Contribution from the Department of Chemistry,
University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

Fluxional Behavior of Potentially Bidentate Phenanthroline, Bipyridine, Naphthyridine, Pyridazine, and Phthalazine Ligands in Platinum Complexes

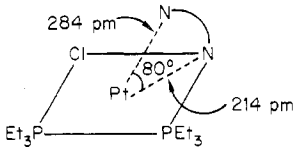
KEITH R. DIXON

Received March 11, 1977 AIC70197T

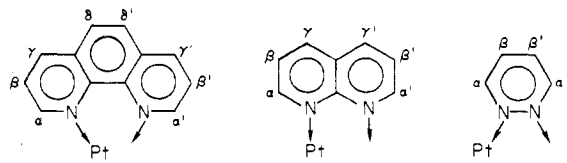
Bridge cleavage reactions of $[Pt_2Cl_2(PR_3)_4][BF_4]_2$ species under mild conditions yield complexes *cis*-$[PtCl(PR_3)_2L][BF_4]$ (R = Et, L = 1,10-phenanthroline, 2,2′-bipyridine, 1,8-naphthyridine, 4-methyl-1,8-naphthyridine, pyridazine, and phthalazine; R_3 = Ph_3 or Me_2Ph, L = 1,8-naphthyridine). When L = ethylenediamine and R = Et the product is $[Pt(PEt_3)_2(en)][BF_4]Cl$. When L = 1,10-phenanthroline or 2,2′-bipyridine the products can be oxidized by methanolic peroxide to $[PtCl(PR_3)L][BF_4]$ and POR_3. X-ray diffraction studies show that the complexes *cis*-$[PtCl(PEt_3)_2L][BF_4]$, L = 1,10-phenanthroline or 1,8-naphthyridine, have an unusual solid-state structure involving square-planar coordination about platinum with an essentially monodentate heterocycle. Detailed ^{31}P and ^1H NMR studies show that these structures persist in solution and further that all the $[PtCl(PR_3)_2L][BF_4]$ complexes are fluxional species in which there is rapid exchange of the site of platinum coordination between the two nitrogen atoms of the heterocycle. The rate of this process is markedly dependent on the suitability of nitrogen lone pair orientation for bidentate coordination (i.e., a transition state involving five-coordinate platinum); e.g., for R = Et and L = 1,10-phenanthroline, 1,8-naphthyridine, or pyridazine the approximate coalescence temperatures in ^1H spectra are respectively <−80, −30, and +50 °C. For L = pyridazine or phthalazine the mechanism is apparently dissociative rather than one involving five-coordinate platinum.

Introduction

Our previous work[1] has shown that the 1,10-phenanthroline (phen) ligand in the complex *cis*-$[PtCl(PEt_3)_2(phen)][BF_4]$ is essentially monodentate in the solid state. Protons in the



rings including the coordinated and "noncoordinated"[2] nitrogen atoms should show clear chemical shift differences in ^1H NMR spectra but in the observed spectra the two rings appear exactly equivalent.[3] Thus, the solution structure of the complex is an unresolved question; the possibilities being a trigonal-bipyramidal structure with phenanthroline in the equatorial plane or a structure similar to that in the solid state but with the phenanthroline rapidly exchanging its point of attachment to platinum. In the present paper we present further evidence which demonstrates that the fluxional hypothesis is most likely the correct one and we also investigate the effect of lone pair orientation upon the rate of fluxion by study of analogous complexes of 1,8-naphthyridine (naph) and pyridazine (pyrid). Thus, in the series



the rate of exchange of platinum between the two nitrogen atoms decreases in the order phen > naph > pyrid, as the orientation of the lone pairs becomes less favorable for formation of a transition state in which both nitrogens are bound to platinum. Related results for complexes of 2,2′-bipyridine, 4-methyl-1,8-naphthyridine, phthalazine, ethylenediamine, and pyridine are also described.

The present work appears to be the first reported example of this type of fluxional behavior for a phenanthroline ligand or for any related ligand having two nitrogen lone pairs suitably orientated for symmetric chelation. However, the reported crystal structure[4] for $[AuCl_3(2,9\text{-}Me_2\text{-}1,10\text{-phen})]$ is very similar to that of *cis*-$[PtCl(PEt_3)_2(phen)]^+$ except that the difference between the in-plane M–N bond (209 pm) and the out-of-plane bond (258 pm) is less pronounced. It is therefore possible that this gold complex could show similar behavior.

X-ray studies in these laboratories[5] have shown that the 1,8-naphthyridine complex *cis*-$[PtCl(PEt_3)_2(naph)][BF_4]$ has a structure closely similar to that of the corresponding phen complex with in-plane Pt–N = 208 pm, out-of-plane Pt–N = 305 pm, and ∠N–Pt–N = 79°. The fluxional behavior of this complex is similar to that reported previously for gold complexes of 2,7-dimethyl-1,8-naphthyridine and it is notable that these gold complexes are the only previous examples of fluxional behavior in naphthyridine complexes. This is surprising since there have been very extensive studies of the coordination chemistry of naphthyridine ligands, notably by Hendricker and co-workers,[6] and several crystal structures which indicate asymmetric binding of a naphthyridine ligand to a metal.[7] For example, in $[Hg_2(naph)_2][ClO_4]_2$ the ligands are bound via one nitrogen (Hg–N = 203 pm) and the second nitrogen is comparatively remote (Hg–N = 278 pm).[7a] This is in contrast to the structure of the phenanthroline complex $[Hg_2(phen)(NO_3)_2]$ where the ligand, although asymmetric, is clearly bidentate with Hg–N lengths of 230 and 248 pm.[8]

The present work appears to be the first report of platinum complexes of pyridazine and phthalazine although the literature does contain brief references to palladium complexes of both ligands[9] and to complexes of pyridazine with several first-row transition elements.[10]

Results

The complexes were all prepared by cleavage reactions of chloro-bridged compounds or by mild oxidation of the initial products of these cleavage reactions. Thus

$$[Pt_2Cl_2(PR_3)_4][BF_4]_2 + 2L \rightarrow 2cis\text{-}[PtCl(PR_3)_2L][BF_4] \quad (1)$$

where L = 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy), 1,8-naphthyridine (naph), 4-methyl-1,8-naphthyridine (Me-naph), pyridazine (pyrid), phthalazine (phth), pyridine (py), or ethylenediamine (en), and

$$cis\text{-}[PtCl(PR_3)_2L][BF_4] \xrightarrow{H_2O_2/CH_3OH} [PtCl(PR_3)L][BF_4] + R_3PO \quad (2)$$

where L = phen or bpy. The specifically cis stereochemistry of the initial bridge cleavage products is consistent with our previous observations on this type of reaction.[11]

Preliminary characterization of the complexes was by analytical and conductance data.[12] In all cases satisfactory C, H, and N analyses were obtained and, except for L = en, the molar conductance values in nitromethane lie within the

range (75–95 Ω^{-1} cm^2) expected for 1:1 electrolytes.[13] For L = en, the product of reaction 1 had molar conductance 155 Ω^{-1} cm^2 in nitromethane. This lies within the expected range (150–180 Ω^{-1} cm^2) for 2:1 electrolytes[13] and thus suggests that this product is more correctly formulated as $[Pt(PEt_3)_2(en)][BF_4]Cl$. In agreement with this formulation, the infrared spectrum showed no significant absorption in the ν(Pt–Cl) region.

Infrared spectra of all the other complexes showed the expected ligand and anion absorptions and also ν(Pt–Cl) ca. 280–310 cm^{-1}. ^{1}H NMR spectra of the triethylphosphine complexes showed the usual[11] complex methylene resonances (ca. τ 7.7–8.3) and, where only a single triethylphosphine was present, the expected[11] methyl resonance (ca. τ 8.6–9.0) consisting of a doublet ($J_{P-CH_3} \sim 17.5$ Hz) of triplets ($J_{H-H} \sim 7.5$ Hz). For *cis*-$[PtCl(PEt_3)_2(phen)][BF_4]$ we have previously shown[3] that 220-MHz spectra are required to resolve the chemical inequivalence of the proton resonances of the mutually cis triethylphosphine ligands. For the present complexes only 90-MHz spectra are available, but for all the $[PtCl(PEt_3)_2L][BF_4]$ species the peak contours are consistent with the presence of chemically inequivalent triethylphosphine ligands. Certainly the spectra are quite different from those expected[11] for mutually trans triethylphosphine ligands and this evidence of cis stereochemistry is confirmed by the ^{31}P spectra described below. Resonances due to phenyl protons in phosphine ligands were generally poorly resolved (ca. τ 2.6–3.0) but, in all cases, resonances due to heterocyclic, phenyl and alkyl protons gave the correct integrated, relative intensities.

Thus, the preliminary data support the assumption that in the $[PtCl(PR_3)_2L][BF_4]$ complexes, all four ligands are coordinated leaving only BF_4^- as counterion (except for L = en) and the stereochemistry is cis in all cases. The structures are probably similar to those established by x-ray crystallographic analysis of *cis*-$[PtCl(PEt_3)_2(phen)][BF_4]$ and *cis*-$[PtCl(PEt_3)_2(naph)][BF_4]$. More detailed information on the coordination geometry, especially the mode of attachment of the potentially bidentate nitrogen ligands, is provided by the ^{1}H NMR spectra of the heterocyclic ligands and by ^{31}P NMR spectra. The assignments compiled in Table I were confirmed by an extensive series of decoupling experiments including irradiation at each proton position in turn and in many cases[14] irradiation at ^{31}P. Presentation of the details of all these experiments would be excessively lengthy but in all cases the expected spectral changes occurred on irradiation and the key features of the assignments are discussed below for each individual compound. The ^{1}H chemical shifts were found to be markedly solvent dependent and, in view of the large variety of solvents and lock signals used in efforts to maximize solubility and resolution, it would be unwise to make comparisons between compounds. The only other general caution arises in cases where chemical shifts between primed and unprimed resonances are very small (τ <0.1). These assignments are probably reliable but the difficulties of irradiating very closely shifted resonances make it impossible to be certain. The labeling scheme for proton positions is explained in footnote *a* to Table I.

^{31}P NMR spectra (with protons decoupled) of the $[PtCl(PR_3)L][BF_4]$ complexes simply showed the expected 1:4:1 triplet due to coupling with ^{195}Pt ($I = {}^1/_2$, relative abundance = 33.8%). For the *cis*-$[PtCl(PR_3)_2L][BF_4]$ complexes, each component of the 1:4:1 triplet appears as a four-line AB pattern (J_{PP} = 20–22 Hz), thus confirming the cis stereochemistry, and the effective value of δ_{AB} varies from $\delta_{AB} + {}^1/_2(J_{Pt-A} - J_{Pt-B})$ for the low-field sideband through δ_{AB} for the center band to $\delta_{AB} - {}^1/_2(J_{Pt-A} - J_{Pt-B})$ for the upfield sideband. The origin of differences of this type between center band and sideband spectra has been discussed in detail previously.[15] Its application to the present spectra is straightforward, and the parameters given in Table I have been derived from analysis of the center bands as AB spectra and the ^{195}Pt sidebands as ABM spectra. In most cases the differences between this analysis and first-order analysis as AX/AMX spectra are small. Since the trans influence of nitrogen is normally greater than that of chloride in platinum complexes,[16] it is likely that the smaller of the two Pt–P coupling constants observed for each *cis*-$[PtCl(PR_3)_2L][BF_4]$ complex should be assigned to phosphorus trans to L. This assumption was shown to be correct for *cis*-$[PtCl(PMe_2Ph)_2(naph)][BF_4]$ by observation of the $\alpha\alpha'$ proton resonance while irradiating at each phosphorus chemical shift in turn. The ^{31}P NMR spectra of *cis*-$[PtCl(PEt_3)_2L][BF_4]$, L = phen or naph, were unchanged by lowering of temperature except for small changes in chemical shifts and J_{Pt-P} coupling constants. Data for L = naph at −70 °C are included in Table I. Corresponding figures for the L = phen case are δ 136.1 and 137.6 ppm and J_{Pt-P} = 3435 and 3694 Hz at −80 °C. We have recently observed[17] similar temperature dependence of Pt–P coupling constants in *cis*- and *trans*-$[PtCl_2(P\text{-}n\text{-}Bu_3)_2]$ and it seems likely that the phenomenon is quite common.

$[PtCl(PEt_3)(phen)][BF_4]$. ^{1}H NMR of the phenanthroline ligand is basically similar to that reported previously[3] except that our recent acquisition of a 90-MHz spectrometer with superior resolution and narrow band decoupling facilities permits a more detailed analysis and, in particular, accurate determination of $J_{\alpha Pt}$, $J_{\alpha' Pt}$, $J_{\alpha P}$, and $J_{\alpha' P}$. The assignment (Table I) of the α, β, γ, and δ protons as trans to phosphorus and α', β', γ', and δ' trans to chlorine is made on the basis that $J_{\alpha Pt} < J_{\alpha' Pt}$, as is expected since the trans influence of phosphorus is greater than that of chlorine, and $J_{\alpha P} > J_{\alpha' P}$, as is expected for a trans vs. a cis coupling.

***cis*-$[PtCl(PEt_3)_2(phen)][BF_4]$.** ^{1}H NMR spectra are again similar to those reported previously[3] except that decoupling experiments permit accurate determination of $J_{\alpha Pt}$ and $J_{\alpha P}$. Despite the chemical inequivalence of the α, β, γ, and δ (coordinated ring) and the α', β', γ', and δ' (noncoordinated ring) positions in the solid-state structure, the spectra show primed and unprimed positions to be chemically equivalent in the NMR spectrum at ambient temperature. Thus the α positions exhibit a single poorly resolved quartet which on irradiation at ^{31}P becomes a pair of doublets (coupling to β and γ) with ^{195}Pt sidebands and on irradiation at β appears as a 1:4:1 triplet (coupling to ^{195}Pt with coupling to γ and P not resolved). The β, γ, and δ resonances similarly show no evidence of inequivalence of primed and unprimed positions. On lowering the temperature, no inequivalence between primed and unprimed positions could be detected even at −80 °C, the lowest temperature accessible before viscosity broadening and solubility problems prevented observation of the spectrum. Unfortunately, this broadening prevented measurement of $J_{\alpha Pt}$ at low temperature but there was no evidence to indicate any change in $J_{\alpha Pt}$ as the temperature was gradually lowered.

***cis*-$[PtCl(PEt_3)_n(bpy)][BF_4]$, n = 1 or 2.** The spectra and analyses were similar to those described above for the phenanthroline complexes except that the presence of δ positions in the same ring introduces extra complexity into β and γ resonances and prevents resolution.

***cis*-$[PtCl(PEt_3)_2(naph)][BF_4]$.** ^{1}H NMR spectra of this complex at various temperatures and under various irradiation conditions are shown in Figure 1. Except for the α resonance, the ambient temperature spectrum (Figure 1C) is similar to the spectrum of free naphthyridine and may be simply analyzed on the assumption that the two rings are chemically equivalent and that the inter-ring couplings are small. Thus the β and γ resonances are pairs of doublets due to intra-ring

Table I. Nuclear Magnetic Resonance Spectra

Compd	^{1}H spectrum of heterocycle[a]									^{31}P spectrum[b]	
	Chem shifts, τ[c]				Coupling constants, Hz						
	α α′	β β′	γ γ′	δ δ′	αβ α′β′	αγ α′γ′	βγ β′γ′	αPt α′Pt	αP α′P	Chem shift, ppm	J_{Pt-P}, Hz
1,10-Phenanthroline[d]	0.86	2.33	1.62	2.15	4.2	1.9	8.0				
[PtCl(PEt$_3$)(phen)][BF$_4$][e]	0.22	1.88	1.18	1.85	5.4	1.3	8.2	22[f]	3.6	135.8	3450
	0.76	1.80	1.12	1.85	5.7	1.1	8.2	46	1.8		
cis-[PtCl(PEt$_3$)$_2$(phen)][BF$_4$][g]	0.68	2.18	1.51	2.11	5.0	1.5	8.0	12[f]	<1.5	138.1	3482
										139.1	3681
2,2′-Bipyridine[h]	1.44	2.78	2.27	1.64	4.9	2.1	8.0				
[PtCl(PEt$_3$)(bpy)][BF$_4$][g]	0.62	~2.1[i]	~1.6[i]		5.3	1.3	*i*	22	3.3	135.7	3442
	1.19	~2.1			5.6	1.5	*i*	48	1.5		
cis-[PtCl(PEt$_3$)$_2$(bpy)][BF$_4$][g,j]	1.27	2.47	~2.0[i]		5.1	1.4	6.5	13	2.5	135.8	3549
										137.3	3214
1,8-Naphthyridine[k]	0.87	2.52	1.78		4.2	2.0	8.0				
cis-[PtCl(PEt$_3$)$_2$(naph)][BF$_4$][l]	0.79	2.16	1.29		4.7	1.5	8.3	15	1.9	134.3	3557
										136.3	3250
cis-[PtCl(PEt$_3$)$_2$(naph)][BF$_4$][l] (−70 °C)	~0.75[i]	2.04	1.15		5.3	*i*	8.0	*i*	*i*	132.5	3566
	~0.75	2.19	1.34		3.9	*i*	7.9	~0	~0	134.0	3194
cis-[PtCl(PPh$_3$)$_2$(naph)][BF$_4$][e]	0.77	2.43	1.79		4.6	1.5	8.3	16	2.2	126.4	3763
										135.5	3415
cis-[PtCl(PPh$_3$)$_2$(naph)][BF$_4$][e] (−70 °C)	0.87	~2.5[i]	1.82		4.9[m]	1.3[m]	~8[i]	34	4.2	*n*	*n*
	0.66	~2.5	1.92		4.5	1.7	~8	~0	~0		
cis-[PtCl(PMe$_2$Ph)$_2$(naph)][BF$_4$][l]	0.62	2.22	1.37		4.7	1.5	8.1	15	2.0	155.7	3609
										161.5	3307
cis-[PtCl(PMe$_2$Ph)$_2$(naph)][BF$_4$][l] (−60 °C)	0.46	~2.1[i]	1.23		*i*	*i*	8.2	32	*i*	*n*	*n*
	0.70	~2.3	1.39				8.2	~0	~0		
4-Methyl-1,8-naphthyridine[k]	1.02	2.68			4.2						
	0.88	2.47	1.62		4.2	2.0	8.2				
cis-[PtCl(PEt$_3$)$_2$(Me-naph)][BF$_4$][e]	1.10	2.41			5.0			20	2.3	134.4	3569
	0.92	2.24	1.35		4.8	1.5	8.4	10	~1[i]	136.5	3240
Pyridazine[o]	0.75	2.42			5.1	1.9	8.3				
cis-[PtCl(PEt$_3$)$_2$(pyrid)][BF$_4$][p]	0.68	1.91[p]			*i*	*i*	8.0	18	*i*	132.0	3503
	0.74	2.05[p]						~0	~0	138.4	3096
Phthalazine[q]	0.41	1.87	2.00		~0	~0	8.2				
cis-[PtCl(PEt$_3$)$_2$(phth)][BF$_4$][r]	−0.16	~1.6[i]			*i*	*i*	*i*	24	*i*	132.2	3525
	0.16							~0	~0	138.3	3083
Pyridine[s]	1.4	2.8	2.4		5.5	1.9	7.5				
cis-[PtCl(PEt$_3$)$_2$(py)][BF$_4$][l]	1.32	2.29	1.90		5.7	*i*	7.6	27	*i*	133.1	3454
										137.4	3057

[a] α, β, γ, and δ positions are labeled relative to the nitrogen atoms. Where a single entry occurs for both primed and unprimed parameters, the two are chemically equivalent. In other cases primes denote positions adjacent to the noncoordinated nitrogen *or* the ring trans to chlorine *or* in the case of 4-methyl-1,8-naphthyridine, the unsubstituted ring. [b] Recorded in CH_2Cl_2 solution using $P(OCH_3)_3$ as external reference. Chemical shifts are in ppm upfield from the reference. For all complexes having two phosphorus atoms in a mutually cis configuration, J_{PP} was in the range 20–22 Hz. See Experimental Section for comments on likely accuracy of parameters. [c] See Results for comments on the variety of solvents and references used. [d] Data from ref 3. [e] Solvent for ^{1}H spectrum CD_2Cl_2; reference and lock CH_2Cl_2. [f] Owing to a computational error, these values were misquoted in ref 3. [g] Solvent for ^{1}H spectrum $CD_2Cl_2/(CD_3)_2CO$; reference and lock CH_2Cl_2. Use of this locking signal is responsible for the chemical shift differences between the present work and those quoted for [PtCl(PEt$_3$)$_2$(phen)][BF$_4$] in ref 3. [h] Data from F. A. Kramer, Jr., and R. West, *J. Phys. Chem.*, 69, 673 (1965). [i] Lack of resolution prevents accurate assignment. Due in some cases to overlap of peaks and in others to viscosity broadening at low temperatures. [j] $J_{\beta\delta} = J_{\beta'\delta'} = 2.6$ Hz. [k] Data from ref 20. [l] Solvent for ^{1}H spectrum $CD_2Cl_2/(CD_3)_2CO$; reference and lock Me_4Si. [m] Determined from spectra with ^{31}P decoupled. [n] Not recorded. [o] Data from ref 18 and C. J. Pouchert and J. R. Campbell, "Aldrich Library of NMR Spectra", Aldrich Chemical Co., 1974. The values listed as $J_{\alpha\gamma}$ and $J_{\beta\gamma}$ are more correctly described as $J_{3,5}$ and $J_{4,5}$. [p] Solvent for ^{1}H spectrum $CDCl_3$; reference and lock Me_4Si. The value listed as $J_{\beta\gamma}$ is more correctly labeled $J_{\beta\beta'}$. $\delta_\beta - \delta_{\beta'} = 12.86$ Hz. It is not possible to determine which chemical shift is β and which β′. [q] Data from P. J. Black and M. L. Heffernan, *Aust. J. Chem.*, 18, 707 (1965). [r] Solvent for ^{1}H spectrum $(CD_3)_2CO$; reference and lock Me_4Si. [s] Data from W. G. Schneider, H. J. Bernstein, and J. A. Pople, *Can. J. Chem.*, 35, 1487 (1957), and C. J. Pouchert and J. R. Campbell, "Aldrich Library of NMR Spectra", Aldrich Chemical Co., 1974.

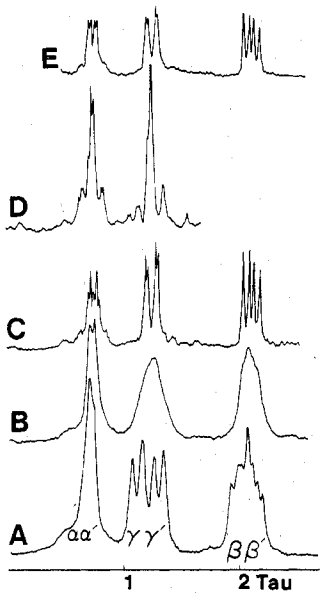


Figure 1. Aromatic region of the ^1H NMR spectrum of *cis*-$[PtCl(PEt_3)_2(naph)]BF_4$ recorded at 90 MHz in $CD_2Cl_2/(CD_3)_2CO$ solution: (A) −70 °C, (B) −40 °C, (C) +35 °C, (D) +35 °C with irradiation at the $\beta\beta'$ resonance, (E) +35 °C with irradiation at ^{31}P.

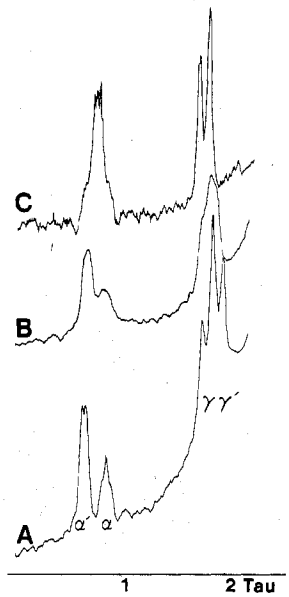


Figure 2. Heterocyclic region of the ^1H NMR spectrum of *cis*-$[PtCl(PPh_3)_2(naph)]BF_4$ recorded at 90 MHz in CD_2Cl_2 solution. The sloping baseline is due to intense phenyl absorption at τ 2.5–3.0. This also obscures the $\beta\beta'$ absorption: (A) −70 °C, (B) −40 °C, (C) +35 °C.

coupling. The α resonance is similar to that observed in *cis*-$[PtCl(PEt_3)_2(phen)][BF_4]$ but better resolved; consisting of a doublet of doublets (coupling to β and γ), doubleted again by ^{31}P and having ^{195}Pt sidebands. The double "triplet" appearance of the resonance is due to overlap caused by the closely similar values of $J_{\alpha\gamma}$ and $J_{\alpha P}$.

As the temperature is lowered, the γ resonance first broadens (ca. −40 °C) and then splits (ca. −60 °C) into two doublets. Thus, the α, β, and γ and α', β', and γ' rings are now chemically inequivalent; the doublets are due to $J_{\beta\gamma}$ and $J_{\beta'\gamma'}$, and the small $J_{\alpha\gamma}$ and $J_{\alpha'\gamma'}$ couplings are not resolved because of viscosity broadening. A similar doubling of the β resonance can also be observed in the low-temperature spectra but the chemical shift difference between α and α' is apparently too small to be resolved. This is somewhat surprising but other results (see *cis*-$[PtCl(PMe_2Ph)_2(naph)][BF_4]$ below) show that the α, α' chemical shifts are very sensitive to the nature of the tertiary phosphine and there is coincidental overlap in the PEt_3 case. However, it is clear that the spectra are most readily explained if the low-temperature form is the same as the solid-state structure[5] (i.e., having the naphthyridine ring coordinated essentially via one nitrogen atom; see Introduction), and as the temperature is raised the two rings are rendered chemically equivalent by a fluxional process in which the ligand rapidly exchanges its point of attachment to platinum from one nitrogen to the other. Inspection of the data in Table I shows that $J_{\alpha\beta}$ is normally increased slightly on coordination to Pt and this effect has been used as a basis for assigning the chemical shifts and coupling constants to the coordinated (α, β, γ) and noncoordinated (α', β', γ') rings of the low-temperature form. Once $J_{\alpha\beta}$ and $J_{\alpha'\beta'}$ are assigned, the remaining assignments follow on the basis of irradiation experiments to establish the mutual coupling relationships.

Variable-temperature NMR spectra recorded in several different solvents and using *cis*-$[PtCl(PEt_3)_2(naph)][ClO_4]$ instead of the above BF_4^- salt were similar to those described above, thus establishing that neither solvent or anion is a significant factor in these phenomena.

***cis*-[PtCl(PPh$_3$)$_2$(naph)][BF$_4$].** ^1H NMR spectra of this complex are shown in Figure 2. The assignments are similar to those described above for the triethylphosphine analogue except that the β resonances are partially overlapped by PPh_3

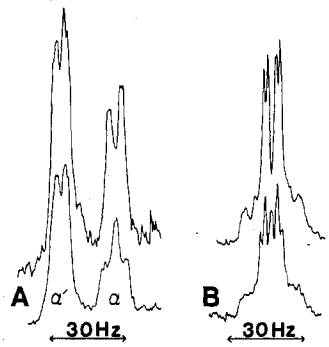


Figure 3. Effect of irradiation at ^{31}P upon the $\alpha\alpha'$ resonances of *cis*-$[PtCl(PPh_3)_2(naph)]BF_4$. Spectra were recorded at 100 MHz in CD_2Cl_2 solution and in each case the lower trace is the spectrum without irradiation: (A) −70 °C, (B) +35 °C.

resonances and, especially at low temperature where there is viscosity broadening, this makes the analysis difficult. A more important difference is that the α and α' resonances are clearly resolved at −70 °C, and the effect of irradiation at ^{31}P (see Figure 3) establishes that the α resonance is coupled to phosphorus whereas α' is not, in agreement with the idea that naphthyridine is bound via only one nitrogen in the low temperature form. Unfortunately the poor signal to noise ratio in the −70 °C spectrum makes the observation of ^{195}Pt sidebands somewhat uncertain. The situation is not improved by irradiation at ^{31}P since irradiation at the phosphorus center band does not decouple phosphorus in those molecules containing ^{195}Pt. However, the assigned value, $J_{\alpha Pt} = 34$ Hz, is approximately double the ambient temperature value, as would be expected if rapid exchange of the naphthyridine point of attachment to platinum is occurring at the higher temperature.

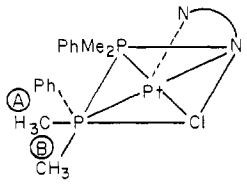
***cis*-[PtCl(PMe$_2$Ph)$_2$(naph)][BF$_4$].** ^1H NMR spectra of this complex were similar to those of the triphenylphosphine analogue described above except that at low temperature the α resonance (coordinated ring) was to low field of α' (noncoordinated ring) whereas in the PPh_3 compound the reverse is true. Clearly, these resonances are very sensitive to the nature of the tertiary phosphine and it is therefore not so surprising that they are not resolved in the triethylphosphine

Table II. NMR Data for the Tertiary Phosphine Ligands in $[PtCl(PMe_2Ph)_2(naph)][BF_4]$

	δ_P, ppm	J_{Pt-P}, Hz	τ_{CH_3} ppm	J_{P-CH_3}, Hz	J_{Pt-CH_3}, Hz
Trans to naph	161.5	3307	8.19[a]	11.2	34.4
Trans to Cl	155.7	3609	8.64[b]	11.2	38.2

[a] At −60 °C this resonance split into two resonances centered at τ 8.14 and 8.19. [b] This resonance split at low temperature in a manner similar to that noted in footnote *a* but the effect was not fully resolved at −60 °C.

complex. A further interesting feature of the spectra of the dimethylphenylphosphine complex is the doubling of the methyl resonances at low temperature. Relevant data from the ^{31}P and ^1H spectra are collected in Table II the assignments having been established by observation of the methyl resonances while irradiating at each phosphorus resonance in turn. Further confirmation is provided by the slightly lower values of J_{Pt-P} and J_{Pt-CH_3} trans to naphthyridine, as expected for a nitrogen ligand having a higher trans influence than chloride. As the temperature is reduced the methyl resonances broaden at the same rate as the naphthyridine resonances and the doublet (coupling to ^{31}P) due to CH_3 trans to naphthyridine splits into two doublets at −60 °C. The chemical shift difference cis to naphthyridine is less and the doublets are not completely resolved. The effect can be understood by considering the possible orientations of the methyl groups as rotation occurs about the Pt–P bond. If the naphthyridine



is static (e.g., always above the plane in the diagram) then the methyl groups A and B are chemically nonequivalent for all rotational positions about the Pt–P bond. However, as the naphthyridine begins to exchange its point of attachment (essentially oscillating above and below the plane) then complete averaging of rotational positions occurs.

***cis*-[PtCl(PEt$_3$)$_2$(Me-naph)][BF$_4$].** Spectra of this complex introduced no new features. Ambient temperature spectra were entirely consistent with a fluxional naphthyridine and spectra recorded in CD_3NO_2 solution were unchanged up to 90 °C. The larger coupling constants from phosphorus and platinum to the substituted ring ($J_{\alpha Pt}$ and $J_{\alpha P}$) as compared to the unsubstituted ring ($J_{\alpha' Pt}$ and $J_{\alpha' P}$) suggest that coordination via the substituted ring is slightly favored. This is expected if electron donation from the methyl group increases the basicity of the nitrogen. At −70 °C the α resonance splits as expected if two isomers are present, one having the heterocycle bound to platinum via the substituted ring and the other having it bound via the unsubstituted ring. However, there is no appreciable effect on the other resonances (except general viscosity broadening) and resolution was generally too poor for definitive conclusions. The methyl group in the naphthyridine ligand was still a single resonance at −70 °C.

***cis*-[PtCl(PEt$_3$)$_2$(phth)][BF$_4$].** ^1H NMR spectra of this complex recorded in $(CD_3)_2SO$ are shown in Figure 4. At 25 °C the $\beta\beta'\gamma\gamma'$ region shows only a broad, poorly resolved absorption but the α and α' resonances are clearly resolved, the former being slightly broader, consistent with unresolved coupling to ^{31}P and consisting of a 1:4:1 triplet due to coupling with ^{195}Pt. Clearly the molecule is static and phthalazine is bound to platinum via only one nitrogen. As the temperature is raised the α and α' resonances coalesce, finally becoming a sharp singlet indicative of a fluxional process in which the

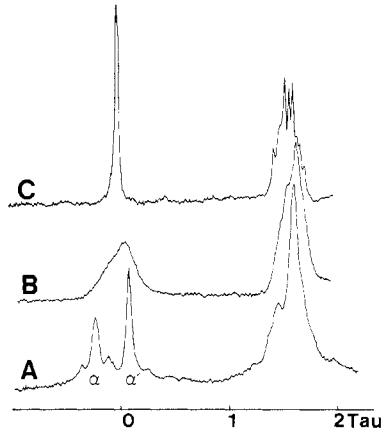


Figure 4. Aromatic region of the ^1H NMR spectrum of *cis*-$[PtCl(PEt_3)_2(phth)]BF_4$ recorded at 90 MHz in $(CD_3)_2SO$ solution: (A) +25 °C, (B) +80 °C, (C) +150 °C.

two protons are rendered chemically equivalent by rapid exchange of platinum coordination between the two nitrogen atoms. The narrow line width of the $\alpha\alpha'$ resonance at 150 °C shows that there is no residual coupling to phosphorus or platinum in the fast exchange limit. For example, sidebands corresponding to $J_{\alpha Pt}$ = 12 Hz (one-half the value at 25 °C) would have been easily visible.

***cis*-[PtCl(PEt$_3$)$_2$(pyrid)][BF$_4$].** The ^1H NMR spectrum of pyridazine has been analyzed[18] as an AA'BB' system with $J_{3,4} = J_{5,6}$ = 5.07 Hz, $J_{3,5} = J_{4,6}$ = 1.88 Hz, $J_{3,6}$ = 1.38 Hz, and $J_{4,5}$ = 8.34 Hz. At ambient temperature in either $CDCl_3$ or $(CD_3)_2SO$ the complex gave only two, broad, poorly resolved peaks of equal intensity due to the 3,6 (α,α') and 4,5 (β,β') protons, respectively. In $CDCl_3$ solution irradiation at the α position converted the β resonance to a four-line AB pattern (J = 8.03 Hz and δ = 12.86 Hz). This suggests that the β and β' positions are chemically inequivalent and the complex is static with only one nitrogen bound to platinum. In a fluxional system irradiation at α would remove the magnetic inequivalence of β and β' and a single resonance would result. This interpretation was confirmed by irradiation at β, β' which gave α and α' resonances similar to those shown in Figure 4 for the phthalazine complex, except that in the pyridazine case the chemical shift difference between α and α' is small and the upfield ^{195}Pt sideband of α is obscured by α'. In $(CD_3)_2SO$ solution irradiation at α failed to resolve the $\beta\beta'$ quartet but irradiation at β still gave clearly resolved α and α' resonances. Raising the temperature (still with irradiation at β) gave coalescence of α and α' at about 50 °C, indicative of a fluxional process similar to that in the phthalazine complex. Moreover, at 70 °C with no irradiation the $\alpha\alpha'$ and $\beta\beta'$ resonances were each poorly resolved triplets very similar to the spectrum of the free ligand and showing no evidence of residual coupling to phosphorus or platinum. Attempts to observe this fluxional behavior in $CDCl_3$ solution were not successful. Evidently the process is to some extent solvent dependent since at 60 °C (near the boiling point of $CDCl_3$) the α and α' resonances showed only slight evidence of coalescence.

***cis*-[PtCl(PEt$_3$)$_2$(py)][BF$_4$].** The ^1H NMR spectrum of pyridine is a representative of a rather complicated spin system,[19] and we have not attempted a detailed analysis of the spectrum of the complex. However, the α resonance appeared as a very broad 1:4:1 triplet and resolution was greatly improved by irradiation at the β resonance, thus permitting accurate measurement of $J_{\alpha Pt}$.

[Pt(PEt$_3$)$_2$(en)][BF$_4$]Cl. As discussed above, conductance and infrared data for this complex suggest that it contains bidentate ethylenediamine and uncoordinated chloride. The

^{31}P NMR spectrum supports this assignment, showing only a single 1:4:1 triplet (δ 137.9 ppm, J_{Pt-P} = 3076 Hz recorded in CH_3NO_2), in contrast to the triplet of AB patterns exhibited by the $[PtCl(PEt_3)_2L]^+$ cations. Thus the two phosphorus atoms are chemically equivalent. Moreover, the ^1H NMR spectrum in CD_3NO_2 has only PEt_3 resonances plus a single 1:4:1 triplet (J_{Pt-H} = 30 Hz) at τ 6.9. Most probably this triplet is due to the NH_2 protons, the fact that it is not doubled demonstrating the symmetric, bidentate character of the ligand, and the CH_2 protons of the diamine are obscured by PEt_3 resonances.

Experimental Section

Data relating to the characterization of the complexes are given in the tables and the Results section. Microanalyses were by D. L. McGillivray of this department. In general the compounds tended to decompose on heating and melting points are not an especially useful method of characterization. Conductance measurements were made on ca. 10^{-3} M solutions in nitromethane using a dip-type cell connected to a Radiometer CDM3 conductivity bridge. IR spectra were recorded from 4000 to 250 cm^{-1} with accuracy ± 3 cm^{-1} on a Beckman I.R. 20 spectrophotometer calibrated against polystyrene film and water vapor. Solid samples were examined as Nujol mulls between cesium iodide plates. ^{31}P NMR spectra were recorded at 40.486 MHz on a JEOL PFT-100 Fourier transform spectrometer using $P(OMe)_3$ as external reference, C_6D_6 as external lock, and CH_2Cl_2 as solvent (except for the ethylenediamine complex for which CH_3NO_2 was the solvent). A total of 8192 data points were used in a 10-kHz sweep, giving a resolution of 2.44 Hz and the ^{31}P parameters are thus subject to uncertainties of this magnitude. ^1H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R32 spectrometer using a variety of solvents and lock signals to optimize solubility and resolution (see Table I). Magnet ambient temperature was 35 °C.

1,8-Naphthyridine and 4-methyl-1,8-naphthyridine were prepared as previously described[20] and the other ligands were commercially available. The phenanthroline complexes were prepared as previously described[3] except that conversion of *cis*-$[PtCl(PEt_3)_2(phen)][BF_4]$ to $[PtCl(PEt_3)][BF_4]$ was achieved rapidly and almost quantitatively by addition of a few drops H_2O_2 solution to the former complex in refluxing methanol. Bipyridine complexes were synthesized in similar yields by analogous methods. *cis*-$[PtCl(PEt_3)_2(py)][BF_4]$ was prepared as previously described.[21] All other complexes were prepared in high yield by cleavage of $[Pt_2Cl_2L_4][BF_4]_2$ complexes by the appropriate ligand under mild conditions in reactions similar to the following example.

***cis*-[PtCl(PEt$_3$)$_2$(naph)][BF$_4$].** 1,8-Naphthyridine (0.106 g, 0.815 mmol) in acetone was added dropwise to a stirred solution of $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (0.450 g, 0.406 mmol) in acetone under a nitrogen atmosphere. After stirring for 15 min, diethyl ether was added to precipitate *the complex* (0.462 g, 0.747 mmol) as colorless crystals which were recrystallized from acetone by the dropwise addition of diethyl ether.

The complex for L = en was prepared from CH_2Cl_2 solution and was too insoluble for effective recrystallization.

Discussion

Solution Structure of *cis*-[PtCl(PEt$_3$)$_2$(phen)]$^+$. As described in the results section, ^1H NMR spectra of this cation show the two nitrogen-containing rings of the phenanthroline ligand to be chemically equivalent at all temperatures down to −80 °C, the lowest temperature accessible before solubility and viscosity problems prevent further observation. It is unlikely that this equivalence is purely accidental since if the solution structure is the same as the solid-state structure, then differences between the coordinated and noncoordinated rings should be clearly observed. For example, no difficulty is experienced in distinguishing the coordinated and noncoordinated rings in low-temperature spectra of *cis*-$[PtCl(PEt_3)_2(naph)]^+$, and in $[PtCl(PEt_3)(phen)]^+$ the small asymmetry introduced by the differing trans influences of chlorine and phosphorus is sufficient to produce a 0.54 ppm shift between the α and α' protons of the phenanthroline. Moreover in ^{13}C NMR spectra the α and α' carbons of the phenanthroline in $[PtCl(PEt_3)(phen)]^+$ resonate at −148.5 and −153.6 ppm downfield from Me_4Si whereas *cis*-$[PtCl(PEt_3)_2(phen)]^+$ shows a single resonance at −151.2 ppm. Given that the equivalence is not purely accidental, there are two possible explanations: (a) that the solution structure is different from the solid-state structure and consists of a trigonal bipyramid with PEt_3 and phenanthroline in the equatorial plane and Cl and PEt_3 in axial positions; (b) that the solution structure is the same as the solid-state structure but the phenanthroline is fluxional by reason of rapid exchange of its point of attachment to platinum.

Despite our failure to obtain NMR spectra corresponding to the static structure, even at −80 °C, we consider that the evidence favors the fluxional hypothesis, "b", for the following reasons.

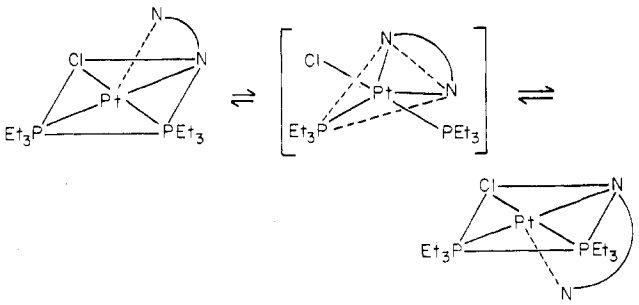
(1) There is close structural analogy with the naphthyridine complexes, whose fluxional nature can be proved by observation of low-temperature spectra corresponding to the static structure.

(2) The ^{31}P NMR spectra of the complexes, *cis*-$[PtCl(PEt_3)_2L]^+$, L = phen, bpy, naph, Me-naph, pyrid, phth, or py, are all closely similar AB patterns (with ^{195}Pt sidebands) and J_{PP} lies in the range 20–22 Hz for all cases. This is a typical value[22] for coupling between cis phosphorus atoms in a square-planar, tertiary phosphine complex. Moreover the values of J_{Pt-P} are all very similar, ranging from 3454 Hz (trans to Cl) and 3057 Hz (trans to N) for L = py, through 3557 and 3250 Hz for L = naph to 3681 and 3482 Hz for L = phen. These coupling constants depend primarily on the s character of the Pt–P bond and they are expected to decrease by ~20% on changing from square-planar (sp^2d) to trigonal-bipyramidal (sp^3d) coordination about platinum provided that the ligand trans to the phosphorus under observation does not change.[22a] Thus the observed similarity for the J_{Pt-P} values in the phenanthroline complex and in the known square-planar pyridine and naphthyridine complexes strongly suggests a square-planar coordination for the phenanthroline complex.

(3) The value of $J_{\alpha Pt}$ (i.e., coupling from Pt to the α proton in the heterocyclic ring trans to phosphorus) in $[PtCl(PEt_3)(phen)]^+$ is 22 Hz whereas in *cis*-$[PtCl(PEt_3)_2(phen)]^+$ the value is 12 Hz, exactly that expected if each heterocyclic ring in the latter complex is coordinated to platinum 50% of the time. This interpretation is supported by comparison with the range, 18–27 Hz, of $J_{\alpha Pt}$ values in the monodentate complexes, $[PtCl(PEt_3)_2L]^+$, L = phth, pyrid, or py, and with the high- and low-temperature spectra of *cis*-$[PtCl(PPh_3)_2(naph)]^+$, *cis*-$[PtCl(PMe_2Ph)_2(naph)]^+$ and *cis*-$[PtCl(PEt_3)_2(Me\text{-}naph)]^+$. In each of the last three cases the fluxional spectra show values of $J_{\alpha Pt}$ approximately half of those obtained for the static spectra.

(4) Examination of Table I shows that the $J_{\alpha P}$ values show a pattern closely similar to that discussed above for $J_{\alpha Pt}$.

Mechanism of the Fluxional Process. Examination of Table I and of the Results section shows that the NMR spectra and in particular the coupling constants for the bipyridine complexes follow a pattern exactly analogous to that analyzed above for the phenanthroline complexes and we therefore conclude that similar fluxional processes occur in *cis*-$[PtCl(PEt_3)_2(bpy)]^+$. Also, as detailed in the Results section, the naphthyridine complexes are fluxional at ambient temperature but static at −60 °C. In all of these cases (i.e., L = phen, bpy, or naph), the mechanism of the fluxional process is most likely a simple oscillatory motion of the potentially bidentate ligand via a trigonal-bipyramidal transition state. The mechanism cannot be dissociative since this would lead to a loss of $J_{\alpha Pt}$ and $J_{\alpha P}$ in the fast-exchange limit NMR spectra. It also appears that the transition state is not sufficiently long-lived to permit Berry rearrangements[23] since



these would lead to an interchange of phosphorus positions and an apparent chemical equivalence of phosphorus atoms in the ^{31}P NMR spectra, in contrast to the observed AB character of these spectra.

As detailed in the Results section, the complexes $[PtCl(PEt_3)_2L][BF_4]$, L = pyrid or phth, are also fluxional but the temperatures required for rapid motion are much higher than those where L = phen or naph. In the L = pyrid or phth examples the orientation of the nitrogen lone pairs in the ligands is unsuitable for the formation of a transition state involving simultaneous coordination of both nitrogens. It is therefore likely that a different exchange mechanism is operative, most likely a dissociative process since the high temperature limit spectra show no evidence of coupling from Pt or P to the $\alpha\alpha'$ protons.

Finally we note that the observed rates of the fluxional processes, phen ~ bpy > naph > pyrid > phth, are fully consistent with the above mechanisms and with our original hypothesis that the orientation of the lone pairs will be a major factor in determining the rates. Thus approximate coalescence temperatures for the phen, naph, pyrid, and phth cases are <−80, −30, +50, and +90 °C, respectively, corresponding to approximate free energies of activation of <40, 51, 71, and 76 kJ mol^{-1}.[24] For L = phen the transition state is an unstrained five-membered ring resulting in very rapid exchange of platinum between the two ligating nitrogens. For L = naph the process is retarded by strain in the four-membered ring transition state—accentuated by the parallel orientation of the nitrogen lone pairs, and for L = pyrid or phth a dissociative process of even higher activation requirements becomes necessary because the nitrogen lone pairs are directed away from each other.

Acknowledgment. We thank the National Research Council of Canada and the University of Victoria for research grants, Dr. A. D. Rattray for the synthesis of *cis*-$[PtCl(PEt_3)_2(Me\text{-}naph)][BF_4]$, Dr. I. Webber for the synthesis of *cis*-$[PtCl(PEt_3)_2(phth)][BF_4]$, Dr. A. Pidcock for the use of ^{31}P NMR facilities at the University of Sussex, and Mrs. M. Rayner Canham for the synthesis of most of the other complexes and for technical assistance during part of this work.

Registry No. $[PtCl(PEt_3)(phen)][BF_4]$, 41586-22-5; *cis*-$[PtCl(PEt_3)_2(phen)][BF_4]$, 53184-01-3; $[PtCl(PEt_3)(bpy)][BF_4]$, 63548-48-1; *cis*-$[PtCl(PEt_3)_2(bpy)][BF_4]$, 63548-50-5; *cis*-$[PtCl(PEt_3)_2(naph)][BF_4]$, 63548-52-7; *cis*-$[PtCl(PPh_3)_2(naph)][BF_4]$, 63548-54-9; *cis*-$[PtCl(PMe_2Ph)_2(naph)][BF_4]$, 63548-56-1; *cis*-$[PtCl(PEt_3)_2(Me\text{-}naph)][BF_4]$, 63548-58-3; *cis*-$[PtCl(PEt_3)_2(pyrid)][BF_4]$, 63588-58-9; *cis*-$[PtCl(PEt_3)_2(phth)][BF_4]$, 63548-60-7; *cis*-$[PtCl(PEt_3)_2(py)][BF_4]$, 34745-07-8; *cis*-$[PtCl(PEt_3)_2(naph)]ClO_4$, 63548-61-8; $[Pt(PEt_3)_2(en)][BF_4]Cl$, 63548-63-0; $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$, 19394-82-2.

Supplementary Material Available: Figures 5–7 showing the ^{31}P NMR spectrum of *cis*-$[PtCl(PEt_3)_2(naph)]ClO_4$ and ^1H NMR spectra of *cis*-$[PtCl(PEt_3)_n(phen)]BF_4$, n = 1 or 2 (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) G. W. Bushnell, K. R. Dixon, and M. A. Khan, *Can. J. Chem.*, **52**, 1367 (1974).
(2) We recognize that in a structure such as that shown there may be a small bonding interaction between the metal and the more distant nitrogen atom. The term "noncoordinated" is used throughout the paper as a convenient piece of nomenclature and is not intended to imply a complete absence of interaction with the metal.
(3) K. R. Dixon and A. D. Rattray, *Can. J. Chem.*, **51**, 618 (1973).
(4) W. T. Robinson and E. Sim, *J. Chem. Soc., Dalton Trans.*, 726 (1975).
(5) G. W. Bushnell and M. A. Khan, unpublished results.
(6) D. G. Hendricker and R. J. Foster, *Inorg. Chem.*, **12**, 349 (1973), and references therein; J. R. Wagner and D. G. Hendricker, *J. Inorg. Nucl. Chem.*, **37**, 1375 (1975), and references therein.
(7) (a) J. C. Dewan, D. L. Kepert, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 490 (1975); (b) P. Singh, A. Clearfield, and I. Bernal, *J. Coord. Chem.*, **1**, 29 (1971).
(8) R. C. Elder, J. Halpen, and J. S. Pond, *J. Am. Chem. Soc.*, **89**, 6877 (1967).
(9) J. J. Porter, J. L. Murray, and K. B. Takvorian, *J. Heterocycl. Chem.*, **10**, 43 (1973); P. Spacu and D. Camboli, *Chem. Abstr.*, **66**, 7964*w* (1967).
(10) J. R. Ferraro, J. Zipper, and W. Wozniak, *Appl. Spectrosc.*, **23**, 160 (1969); J. R. Ferraro, W. Wozniak, and G. Roch, *Ric. Sci.*, **38**, 433 (1968).
(11) K. R. Dixon, K. C. Moss, and M. A. R. Smith, *Can. J. Chem.*, **52**, 692 (1974), and references therein.
(12) Microanalytical figures were supplied for perusal by the referees.
(13) W. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(14) This experiment was carried out for all complexes except those having L = bpy, pyrid, phth, py, or en.
(15) T. W. Dingle and K. R. Dixon, *Inorg. Chem.*, **13**, 846 (1974).
(16) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
(17) K. R. Dixon, M. Fakley, and A. Pidcock, *Can. J. Chem.*, **54**, 2733 (1976).
(18) V. M. S. Gill and A. J. L. Pinto, *Mol. Phys.*, **16**, 623 (1969); **19**, 573 (1970).
(19) W. G. Schneider, H. J. Bernstein, and J. A. Pople, *Can. J. Chem.*, **35**, 1487 (1957).
(20) W. W. Pandler and T. J. Kress, *J. Org. Chem.*, **32**, 832 (1967).
(21) K. R. Dixon and D. J. Hawke, *Can. J. Chem.*, **49**, 3252 (1971).
(22) (a) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, **2**, 345 (1969); (b) M. A. Cairns, K. R. Dixon, and J. J. McFarland, *J. Chem. Soc., Dalton Trans.*, 1159 (1975); T. W. Dingle and K. R. Dixon, *Inorg. Chem.*, **13**, 846 (1974).
(23) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
(24) Derived from the equation $\Delta G^{\ddagger} = 2.303RT_c(10.319 - \log k' + \log T_c)$ where T_c = coalescence temperature and $k' = \pi\Delta\nu/2^{1/2}$ (I. C. Calder and P. J. Garratt, *J. Chem. Soc. B*, 660 (1967)). $\Delta\nu$ is the frequency separation of the coalescing peaks and the equation is strictly valid only for coalescence of two singlets. Consequently the present results should be used only as an approximate indication of $\Delta G^{\ddagger}$.