX}''} + J_{\text{AX}'''} + J_{\text{A}''\text{X}} + J_{\text{A}'''\text{X}}$) is 11.8 Hz for $\text{Ni}[\text{P}(\text{OCH}_3)_3]_3^{2+}$, a value very similar to the doublet separation at high temperature. A-X coupling through the metal (five bonds) should be very small, and the separation of the two outer lines approximates J_{AX} . It is commonly observed^{19,26} that J_{POCH} for $\text{P}(\text{OCH}_3)_3$ (10.5 Hz) changes very little upon coordination; hence the value of 11.8 Hz for the separation of the two outer lines is consistent with this type of spin system. Also, the fractional intensity of the two outer lines is predicted to be $(1/2)^{r-1}$ (r = number of A nuclei) that of the entire resonance.¹⁴ For these complexes $r = 5$; hence, the intensity of the two outer lines is calculated to be $1/16$ th that of the sextet—close to what is observed.

The symmetrical nature of the six-line proton NMR pattern for the ML_5^{n+} complexes is interesting, since there are two chemically different ligands in the trigonal-bipyramidal geometry, the two axial ligands and the three equatorial ligands. (Other five-coordinate geometries would also result in at least two chemically different ligands.) The ^{31}P spectra were recorded for some of these complexes; however, the resonances are very broad and poorly resolved, and, hence, no information could be obtained from them. The ^1H resonance is symmetrical (even at 100 MHz), indicative of only one type of ligand, and may suggest that the ligands are rapidly exchanging sites intramolecularly, whereby all ligands would be equivalent. This process could be similar to the Berry²⁷ mechanism postulated for pentavalent phosphorus compounds and $\text{M}(\text{PF}_3)_5$ complexes ($\text{M} = \text{Fe}, \text{Rh}, \text{Os}$). We have attempted to look at the spectra of these complexes at temperatures lower than that of the sextet, but presently all we observe is a slight broadening of the spectra before precipitation occurs. This problem is presently being pursued with other solvent systems.²⁸

Rates of Ligand Exchange. If it is assumed that there is a similar ligand-exchange rate at temperatures where each $\text{NiL}_3(\text{CN})_2$ complex exhibits a maximum singlet, those temperatures (Table I) should provide a measure of the relative exchange rates.²⁹ For example, $\text{Ni}[(\text{CH}_3)_3\text{P}]_3(\text{CN})_2$ exhibits a maximum singlet (-24°) at a lower temperature than $\text{Ni}[(\text{CH}_3)_2\text{POCH}_3]_3(\text{CN})_2$ ($+25^\circ$). Therefore, $(\text{CH}_3)_3\text{P}$ should exchange more rapidly at a given temperature. A comparison of these "singlet" temperatures gives the following relative exchange rates: $(\text{CH}_3)_3\text{P} > \text{P}(\text{OCH}_3)_3 > \text{CH}_3\text{P}(\text{OCH}_3)_2 > (\text{CH}_3)_2\text{POCH}_3$. This ordering has been observed

before in the instability constants (K_{inst}) for the same $\text{NiL}_3(\text{CN})_2$ complexes² where the $(\text{CH}_3)_3\text{P}$ complex has the largest K_{inst} . Also, the order of ligand field strengths, as determined by the positions of the d-d transitions, is approximately the same; the $(\text{CH}_3)_3\text{P}$ complex has the lowest ligand field strength.² For the $\text{P}(\text{OCH}_3)_3$ complexes of Co^+ , Rh^+ , and Ni^{2+} (Table I) the order of exchange rates is $\text{Co}^+ > \text{Rh}^+ > \text{Ni}^{2+}$.

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Registry No. $\text{Ni}[(\text{CH}_3)_3\text{P}]_3(\text{CN})_2$, 54515-54-7; $\text{Ni}[(\text{CH}_3)_2\text{POCH}_3]_3(\text{CN})_2$, 55299-03-1; $\text{Ni}[(\text{CH}_3)_2\text{POCH}_3]_2(\text{CN})_2$, 55299-05-3; $\text{Ni}[\text{P}(\text{OCH}_3)_3]_3(\text{CN})_2$, 21007-23-8; $\text{Ni}[(\text{CH}_3)_3\text{P}]_2(\text{CN})_2$, 38889-86-0; $\text{Ni}[\text{P}(\text{OCH}_3)_3]_2(\text{ClO}_4)_2$, 55009-50-2; $\text{Co}[\text{P}(\text{OCH}_3)_3]_3(\text{ClO}_4)_2$, 55299-07-5; $\text{Rh}[\text{P}(\text{OCH}_3)_3]_3\text{B}(\text{C}_6\text{H}_5)_4$, 41655-78-1; $\text{Ni}[(\text{CH}_3)_2\text{POCH}_3]_2(\text{ClO}_4)_2$, 55299-01-9.

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- To whom correspondence should be addressed at the Department of Chemistry, State University of New York, College at Potsdam, Potsdam, N.Y. 13676.
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- This assumption is valid only if the respective values of J_{PP} , J_{PH} , and J_{PH} in each $\text{NiL}_3(\text{CN})_2$ complex are nearly equal.