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Palladium(II) and Platinum(II) Complexes of Some "Mixed" Nitrogen-Phosphorus Polydentate Ligands¹

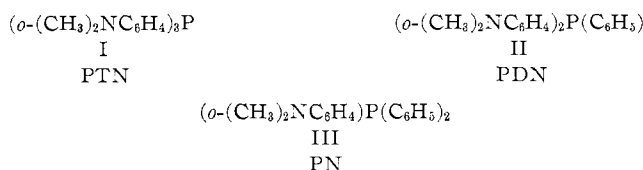
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Various types of palladium(II) and platinum(II) complexes have been prepared with three polydentate ligands: 1-(diphenylphosphino)-2-(diethylamino)ethane (NP), bis(diethylaminoethyl)phenylphosphine (NPN), and 1,3-(diethylamino)-2-(diphenylphosphino)propane (T-NPN). Square-planar complexes of the general formula MX_2L ($\text{M} = \text{Pd(II)}, \text{Pt(II)}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = \text{NP}, \text{NPN}, \text{T-NPN}$) have been characterized by elemental analysis, proton magnetic resonance, spectrophotometric, and conductivity studies. Ionic complexes of the type $[\text{MCl(L)}][(\text{C}_6\text{H}_5)_4\text{B}]$, where $\text{L} = \text{NPN}$ and T-NPN , have been prepared in which all of the donor atoms are coordinated to the central metal atom. A complex of the formula $[\text{PdCl(NP)}_3][(\text{C}_6\text{H}_5)_4\text{B}]$ has also been prepared. Possible explanations for the inability to prepare five-coordinate complexes are discussed.

Introduction

Numerous investigations of transition metal complexes of group Va polydentate ligands have been reported;³ Ni(II), Pd(II), and Pt(II) complexes have often been found to be five-coordinate. Venanzi and coworkers⁴ recently investigated the reactions of certain "mixed" polydentate ligands containing both nitrogen and phosphorus donor atoms with Pd(II) and Pt(II) halides. The coordinating atoms in these ligands are joined by *o*-phenylene bridges (I-III). These com-



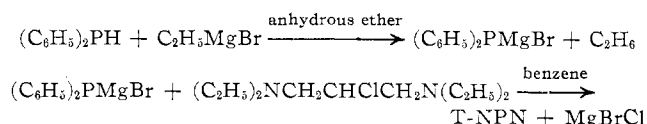
plexes exhibited, instead of five-coordinate stereochemistries, normal square-planar configurations in which the phosphorus atom and a single nitrogen atom were bonded to the metal atom. It was suggested that the failure of these ligands to stabilize five-coordinate complexes might be attributed to the deactivation of the remaining nitrogen atoms by coordination effects transmitted through the aromatic ring system. If this interpretation was correct, five-coordinate "mixed" nitrogen-phosphorus complexes of Pd(II) and Pt(II) might be stabilized if aliphatic rather than aromatic linkages joined the coordinating atoms. Accordingly, three such ligands—1-(diphenylphosphino)-2-(diethylamino)ethane (NP), bis(diethylaminoethyl)phenylphosphine (NPN), and 1,3-(diethylamino)-2-(diphenylphosphino)propane (T-NPN)—were prepared and their Pd(II) and Pt(II) halide complexes were characterized.

Experimental Section

All reagents were used without further purification. The ligands were prepared under an atmosphere of nitrogen. All complexes were dried *in vacuo*.

Ligands.—The three ligands were prepared from the appropriate phenylphosphorus Grignard reagent⁵ and the corresponding haloalkylamine in a manner analogous to that used by Mann and Millar⁶ for the synthesis of $(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_2\text{H}_5)_2\text{N}(\text{C}_6\text{H}_5)$. We have briefly sketched the preparation of NP and NPN in a previous paper.⁷ NP has also been prepared by Issleib and Rieschel⁸ by a different method.

Preparation of 1,3-(Diethylamino)-2-(diphenylphosphino)propane, T-NPN.⁹—This ligand was prepared by the reaction scheme



One mole of ethylmagnesium bromide (in 500 ml of ether) was prepared in a 2-l., three-neck flask equipped with nitrogen bleed, mechanical stirrer, and reflux condenser. A solution of 1 mol of diphenylphosphine in 500 ml of ether was added dropwise to the above Grignard reagent, and after complete addition the dark green solution was refluxed for 2 hr. The ether lost through evaporation was replaced by benzene. The solution was cooled to room temperature and a solution of 1 mol of 2-chloro-*N,N,N',N'*-tetraethyl-1,3-propanediamine in 250 ml of benzene was added at such a rate so as to maintain a steady reflux. The mixture was refluxed for an additional 2 hr and then cooled to room temperature. The reaction mixture was hydrolyzed with 1 l. of 1 *M* aqueous ammonium chloride, the organic layer was isolated and dried with anhydrous sodium sulfate, and the solvent was removed *in vacuo*. The T-NPN was vacuum distilled as a colorless oil, bp 146–149° (0.04 mm). *Anal.* Calcd for $\text{C}_{23}\text{H}_{35}\text{N}_2\text{P}$: C, 74.6; H, 9.5; N, 7.6; P, 8.4. Found: C, 74.8; H, 9.4; N, 7.6; P, 8.5.

Preparation of the Palladium Complexes. Dichloro(1-(diphenylphosphino)-2-(diethylamino)ethane)palladium(II), $\text{PdCl}_2(\text{C}_{18}\text{H}_{24}\text{NP})$.—A solution of NP (2 mmol) in 25 ml of absolute ethanol was added to a boiling ethanolic solution (25 ml) containing sodium tetrachloropalladate (2 mmol). After refluxing for 10 min the yellow-orange solution was filtered and allowed

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to cool, whereupon bright yellow crystals precipitated. The crystals were collected and recrystallized twice from hot ethanol.

Dibromo(1-(diphenylphosphino)-2-(diethylamino)ethane)palladium(II), $\text{PdBr}_2(\text{C}_{18}\text{H}_{24}\text{NP})$, and **Diiodo(1-(diphenylphosphino)-2-(diethylamino)ethane)palladium(II)**, $\text{PdI}_2(\text{C}_{18}\text{H}_{24}\text{NP})$.—A solution of $\text{PdCl}_2(\text{NP})$ (0.5 mmol) in 10 ml of hot ethanol was added to 10 ml of a hot ethanolic solution containing an excess of sodium bromide or sodium iodide. The sodium chloride was removed by filtration and after cooling the complexes crystallized. They were recrystallized twice from hot ethanolic solutions containing sodium bromide or sodium iodide to ensure complete conversion of the original chloride complex.

The complexes PdX_2L ($\text{X} = \text{Cl, Br, I}$ and $\text{L} = \text{NPN}$ and T-NPN) were prepared in a manner wholly analogous to that described for the PdX_2NP complexes.

Chlorobis(1-(diphenylphosphino)-2-(diethylamino)ethane)palladium(II) Tetraphenylborate, $[\text{PdCl}(\text{C}_{18}\text{H}_{24}\text{NP})_2][(\text{C}_6\text{H}_5)_4\text{B}]$.—To 25 ml of a hot ethanolic solution of sodium tetrachloropal-ladate(II) (1 mmol) was added NP (4 mmol) in hot ethanol (25 ml). Sodium tetraphenylboron (4 mmol) in 25 ml of ethanol was added to the above deep reddish orange solution. The resulting solution was heated to boiling and filtered hot to remove sodium chloride. The original volume was reduced by half and after cooling for 24 hr pale yellow crystals were deposited. Recrystallization was effected from hot ethanol.

Chloro(bis(diethylaminoethyl)phenylphosphine)palladium(II) Tetraphenylborate, $[\text{PdCl}(\text{C}_{18}\text{H}_{33}\text{N}_2\text{P})_2][(\text{C}_6\text{H}_5)_4\text{B}]$.— $\text{PdCl}_2(\text{NPN})$ (0.5 mmol) was dissolved in 25 ml of 1-butanol and this solution was then added to a solution containing sodium tetraphenylboron (4 mmol) in 25 ml of 1-butanol. The resulting solution was refluxed for 5 min. The hot solution was filtered to remove sodium chloride; after cooling a pale yellow solid precipitated. The complex was washed with water before being recrystallized from ethanol.

Attempts to prepare the corresponding T-NPN complex led only to decomposition.

Preparation of Platinum Complexes. Dichloro(bis(diethylaminoethyl)phenylphosphine)platinum(II), $\text{PtCl}_2(\text{C}_{18}\text{H}_{33}\text{N}_2\text{P})$.—Tetrachloro(diethylene)diplatinum(II)¹⁰ (2 mmol) was dissolved in 20 ml of ethanol and this solution was added to a solution containing NPN (2 mmol) in 10 ml of ethanol. The mixture was heated at reflux temperature for 5 min and filtered hot. The cooled solution yielded cream-colored crystals. The crystals were filtered and recrystallized from a minimum amount of 1-butanol.

Dichloro(1,3-(diethylamino)-2-(diphenylphosphino)propane)-platinum(II), $\text{PtCl}_2(\text{C}_{23}\text{H}_{35}\text{N}_2\text{P})$.—T-NPN (5 mmol) was dissolved in hot ethanol (50 ml) and added with stirring to a solution of sodium tetrachloroplatinate(II) (5 mmol) dissolved in 25 ml of ethanol. The resulting solution was refluxed for 5 min and after filtration of the hot solution, the complex separated as pale cream-colored crystals. The complex was recrystallized twice from hot ethanol.

$\text{PtX}_2(\text{C}_{23}\text{H}_{35}\text{N}_2\text{P})$ ($\text{X} = \text{Br, I}$).—These complexes were prepared from $\text{PtCl}_2(\text{T-NPN})$ in a manner analogous to that described for the palladium NP complexes.

Chloro(bis(diethylaminoethyl)phenylphosphine)platinum(II) Tetraphenylborate, $[\text{PtCl}(\text{C}_{18}\text{H}_{33}\text{N}_2\text{P})_2][(\text{C}_6\text{H}_5)_4\text{B}]$.—To a solution of $\text{PtCl}_2(\text{NPN})$ (0.5 mmol) in 10 ml of hot ethanol was added 25 ml of a hot ethanolic solution containing sodium tetraphenylboron (2 mmol). The resulting solution was heated to reflux and precipitation occurred immediately upon cooling to room temperature. The solid was collected, washed with water to remove sodium chloride, and then recrystallized twice from hot ethanol.

Chloro(1,3-(diethylamino)-2-(diphenylphosphino)propane)-platinum(II) Tetraphenylborate, $[\text{PtCl}(\text{C}_{23}\text{H}_{35}\text{N}_2\text{P})_2][(\text{C}_6\text{H}_5)_4\text{B}]$.— $\text{PtCl}_2(\text{T-NPN})$ (1 mmol) was dissolved in 100 ml of hot ethanol, and 25 ml of a hot ethanolic solution containing sodium tetraphenylboron (4 mmol) was added. The solution was heated to

boiling and then cooled to room temperature whereupon the complex precipitated together with sodium chloride. After removal of the sodium chloride with water the complex was recrystallized from hot ethanol.

Analyses.—Microanalyses were determined by Weiler and Strauss, Microanalytical Laboratories, Oxford, United Kingdom, and by Midwest Microanalytical Laboratories, Indianapolis, Ind.

Spectra.—Ultraviolet and visible spectra of the complexes in solution were taken with a Cary Model 14 recording spectrophotometer using a set of matched 1-cm quartz cells. The proton magnetic resonance spectra were obtained on Varian HA 100 and Varian A-60 spectrometers in chloroform-*d* solutions with tetramethylsilane as an internal reference.

Conductance Measurements.—Conductivity measurements were performed at 24° with an Industrial Instruments Model RC 16B2 conductivity bridge on approximately 10^{-3} M solutions of the complexes. The nonionic NPN and T-NPN complexes were tested for uncoordinated donor atoms through addition of methyl iodide to acetonitrile solutions of these complexes. An increase in conductivity to values in the range expected for 1:1 electrolytes constituted evidence for uncoordinated donor atoms.

Results and Discussion

The complexes to be described have the stoichiometries MX_2L , $(\text{MXL})(\text{TPB})$, and $[\text{PdCl}(\text{NP})_2]$ (TPB) where L is the "mixed" nitrogen-phosphorus polydentate ligand, X is a halide, M is Pd(II) or Pt(II), and TPB is tetraphenylborate. Analytical and conductivity data are presented in Table I. Ultraviolet and visible spectra are presented in Tables II and III. Proton magnetic resonance spectra are reported in Table IV.

NP and NPN Complexes.—The data presented in Tables I, II, and IV for the $\text{PdX}_2(\text{NP})$, $\text{PdX}_2(\text{NPN})$, and $\text{PtCl}_2(\text{NPN})$ complexes indicate the usual square-planar configuration of ligands about the central metal atom. The band intensities and positions are in close agreement with those complexes reported by Venanzi.⁵ The values of the molar extinction coefficients for the low-energy bands in these complexes are in the range expected for a square-planar configuration about Pd(II) and Pt(II). Five-coordination would be accompanied by an increase in the magnitude of the extinction coefficients and a shift in the position of the lowest energy electronic transition to longer wavelengths.¹¹ Since the extinction coefficients for the lowest energy transition in the NP complexes (which can only be four-coordinate) are essentially identical in magnitude with those for the neutral NPN complexes, the latter must necessarily be four-coordinate. Changing the halide in any series of complexes closely follows the pattern expected on the basis of the difference in ligand field strength; *i.e.*, the lowest energy electronic transition is shifted to longer wavelength as one proceeds from the chloride to the iodide. Furthermore, the ratio of the frequencies of these bands in the palladium and platinum iodide complexes is 1:1.2, in excellent agreement with the order of increase in ligand field splitting expected (1:1.21) between second- and third-row transition metals.^{4,12}

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TABLE I
 ANALYTICAL AND CONDUCTIVITY^a DATA FOR THE PALLADIUM(II) AND PLATINUM(II) COMPLEXES

Complexes ^b	Color	Conductance, Λ_M , $\text{cm}^2/\text{ohm mol}$		Analyses, %									
		Without CH ₃ I	With CH ₃ I	C		H		Halide		N		P	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
PdCl ₂ (NP)	Yellow	0.08	No change	46.8	46.7	5.2	5.2	15.4	15.6 (Cl)				
PdBr ₂ (NP)	Yellow-orange	0.03	No change	39.3	38.7	4.4	4.5	29.0	30.4 (Br)				
PdI ₂ (NP)	Red-orange	0.06	No change	33.5	33.2	3.8	3.8						
PdCl ₂ (T-NPN)	Yellow	0.2	No change	50.5	50.1	6.4	6.8			5.1	5.4		
PdBr ₂ (T-NPN)	Yellow-orange	0.08	No change	43.4	43.8	5.5	5.6	25.2	24.9 (Br)				
PdI ₂ (T-NPN)	Deep red	0.4	No change	37.8	36.7	4.8	4.7	34.8	35.7 (I)				
PdCl ₂ (NPN)	Yellow	0.1	14	44.6	44.3	6.8	7.0	14.6	14.3 (Cl)	5.8	5.6	6.4	6.7
PdBr ₂ (NPN)	Yellow	0.2	17	37.6	37.9	5.7	5.8	27.8	28.2 (Br)				
PdI ₂ (NPN)	Orange	0.09	11	32.3	32.5	4.9	4.9						
PtCl ₂ (NPN)	Cream	9.6	35	37.6	37.8	5.8	5.8	12.4	12.0 (Cl)	4.9	5.0		
PtCl ₂ (T-NPN)	Cream	0.4	No change	43.4	43.2	5.5	5.3	11.2	10.8 (Cl)	4.4	4.6		
PtBr ₂ (T-NPN)	Pale yellow	0.6	No change	38.1	38.3	4.8	5.0						
PtI ₂ (T-NPN)	Yellow	0.5	No change	33.7	34.4	4.3	4.5						
[PdCl(NPN)](TPB)	Pale yellow	65	No change	65.6	65.3	6.9	6.8	4.6	4.7 (Cl)				
[PdCl(NP) ₂](TPB)	Yellow	44	No change	69.8	69.6	6.6	6.6	3.4	3.3 (Cl)				
[PtCl(NPN)](TPB)	White	53	No change	58.8	57.4	6.2	6.2						
[PtCl(T-NPN)](TPB)	White	49	No change	61.3	62.8	6.0	6.5	3.9	3.6 (Cl)				

^a Molar conductivity values on approximately 10^{-3} M solutions. Data for the palladium nonionic complexes were determined in nitrobenzene; the platinum and the ionic complexes were run in acetonitrile. ^b TPB = tetraphenylborate.

 TABLE II
 ULTRAVIOLET AND VISIBLE SPECTRA OF THE COMPLEXES^a

Complex	E_{max} , cm^{-1}	ϵ_{max} , l./ mol cm^2	Complex	E_{max} , cm^{-1}	ϵ_{max} , l./ mol cm^2
PdCl ₂ (NP)	37,200	14,100	PtCl ₂ (T-NPN)	38,800	sh
	28,400	1,900		37,400	4,460
PdBr ₂ (NP)	35,200	15,500		36,400	3,700
	29,100	2,200		33,300	910
	26,500	sh		29,500	380
PdI ₂ (NP)	31,900	16,000	PtBr ₂ (T-NPN)	37,500	5,500
	26,000	2,000		36,400	4,430
	22,400	3,000		31,500	1,100
PdCl ₂ (NPN)	35,700	sh	PtI ₂ (T-NPN)	30,800	1,730
	34,500	sh		26,900	2,290
	28,300	1,620	[PdCl(NPN)](TPB)	36,660	sh
PdBr ₂ (NPN)	42,500	21,000		31,100	1,850
	37,600	sh	[PtCl(NPN)](TPB)	38,800	sh
	36,700	sh		37,800	5,500
	30,300	sh		36,700	3,900
	27,350	2,160		32,500	500
PdI ₂ (NPN)	33,300	9,400	[PtCl(T-NPN)](TPB)	37,600	sh
	26,700	sh		36,500	sh
	22,900	2,650	[PdCl(NP) ₂](TPB)	37,300	21,400
PtCl ₂ (NPN)	44,500	13,400		36,300	21,800
	38,600	sh		31,000	sh
	37,800	2,110			
	36,800	1,760			
	34,500	910			
	30,300	sh			

^a The average of three independent determinations, all run in dichloromethane. ^b sh signifies a definite shoulder on an intense absorption.

 TABLE III
 COMPARISON OF THE ULTRAVIOLET AND VISIBLE SPECTRA FOR THE
 COMPLEXES PdX₂(T-NPN) AND
 PdX₂(PDN) IN DICHLOROMETHANE

X	E_{max} , cm^{-1}		ϵ_{max} , l./mol cm^2	
	a	b	a	b
Cl	37,200	37,200	13,200	13,200
		34,000		sh
Br	27,900	27,400	2,000	1,930
	35,400	35,200	15,000	13,000
	28,800	29,600	sh	sh
I	27,100	26,000	2,600	2,100
	44,000		sh	
		38,700		sh
		36,200		sh
	32,000	31,400	13,700	13,100
	26,300	25,900	sh	sh
	22,250	21,800	2,700	3,260

^a PdX₂(T-NPN). ^b PdX₂(PDN) from ref 4.

 TABLE IV
 PROTON MAGNETIC RESONANCE SPECTRA OF THE
 METHYL GROUPS IN THE LIGANDS AND COMPLEXES^a

Compound	Chem shift of	
	H(methyl)(coord)	H(methyl)(uncoord)
NP		0.87
NPN		0.87
T-NPN		0.87
PdBr ₂ (NPN)	1.25 (1), 1.38 (1)	1.03 (2)
PdCl ₂ (T-NPN) ^b	1.47 (1), 1.91 (1)	0.96 (2)
PtCl ₂ (T-NPN) ^b	1.41 (1), 1.79 (1)	0.95 (2)
[PdCl(NP) ₂](TPB)	1.16 (1)	0.95 (1)

^a The resonances refer to the center of the triplet. In all cases the coupling constants for the coupling of the methylene protons with the methyl protons is of the order of 6–7 cps. All reported values are in ppm from tetramethylsilane. H(methyl)(coord) and H(methyl)(uncoord) refer to the methyl groups on a coordinated and uncoordinated nitrogen, respectively. Relative intensities are given in parentheses. ^b At 100 Mcps in chloroform-*d* with tetramethylsilane as internal reference. All other samples at 60 Mcps.

The nmr spectrum (Table IV) of the PdBr₂(NPN) complex exhibits three overlapping triplets; the two low-field resonances are due to the nonequivalence of the methyl groups on the coordinated nitrogen whereas the high-field triplet is very close to the methyl resonance of the free ligand.

The conductivity data for the NP and NPN complexes lend further support for the square-planar configuration. As expected, these complexes are nonionic in acetonitrile and nitrobenzene. The uncoordinated nitrogen in the NPN complexes readily reacts with a molecule of methyl iodide resulting in a conducting solution with a Λ_M in the range of a 1:1 electrolyte.^{11,13} This reaction presumably proceeds at the uncoordinated nitrogen yielding quaternary ammonium salts, although these salts were not isolated.

Excess NP reacts with sodium tetrachloropalladate(II) in ethanol to form the ionic complex [PdCl(NP)₂]⁺ which can be isolated as the tetraphenylborate salt, [PdCl(NP)₂](TPB). This complex is also square

planar based on its electronic spectrum (Table II); the low-energy band in the original complex is shifted to higher energies and is practically obscured by the charge-transfer bands. The nmr of this compound exhibited two distinct methyl groups; the high-field resonance is very close to that found for the free ligand (Table IV). This result would be expected for the complex in which the second NP molecule is bonded at the phosphorus end. Two possible geometrical isomers result; the phosphorus atoms are either *cis* or *trans* to one another (IV or V).



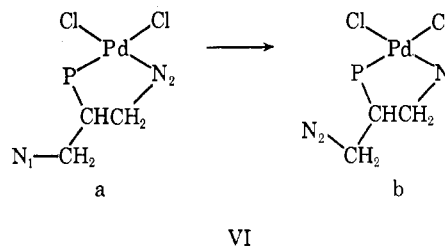
[PdCl(NPN)](TPB) can be prepared directly from PdCl₂(NPN) by allowing the latter to react with sodium tetraphenylboron in ethanol. The chloride replaced presumably is the one *trans* to the phosphorus atom. The over-all shift of the electronic transitions to higher energies (Table III) upon replacement of the chloride by the nitrogen is readily explicable on the basis of the spectrochemical series. The inability of the second nitrogen of NPN to coordinate to the central metal atom in the neutral complexes appears to be due to a combination of electronic and steric requirements. Westland¹⁴ has pointed out that nitrogen-containing ligands show little tendency to form five-coordinate complexes with Pd(II) or Pt(II) because of the poor π -acceptor and strong σ -donor abilities of nitrogen which work together to destabilize coordination of a fifth negatively charged ligand. Steric effects may also be important since an examination of a molecular model of the PdCl₂(NPN) complex reveals that there is considerable crowding of the ethyl groups on the uncoordinated nitrogen with the rest of the molecule. These two effects (electronic and steric) apparently prevent five-coordination in the NPN complexes investigated. Which of these effects predominates requires further study.

T-NPN Complexes.—Examination of the complexes formed by T-NPN proved to be extremely interesting especially with regard to the conductivity data (Table I). Although NPN and T-NPN are quite similar ligands (both have ethyl groups on the nitrogens), the T-NPN complexes do not react with added methyl iodide. Three possibilities exist which may explain this seemingly anomalous behavior: (1) the MX₂(T-NPN) complexes are five-coordinate, (2) the nitrogens of T-NPN are rapidly exchanging with one another in the coordination sphere of the metal thereby deactivating the nitrogens toward attack by methyl iodide, and (3) methyl iodide cannot react with the uncoordinated nitrogen because of the steric requirements of the rest of the molecule.

The first of these explanations was eliminated since the absorption spectra of the T-NPN complexes are

virtually identical with those obtained for the square-planar complexes prepared by Venanzi⁴ (Table III). The colors, band intensities, and band positions are also very similar to the four-coordinate NPN complexes (Table II).

The nitrogen atoms, N₁ and N₂ in VI, may rapidly exchange with one another in the coordination sphere of the central metal atom provided there can be free rotation about the P-C bond. The labilizing effect of the chloride ion *trans* to N₂ in VIa might tend to



promote this possibility by weakening the Pd-N₂ bond. Venanzi⁴ presented nmr evidence in support of a similar exchange process for PdI₂(PDN). The nmr spectrum of the methyl region of the PdCl₂(T-NPN) complex exhibits three resonances whose triplet structures are centered at 0.96, 1.47, and 1.91 ppm downfield from tetramethylsilane and with relative areas 2:1:1 (Figure 1). The high-field triplet, which is assigned to

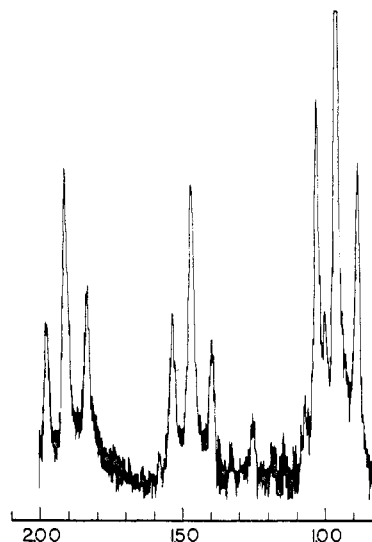


Figure 1.—Pmr spectrum of the methyl region of PdCl₂(T-NPN) in chloroform-*d* solution at 30°, in ppm from tetramethylsilane.

the two equivalent methyl groups on the uncoordinated nitrogen, occurs 0.09 ppm downfield from the methyl resonance in the free ligand (Table IV). The two nmr triplets are assigned to the nonequivalent methyl groups on the coordinated nitrogen, the nonequivalency arising from the difference in shielding by the central metal atom. Increasing the temperature to 60° has no effect on the spectrum. The corresponding platinum complex shows identical behavior. These results, although not ruling out the possibility of exchange,

indicate that the rate of exchange, should it occur, is too slow to observe on the nmr time scale over the temperature range investigated. The reactivity of the amine function toward methyl iodide may be quite sensitive to electronic perturbations caused by even a slow exchange process.

An examination of molecular models indicates the third possibility to be the most likely explanation. The two ethyl groups on the uncoordinated nitrogen and the bulkiness of the rest of the molecule make attack by methyl iodide sterically inaccessible. The differences in the geometries of the two potentially tridentate ligands may account for the ability of T-NPN to add methyl iodide and the inability of T-NPN to do the same. An X-ray investigation of $\text{PdCl}_2(\text{T-NPN})$ is currently underway.

Conclusions

The polydentate ligands investigated in the course of this study did not yield five-coordinate palladium(II) and platinum(II) halide complexes. When compared with other group Va polydentate ligands^{14,15} substitution of a nitrogen atom for a heavier group Va atom drastically reduces the chances for five-coordination. This trend appears to result from both electronic effects and (in the case of our ligands) steric effects. These conclusions agree with those reached by Venanzi.⁴

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Stereochemical Studies of Metal Chelates. II. Stereospecific Coordination of N-Methyl-L-alanine to the Cobalt(III) Ion

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Cobalt(III) complexes containing N-methyl-L-alanine and related N-substituted amino acids have been prepared. Rotatory dispersion, circular dichroism, and pmr evidence has been collected to show that N-methyl-L-alanine is coordinated stereospecifically with regard to the secondary nitrogen atom. The contributions to optical activity from the vicinal effects of asymmetric carbon and asymmetric secondary nitrogen were found to be qualitatively additive.

In a recent study, three possible geometrical isomers of the dichlorotriethylenetetraminecobalt(III) ion, that is, the *cis- α* , *cis- β* , and *trans* isomers, were prepared under controlled conditions.¹ The first study of a triethylenetetramine cobalt(III) complex² pointed out that the violet dichloro complex was obtained by a method similar to that for preparing green *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$. One of the present authors observed that the green *trans* isomer was isolated in the same procedure using L,L-3,8-dimethyltriethylenetetramine (one of the optically active derivatives of triethylenetetramine) in the place of unsubstituted triethylenetetramine.³ On the other hand, L,L-2,9-dimethyltriethylenetetramine, also an optically active derivative of triethylenetetramine, was revealed to give the *cis- α* form in the similar preparative conditions.⁴ It is considered that in L,L-3,8-dimethyltriethylenetetramine coordinated in the form of *cis- α* (and *cis- β*), there are repulsive interactions among the methyl groups substituted on the carbon atoms adjacent to secondary nitrogen atoms and hydrogen atoms of the central ethylene bridge of triethylenetetramine. The in-

fluence of such interactions may be one of the reasons for obtaining only the *trans* isomer in the case of this ligand.

An N-methylamino acid coordinated to a metal ion can be regarded as a simple model system of a chelate ring which contains such an alkyl-substituted carbon atom adjacent to a coordinated secondary nitrogen. Therefore, investigation of the steric interaction between the N and C substituents in the five-membered chelate ring would aid in understanding the mode of wrapping with a ligand chain such as L,L-3,8-dimethyltriethylenetetramine.

Sargeson and his coworkers showed the possibility of resolving a secondary amine coordinated to a metal ion using the $\text{Co}(\text{NH}_3)_4\text{sar}^{2+}$ ion (*sarH* = sarcosine, N-methylglycine) and reported the RD and CD curves of the optically active form.⁵ Shimura and his coworkers pointed out that the L-proline complex shows a considerably different CD curve from the other L-amino acid complexes.^{6,7} It was thought that the anomalous CD curve of the L-proline complex is probably due to the

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