

(triglycine)⁻ is diamagnetic in solution,³ solid nickel triglycine chloride exhibits an unusual magnetic moment of 1.4 BM.⁴ A relatively unstable mixed complex is indicated in the reaction of square-planar, diamagnetic Ni(CN)₄²⁻ with a large excess of EDTA.¹² This paper reports the occurrence of complicated mixed complexes of NiG²⁻; their detailed structural elucidation awaits further study.

The mixed complexes formed from NiG²⁻ and polydentate amine undergo, in the presence of excess amine, slower decomposition reactions to yield octahedral nickel complexes of the amines and tetraglycine. In general the decomposition reactions appear to be independent of buffer concentration and pH from pH 10.5 to 11.5. They exhibit a first-order dependence on mixed complex and a zero- and first-order dependence on excess polydentate amine.

The metal ion exchange reaction to EDTA from square-planar complexes of Ni(II) with aliphatic amine oximes¹³ and cysteine¹⁴ have been studied. No buildup

(12) D. W. Margerum, T. J. Bydalek, and J. J. Bishop, *J. Am. Chem. Soc.*, **83**, 1791 (1961).

of mixed-complex intermediates is reported. Two ligand molecules are required to produce the square-planar complexes in both studies while one tetraglycine molecule wraps around the plane of the nickel ion. EDTA was present in much greater excess than were the polydentate amines of this study. Conversions of square-planar nickel to the octahedral EDTA complexes followed a rate law of the form of eq 1. Neglecting the initial rapid reaction to form mixed complexes described above for the tetraglycine complex, rate constants for EDTA reactions with the nickel complexes of cysteine appear more rapid than those of amine oximes or tetraglycine which seem comparable.

Considering the multiplicity of functional groups on both reactants, NiG²⁻ and polydentate amines, it is not surprising that the two reactions possess rates so that they are measurable by conventional techniques. Indeed, in cases as complicated as that reported here, a pertinent question is whether three or more measurable reactions would be recognized if they did occur.

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Reaction of *trans*-[Ni(PR₃)₂X₂] Complexes with Phosphines and Amines. Formation of Stable Five-Coordinate Intermediates

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Tertiary phosphines PR₃ do not yield five-coordinated adducts by reaction with the planar complexes *trans*-Ni(PR₃)₂X₂ (PR₃ = P(C₂H₅)₃, P(C₂H₅)₂C₆H₅ and X = Cl, Br, NCO, NCS; PR₃ = P(C₂H₅)₂Cy, PC₂H₅Cy₂, PCy₃ (Cy = cyclohexyl) and X = Cl, Br, NCS; PR₃ = PC₂H₅(C₆H₅)₂ and X = NCS). However, P(C₂H₅)₃ and P(C₂H₅)₂C₆H₅ immediately replace PCy₃ and PC₂H₅Cy₂ in the reactions with the halide complexes. Since the reverse reactions are also observable, the result of these reactions is actually the exchange of the coordinated by the free phosphine. However, the reactions of the complexes *trans*-Ni(PR₃)₂(CN)₂ with the corresponding phosphines give in solution the stable five-coordinated intermediates as shown by the visible spectra. The compound Ni(P(C₂H₅)₂C₆H₅)₂(CN)₂ has also been isolated in the solid state. The five-coordinate compounds are discussed in terms of the binding properties of the ligands, the kinetic behavior toward the substitution, and their thermodynamic stability. With ethyl- and *n*-butylamine only substitution reactions occur.

Introduction

Whereas there are a number of five-coordinate complexes of nickel(II) with polydentate ligands,¹ little is known about the complexes with monodentate ligands in which coordination number and geometry are essentially determined by the tendency of the metal ion to attain a particular type of coordination.

Recent work on the stability of five-coordinated low-spin complexes of cobalt(II) has shown that the tris-(phosphine) compounds Co(PR₃)₃X₂ (R = alkyl, aryl) are thermodynamically unstable when X = Cl, Br, NCO but are easily formed by addition of PR₃ to the

four-coordinated Co(PR₃)₂X₂ when X = NCS.^{2,3} This behavior has been attributed to the ability of NCS⁻ to give better covalent bonds and it has been suggested that other "good" ligands such as NO₂⁻ and CN⁻ should promote stabilization of the five-coordinated compounds.⁴

As an extension of our work on the cobalt(II) complexes^{2,3} we have now investigated the similar compounds of nickel(II). In complexes of the type M(PR₃)₂X₂ the behavior of nickel(II) apparently parallels

(2) M. Nicolini, C. Pecile, and A. Turco, *J. Am. Chem. Soc.*, **87**, 2379 (1965).

(3) T. Boschi, M. Nicolini, and A. Turco, *Coord. Chem. Rev.*, **1**, 269 (1966).

(4) T. Boschi, P. Rigo, C. Pecile, and A. Turco, *Gazz. Chim. Ital.*, in press.

(1) E. L. Muetterties and R. A. Schunn, *Quart. Rev. (London)*, **20**, 245 (1966), and references therein.

TABLE I
 ANALYTICAL DATA FOR SOME Ni(II) COMPLEXES WITH TRISUBSTITUTED PHOSPHINES

Compound ^a	Mp, ^b °C	Color	% C		% H		% Ni		% other		
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
Ni(PC ₂ H ₅ Cy ₂) ₂ Cl ₂	169–170	Red	57.7	56.8	9.35	9.46	10.1	10.0	Cl	12.2	12.7
Ni(PC ₂ H ₅ Cy ₂) ₂ Br ₂	150–152	Red	50.1	50.1	8.11	8.10	8.74	8.71	Br	23.8	24.3
Ni(PC ₂ H ₅ Cy ₂) ₂ (NCS) ₂	200–201	Orange	57.4	56.6	8.67	8.76	9.35	9.48	N	4.47	4.49
Ni(P(C ₂ H ₅) ₂ Cy) ₂ Cl ₂	97–98	Red	50.7	50.7	8.93	8.9	12.4	12.4	Cl	14.9	15.0
Ni(P(C ₂ H ₅) ₂ Cy) ₂ Br ₂	82–83	Red	42.7	42.5	7.52	7.41	10.4	10.5	Br	28.4	28.6
Ni(P(C ₂ H ₅) ₂ Cy) ₂ (NCS) ₂	145–146	Orange	50.9	51.8	8.15	8.15	11.3	11.2	N	5.40	5.39
Ni(P(C ₂ H ₅) ₂ C ₆ H ₅) ₂ (NCO) ₂	139–140	Red-orange	55.6	55.0	6.36	6.44	12.3	12.2	N	5.90	5.83
Ni(P(C ₂ H ₅) ₂ C ₆ H ₅) ₂ (CN) ₂	169–170	Yellow	59.6	59.3	6.82	6.85	13.2	13.0	N	6.32	6.20
Ni(PC ₂ H ₅ (C ₆ H ₅) ₂) ₂ (CN) ₂	215–217 dec	Yellow	66.8	65.5	5.60	5.62	10.9	11.1	N	5.20	4.97
Ni(P(C ₂ H ₅) ₂ C ₆ H ₅) ₃ (CN) ₂	126–128	Red	63.1	61.0	7.45	7.37	9.63	9.71	N	4.60	4.67

^a Cy = cyclohexyl. ^b All melting points are uncorrected.

that of cobalt(II). In fact the only known compounds with the general formula Ni(PR₃)₃X₂ are Ni(P(C₂H₅)₂-C₆H₅)₃(C≡CC₆H₅)₂,⁵ Ni(P(C₄H₉)₃)₃(CN)₂,⁶ and Ni[(C₂H₅O)₂PC₆H₅]₃(CN)₂.⁷

The present paper reports the reactions between the planar complexes *trans*-Ni(PR₃)₂X₂ and tertiary phosphines and amines, in weakly coordinating solvents such as CH₂Cl₂ and ClCH₂CH₂Cl. The chief aim of this work was to investigate the factors which determine the tendency of such complexes to attain five-coordination by addition of a neutral ligand.

Experimental Section

Apparatus.—All preparative work was carried out under an atmosphere of dry nitrogen. Compounds were handled in a drybox under dry nitrogen.

Electronic spectra were obtained with an Optica CF4 spectrophotometer, and infrared spectra, with a Beckman IR9 spectrophotometer.

All the solutions were freshly prepared. The absence of quaternization processes of the phosphines and the amines by reaction with the solvent was ascertained by conductivity measurements. No significant increase of the conductivity was found during the time necessary for the spectrophotometric measurements (less than 20 min). That no side reaction occurred in the solutions under investigation was confirmed by the rigorous constancy of the absorption intensities of the spectra measured at different times.

Starting Materials.—The phosphines used were prepared by standard Grignard syntheses. The previously unreported diethylcyclohexylphosphine was prepared in the following way. A solution of diethylchlorophosphine (12.0 g) in anhydrous ether (50 ml) was added dropwise to a rapidly stirred Grignard solution prepared from magnesium (2.8 g) and cyclohexyl chloride (12.0 g) and then cooled to -20°. The mixture was refluxed for 1 hr; then a 25% aqueous solution of ammonium chloride (100 ml) was added at 0° and the ethereal layer was separated and dried. The ether was distilled off and the liquid phosphine was purified by distillation under reduced pressure collecting the fraction boiling at 98–100° (15 mm). *Anal.* Calcd for C₁₀H₂₁P: C, 69.7; H, 12.3. Found: C, 69.0; H, 12.1.

Complexes.—The preparative methods used for all complexes of the type Ni(PR₃)₂X₂ (X = Cl, Br, and NCS) are essentially alike. The complexes were prepared according to standard methods by addition of a slight excess of the phosphine to a solution of the appropriate nickel salt in absolute ethanol. The analytical data and physical properties of the previously unreported complexes are given in Table I.

Ni(P(C₂H₅)₂C₆H₅)₂(NCO)₂.—A filtered aqueous solution (50

ml) of nickel sulfate (2.8 g) and potassium cyanate (1.7 g) was treated with diethylphenylphosphine (3.4 ml) under vigorous stirring. The precipitate, which was obtained immediately, was filtered, washed with a small amount of ethanol, and dried *in vacuo*. The solid was recrystallized from ethanol.

Ni(P(C₂H₅)₂C₆H₅)₃(CN)₂.—Anhydrous nickel cyanide was slowly dissolved in a refluxing solution of diethylphenylphosphine in dichloromethane to obtain a dark red solution. The unreacted nickel cyanide was filtered off, the solvent was evaporated to a small volume, and enough light petroleum ether (bp 30–50°) was added to start crystallization. The red crystals of the complex are stable as long as they are stored under nitrogen.

Ni(P(C₂H₅)₂C₆H₅)₂(CN)₂.—When Ni(P(C₂H₅)₂C₆H₅)₃(CN)₂ was boiled with petroleum ether (bp 70–120°), it rapidly gave the yellow tetracoordinate complex which was recrystallized from dichloromethane and petroleum ether solution.

Ni(PC₂H₅(C₆H₅)₂)₂(CN)₂.—The reaction of nickel cyanide with a refluxing solution of ethyldiphenylphosphine in dichloromethane gave a red solution. The solid, obtained by evaporating the solvent *in vacuo*, was dissolved in boiling petroleum ether. Precipitation of the yellow Ni(PC₂H₅(C₆H₅)₂)₂(CN)₂ occurred by cooling the solution at 0°.

Ni(P(C₂H₅)₂(CN)₂).—This complex, previously obtained by Jensen,⁸ was prepared by the same method described above for Ni(PC₂H₅(C₆H₅)₂)₂(CN)₂.

Results and Discussion

The visible spectra of some compounds, which are relevant for the discussion, are reported in Figure 1. No change in the visible spectra of Ni(PR₃)₂X₂ (where PR₃ = P(C₂H₅)₃, P(C₂H₅)₂C₆H₅, P(C₂H₅)₂Cy, PC₂H₅-Cy₂, PCy₃, PC₂H₅(C₆H₅)₂⁹ and X = Cl, Br, I, NCS, NCO) occurs in the presence of even a large excess of phosphine (1:10³ M) and at temperatures as low as -25°, showing that the tris(phosphine) complexes are not formed in the presence of these anions. However, the yellow solutions of Ni(PR₃)₂(CN)₂ (where PR₃ = P(C₂H₅)₂C₆H₅, PC₂H₅(C₆H₅)₂, P(C₂H₅)₃) immediately turn red on addition of PR₃. By reaction of Ni(CN)₂ with P(C₂H₅)₂C₆H₅ in CH₂Cl₂ it was also possible to obtain the solid compound Ni(P(C₂H₅)₂C₆H₅)₃(CN)₂, which is diamagnetic and a nonelectrolyte in C₂H₄Cl₂. A comparison of the reflectance spectrum (Figure 2) with the solution spectra in the presence of a great excess of phosphine indicates that there is no substantial change in coordination from the solid state to the

(8) K. A. Jensen, P. H. Nielsen, and C. T. Pedersen, *Acta Chem. Scand.*, **17**, 1115 (1963).

(9) For PR₃ = PC₂H₅(C₆H₅)₂, only the thiocyanate derivative Ni(PC₂H₅(C₆H₅)₂)₂(NCS)₂ was examined, since the halide complexes are known to exist in both planar and tetrahedral forms in solution.

(5) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

(6) G. N. Schrauzer and P. Glockner, *Chem. Ber.*, **97**, 2451 (1964).

(7) E. A. Rick and R. L. Pruett, *Chem. Commun.*, 697 (1966).

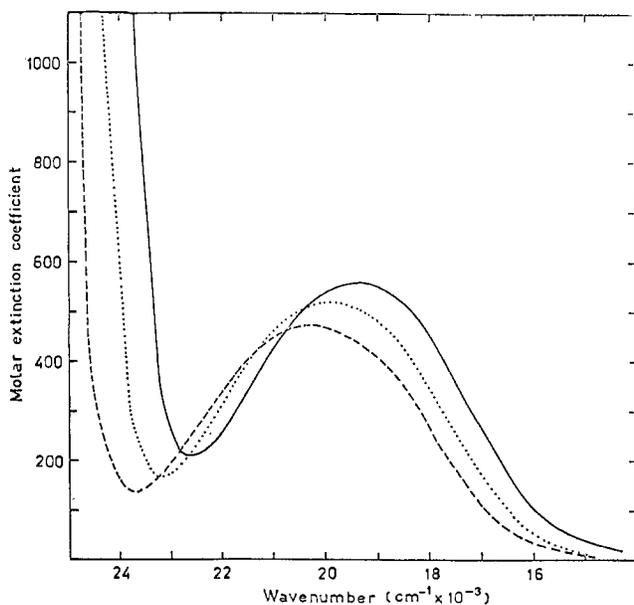


Figure 1.—Absorption spectra in $C_2H_4Cl_2$: $Ni(P(C_2H_5)_2C_6H_5)_2Cl_2$, — — —; $Ni(P(C_2H_5)_2Cy)_2Cl_2$,; $Ni(P(C_2H_5)Cy)_2Cl_2$, ———.

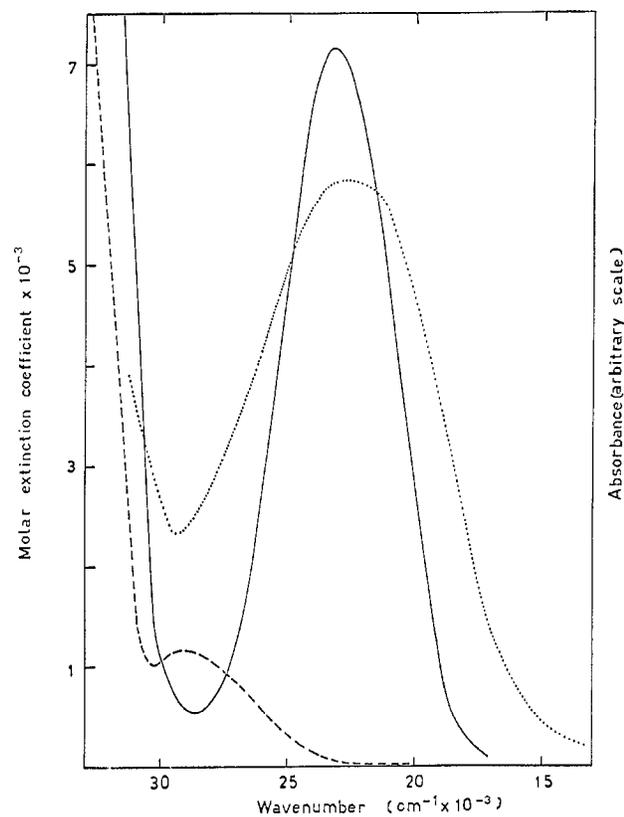


Figure 2.—Absorption spectra: — — —, $Ni(P(C_2H_5)_2C_6H_5)_2(CN)_2$ in $C_2H_4Cl_2$; ———, $8.5 \times 10^{-4} M Ni(P(C_2H_5)_2C_6H_5)_2(CN)_2$ in $C_2H_4Cl_2$ containing $0.1 M P(C_2H_5)_2C_6H_5$. Reflectance spectrum: , $Ni(P(C_2H_5)_2C_6H_5)_3(CN)_2$.

solution. The intensity and location of the visible bands are in agreement with the spectral patterns of other low-spin five-coordinated complexes of nickel(II).^{7, 10, 11}

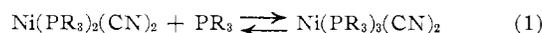
(10) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).

(11) G. Dyer and D. W. Meek, *Inorg. Chem.*, **4**, 1398 (1965); **6**, 149 (1967); G. Dyer and L. M. Venanzi, *J. Chem. Soc.*, 2771 (1965).

The infrared spectrum of the planar compound $Ni(P(C_2H_5)_2C_6H_5)_2(CN)_2$ in $C_2H_4Cl_2$ shows a single peak at 2112 cm^{-1} , and the spectrum of $Ni(P(C_2H_5)_2C_6H_5)_3(CN)_2$ in the same solvent in the presence of a large excess of phosphine shows one band at 2100 cm^{-1} . Thus the infrared spectra indicate that in both compounds the CN^- groups are in *trans* positions. The occurrence of an isosbestic point at $368\text{ m}\mu$ in solutions of $Ni(P(C_2H_5)_2C_6H_5)_2(CN)_2$ ($7.6 \times 10^{-3} M$) containing increasing amounts of phosphine (10^{-2} – $4.5 \times 10^{-2} M$) confirmed that only the four- and five-coordinated species were present at 35° , under the conditions used in recording the infrared spectra.

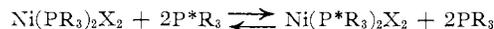
It is not possible on the basis of the infrared spectra alone to decide unambiguously whether the molecule is trigonal bipyramidal or square pyramidal. However, the structural equivalence of the three phosphine molecules is suggested by the gaussian shape of the band at $430\text{ m}\mu$.¹¹

Further evidence to support five-coordination is given by the fact that the mass law is perfectly obeyed at 20° for the equilibrium



The tris(phosphine) compound dissociates reversibly in $C_2H_4Cl_2$, reforming the original *trans*- $[Ni(PR_3)_2(CN)_2]$. The value of the stability constant determined spectrophotometrically for $PR_3 = P(C_2H_5)_2C_6H_5$ is $93\text{ mole}^{-1} l.$, and ΔF is -2.6 kcal/mole .¹²

Except for the cyanide complexes, as stated above, the changes in the spectra of the solutions of the planar compounds upon addition of the phosphine are below the limits of spectrophotometric detection. However, it was suspected that the following exchange reaction occurs, although it is obviously not revealed if the added phosphine is the same as that coordinated in the planar compound



The red shift which occurs in the visible region when $P(C_2H_5)_3$ is replaced by $PC_2H_5Cy_2$ (Figure 1) confirms that this exchange actually takes place. As shown by the spectral changes in the visible region, the addition of $P(C_2H_5)_3$ and $P(C_2H_5)_2C_6H_5$ ($2.1 \times 10^{-2} M$) to a solution of *trans*- $Ni(PC_2H_5Cy_2)_2Cl_2$ ($4.6 \times 10^{-3} M$) at 25° in $C_2H_4Cl_2$ immediately gives *trans*- $Ni(P(C_2H_5)_3)_2Cl_2$ and *trans*- $Ni(P(C_2H_5)_2C_6H_5)_2Cl_2$. The same substitution occurs by treatment of $Ni(PCy_3)_2Cl_2$ with $P(C_2H_5)_3$ and $P(C_2H_5)_2C_6H_5$; the reverse reactions also take place. Similarly, the addition of $P(C_2H_5)_2C_6H_5$ to a solution of $Ni(P(C_2H_5)_3)_2(CN)_2$ brings about the complete replacement of the phosphines, leading to $Ni(P(C_2H_5)_2C_6H_5)_3(CN)_2$.

(12) The data have been deposited as Document No. 9503 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington D. C. 20540. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints, or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

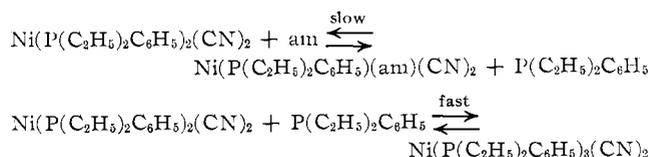
The reactions of all of these compounds with phosphines invariably lead to the replacement of the coordinated phosphines, and not of the coordinated anionic ligands, showing that the transition states are always of the same type. These results indicate that the only difference between the cyano complexes and those of the other anionic ligands in their reaction with phosphine is that a stable five-coordinated intermediate can be formed when the CN^- ligand is present. It is important to note that all of these reactions, including equilibrium 1, occur without changes in the configuration.

Since the two phosphine molecules are in *trans* positions in both the starting material and in the reaction products, it follows, from the generally accepted picture for the substitution mechanism in planar complexes of d^8 ions,¹³ that the transition state is a trigonal bipyramid with the three phosphines in the equatorial plane. If, as strongly suggested by the visible spectra, this is also the structure of the stable intermediate, this differs from the transition state in having different bond strengths.

The planar complexes $\text{Ni}(\text{PR}_3)_2\text{X}_2$ cannot attain five-coordination by addition of purely σ -donor ligands. For all compounds reported here, the addition of *n*-butylamine to the solutions of the complexes in $\text{C}_2\text{H}_4\text{Cl}_2$ invariably led to the displacement of the phosphine by the amine. However, the cyanide complexes still differ from the other compounds in their much greater kinetic stability. Whereas an immediate substitution of the phosphine is observable for $\text{Ni}(\text{PR}_3)_2\text{Cl}_2$ or $\text{Ni}(\text{PR}_3)_2(\text{NCS})_2$ in $\text{C}_2\text{H}_4\text{Cl}_2$ at -20° , the same reaction for $\text{Ni}(\text{P}(\text{C}_2\text{H}_5)_2)_2(\text{CN})_2$ is slower by many orders of magnitude and can be followed spectrophotometrically at room temperature. For $\text{Ni}(\text{P}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2)_2(\text{CN})_2$, the reaction is fast but still observable at room temperature and is much slower at -20° . If one accepts that substitution in planar complexes consists of an addition process with two transition states, one involving bond making and the other bond breaking,^{13,14} there is little doubt that this retardation observed for the cyanide complexes is due to the fact that bond breaking is more difficult. In fact, bond making, *i.e.*, the first transition state, is expected to be favored by the presence of CN^- which should enhance the electrophilic character of the substrate, as indicated by the stability of the tris(phosphine) complexes.

The behavior of $\text{Ni}(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2(\text{CN})_2$ in the reaction with ethyl- and *n*-butylamine is rather unusual. Whereas the substitution reactions on the complexes mentioned above eventually lead to the formation of octahedral amino complexes, the addition of *n*-butylamine ($10^{-1} M$) to a $10^{-3} M$ solution of $\text{Ni}(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2(\text{CN})_2$ in $\text{C}_2\text{H}_4\text{Cl}_2$ at -25° gives the typical spectrum of the five-coordinated complex $\text{Ni}(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_3(\text{CN})_2$.

The intensity of the band at $430 m\mu$ increases progressively and reaches a maximum (constant) value in about 10 min. Since these addition reactions are instantaneous, the present results suggest the successive steps



It may be concluded that *n*-butylamine does not form the five-coordinate compound or that the tendency of the planar complexes to coordinate an amine is very much smaller than the tendency to coordinate a third phosphine molecule.

The ability to form stable five-coordinated complexes of the type discussed here appears to be associated in some way with the good coordinating properties of the anions and perhaps to π back donation which enhances the acceptor power of the metal ion. It is noteworthy that the formation of complexes with coordination numbers greater than four with other d^8 metal ions, such as Pt(II) and Au(III), generally occurs when the metal is coordinated to ligands which leave a relatively high positive charge on the metal.¹⁴ In fact, our results show that the fifth ligand cannot be of a purely σ -donor type, such as an amine, although the amine is a much stronger base than the phosphines.

The requirement that good π -bonding ligands are present in the molecule appears to be more restrictive for Ni(II) than for Co(II). In fact, whereas Co(II) forms the tris(phosphine) complexes even when X is NCS^- with nickel(II), the anions necessary are stronger ligands such as CN^- and $\text{C}\equiv\text{CR}^-$. Steric factors do not appear to be important, because $\leftarrow\text{C}\equiv\text{CPh}$ is more bulky than $\leftarrow\text{NCO}$, and yet five-coordination is not attained with this anion.

These observations are in agreement with the fact that both Ni(II) and Co(II) give the tris complexes with secondary phosphines $\text{PH}(\text{C}_6\text{H}_5)_2$ even when X = Br or I.^{15,16} Although steric restrictions are surely less severe with the secondary phosphines, this factor alone cannot explain the higher stability of the complexes $\text{M}(\text{PHR}_2)_3\text{X}_2$ as compared to that of $\text{M}(\text{PR}_3)_3\text{X}_2$. Tertiary phosphines are much more basic than secondary phosphines,¹⁷ thus decreasing the positive charge upon the metal and consequently its tendency to coordinate a fifth ligand.

That steric factors are not important in the formation of the five-coordinate complexes is also suggested by the linear dependence of the reactivity of the planar complexes on the basicity of the coordinated phosphines in substitution reactions with 2,2-dipyridyl.¹⁸

We conclude this discussion with the observation that

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kinetic inertness toward the substitution of phosphines by amines and the thermodynamic stability of the tris-(phosphine) intermediates appear to be related. In fact, both are a consequence of the presence of CN⁻ groups in the molecule and are most likely attributable

to the increased strength of the nickel-phosphorus bonds in the cyanide complexes.

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Studies of Some Nickel(II) Nitrite Complexes

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Complexes of the type NiD₂(NO₂)₂ were prepared where D represents any of the following chelating ligands: 2-(aminomethyl)pyridine, 2-(methylaminomethyl)pyridine, 2-(aminomethyl)-6-methylpyridine, and their saturated derivatives. Infrared and electronic spectra were used to determine the mode of bonding of the nitrite group in the complexes. Ni[2-(aminomethyl)piperidine]₂(NO₂)₂ was found to be a nitro complex whereas Ni[2-(methylaminomethyl)pyridine]₂(ONO)₂, Ni[2-(aminomethyl)-6-methylpyridine]₂(ONO)₂, and the corresponding piperidine complexes contained nitrito groups. It is suggested that Ni[2-(aminomethyl)pyridine]₂(NO₂)₂ may contain both nitro and nitrito groups. The nitrito complexes were stable in the solid state as well as in solution and did not show any isomerization.

Introduction

Earlier studies of nitrito complexes have been concerned with complexes of the type [M(NH₃)₅ONO]ⁿ⁺, where M = Co(III), Cr(III), Rh(III), Ir(III), and Pt(IV), which with the exception of the Cr(III) compound rearrange to the corresponding nitro complexes.^{2,3} Recently Goodgame⁴ isolated some nitrito complexes of nickel(II) with disubstituted ethylenediamines and pyridine which in the solid state are quite stable with respect to isomerization to the nitro compounds. Further investigations seemed necessary to understand better the factors influencing the mode of bonding of the nitrite group.

Since nitrite complexes of nickel(II) with ethylenediamine and monosubstituted ethylenediamine gave nitro complexes⁵ and the pyridine adduct formed a nitrito complex,⁴ it was of interest to investigate 2-(aminomethyl)pyridine as a ligand. 2-(Aminomethyl)pyridine was considered since it is a chelating ligand which is structurally intermediate between ethylenediamine and 2,2'-bipyridine. The methyl derivatives, 2-(methylaminomethyl)pyridine and 2-(aminomethyl)-6-methylpyridine, were also used as bases, together with the corresponding saturated derivatives, 2-(aminomethyl)piperidine, 2-(methylaminomethyl)piperidine, and 2-(aminomethyl)-6-methylpiperidine.

Experimental Section

Materials.—2-(Aminomethyl)pyridine, 2-(methylaminomethyl)pyridine, and 2-(aminomethyl)-6-methylpyridine, from

Aldrich Chemical Co., were used without further purification. Their saturated derivatives were obtained by reduction with sodium and alcohol⁶ with a 40% yield. 2-(Aminomethyl)piperidine was obtained as a colorless oil (bp 51–52° (5 mm)) which turned yellow by exposure to the air. 2-(Methylaminomethyl)piperidine (bp 55–56° (8 mm)) and 2-(aminomethyl)-6-methylpiperidine (bp 59–60° (6 mm)) were also obtained as yellow oils.

Preparation of the Nickel(II) Nitrite Complexes.—The nickel(II) nitrite complexes were prepared in methanol by the addition of the stoichiometric amount of the chelating ligand to the nickel(II) nitrite solution.⁷ The reacting mixture was left overnight.

Ni[2-(aminomethyl)piperidine]₂(NO₂)₂.—Red crystals were obtained in a blue solution. They were filtered, washed with cold ethanol and dry ether, and then dried under vacuum. The compound started to decompose at about 230° turning brown without melting. *Anal.* Calcd for C₁₂H₂₈N₆NiO₄: C, 38.01; H, 7.44; N, 22.16. Found: C, 37.59; H, 7.08; N, 21.76.

Ni[2-(aminomethyl)pyridine]₂(NO₂)₂.—Reddish violet crystals were formed in the methanol solution. They were washed and dried as described above. *Anal.* Calcd for C₁₂H₁₆N₆NiO₄: C, 39.27; H, 4.39; N, 22.90. Found: C, 38.93; H, 4.43; N, 22.52.

Ni[2-(methylaminomethyl)pyridine]₂(ONO)₂.—Blue-violet crystals were obtained after evaporation of the methanol solution to dryness and recrystallization of the crude product from absolute ethanol. *Anal.* Calcd for C₁₄H₂₀N₆NiO₄: C, 42.56; H, 5.10; N, 21.27. Found: C, 42.74; H, 5.36; N, 20.89.

Ni[2-(methylaminomethyl)piperidine]₂(ONO)₂.—Blue crystals were obtained after recrystallization from absolute ethanol. *Anal.* Calcd for C₁₄H₃₂N₆NiO₄: C, 41.29; H, 7.92; N, 20.64. Found: C, 41.23; H, 7.66; N, 21.24.

Ni[2-(aminomethyl)-6-methylpyridine]₂(ONO)₂.—Blue crystals were obtained on recrystallization of the crude product from absolute ethanol. *Anal.* Calcd for C₁₄H₂₀N₆NiO₄: C, 42.56; H, 5.10; N, 21.27. Found: C, 42.10; H, 5.31; N, 20.55.

Ni[2-(aminomethyl)-6-methylpiperidine]₂(ONO)₂.—Blue-gray crystals were recrystallized from absolute ethanol. *Anal.*

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