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Platinum(II) Complexes of (Cyanoethyl)phosphines

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A series of platinum(II) complexes of the type L_2PtX_2 ($L = Ph_nP(CH_2CH_2CN)_{3-n}$; $n = 0$–2; X = Cl, Br, I) have been prepared and characterized by elemental analyses, physical properties, conductance measurements, infrared spectroscopy, and $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectroscopy. All complexes are nonelectrolytes and possess geometries that are dictated by the steric bulk of the phosphines and halides. The complex $[P(CH_2CH_2CN)_3]_2PtCl_2$ undergoes reversible cis–trans geometrical isomerization in dimethyl sulfoxide solution, which is also catalyzed by $P(CH_2CH_2CN)_3$. Equilibrium thermodynamics for this isomerization demonstrate that the cis isomer is thermodynamically more stable than the trans isomer. The complexes of $PhP(CH_2CH_2CN)_2$ all react with $PhP(CH_2CH_2CN)_2$ in dimethyl sulfoxide solution to give broadened ^{31}P NMR resonances, showing that the equilibrium $L_2PtX_2 + L \rightleftharpoons L_3PtX_2$ occurs at an intermediate rate on the NMR time scale. The complexes with $L = Ph_2PCH_2CH_2CN$ react with L in chloroform to produce equilibrium mixtures of L_3PtX_2 and L_2PtX_2. The relationship of these observations to the relative thermodynamic stabilities of *cis*-L_2PtX_2, *trans*-L_2PtX_2, and L_3PtX_2 is discussed.

Introduction

Many studies have examined cis–trans geometrical isomerizations of square-planar d^8 metal complexes.[1] Thermal isomerization of platinum(II) phosphine complexes is well-known.[2] Catalysis of this geometrical isomerization by small amounts of added phosphine has also been well studied.[3] Studies of (2-cyanoethyl)phosphine ligands have focused on their basicity,[4–6] π-acidity,[7,8] or ability to form polymeric complexes[9–13] by simultaneous phosphorus and nitrile coordination. In order to further study the steric and electronic nature of these ligands, the platinum(II) complexes $Pt[Ph_nP(CH_2CH_2CN)_{3-n}]_2X_2$ ($n = 0$–2; X = Cl, Br, I) have been prepared and characterized. In addition, phosphine catalysis of geometric isomerization was investigated.

Experimental Section

(A) Reagents and Physical Measurements. All chemicals were reagent grade and were used as received or synthesized as described below. All solvents were dried, when necessary, by standard procedures and stored over Linde 4-Å molecular sieves. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer as Nujol mulls between CsBr plates. Far-infrared spectra were recorded on a Polytec FIR 30 FT interferometer as polyethylene pellets. The ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra were recorded at 99.54, 25.00, 40.26, and 21.30 MHz, respectively, on a JEOL FX-100 spectrometer in the FT mode. Proton and carbon-13 chemical shifts are downfield relative to internal Me_4Si, while the phosphorus-31 chemical shifts are relative to external 85% H_3PO_4. A positive value of $\delta(^{31}P)$ indicates a downfield position relative to that of the reference. Platinum-195 chemical shifts are referenced to the standard frequency[14] 21.4 MHz relative to the proton resonance of Me_4Si at exactly 100 MHz. NMR solvents were spectroscopic grade and were used as received from the manufacturer. Preparation of samples for NMR analyses has been described.[15] Conductivity studies were performed ass described previously.[16]

Equilibrium constants for the cis–trans isomerizations and for the equilibria $L_2PtX_2 + L \rightleftharpoons L_3PtX_2$ were obtained at various temperatures by integrating the areas under the appropriate $^{31}P\{^1H\}$ NMR signals. Plots of $\ln K_{eq}$ vs. T^{-1} were treated by least-squares analyses to obtain ΔH_{eq} and ΔS_{eq}.

(B) Syntheses. Tris(2-cyanoethyl)phosphine (CEP) and phenylbis-(2-cyanoethyl)phosphine) (PhCEP) were obtained from Strem Chemicals and were used without further purification. Diphenyl(2-cyanoethyl)phosphine (Ph_2CEP) was prepared by literature methods.[17] The platinum chloride complexes of all three ligands were prepared by reacting 2 equiv of the appropriate phosphine with 1 equiv of dichlorobis(benzonitrile)platinum(II) in chloroform. The complexes immediately precipitated in nearly quantitative yield and were separated by filtration, washed with ethanol, and dried under vacuum. The bromide and iodide complexes were prepared by metathesis of the chloride complexes in dimethyl sulfoxide solution with 4 equiv of sodium bromide or iodide at ambient temperature for several days. Addition of water to the dimethyl sulfoxide solutions resulted in precipitation of the complexes, which were isolated by filtration, washed with ethanol and anhydrous diethyl ether, and vacuum-dried. In each case the yields were nearly quantitative. The physical properties and elemental analyses (Galbraith Laboratories, Knoxville, TN 37921) for the complexes are given in Table II, while the data for the ligands are given in Table I.

Results and Discussion

Four-Coordinate Complexes. (Cyanoethyl)phosphine ligands have been shown to be sterically flexible ligands that have moderately low basicity but are good π-acceptors.[18,19] Because sterically undemanding ligands that form strong metal–phosphorus bonds have been thought to promote pentacoordination,[20] these ligands provide an opportunity to explore the limits of these two conditions.

Complexes of primary and secondary (cyanoethyl)phosphines of the type L_3PtX_2 have been reported,[21,22] but they have been thought to be ionic complexes $[L_3PtCl]^+Cl^-$ rather than pentacoordinate species. In this study, tertiary (cyanoethyl)phosphines of the type $Ph_nP(CH_2CH_2CN)_{3-n}$ ($n = 0$–2) have been used as ligands.

Despite the low basicity of these (cyanoethyl)phosphines toward a proton[23] (Table I), they readily form stable typical square-planar

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Table I. IR and Physical Data for Free Ligands

L	mp[a]	color	$\delta(^{31}P)$[b]	pK_a	cone angle[c]	ν_{CN}[d]	other vib[d] (700–200 cm^{-1})
$P(CH_2CH_2CN)_3$ (CEP)	97–98	white	−25.5	1.36[e] (1.44)[f]	132	2240	700, 655, 572, 495, 360, 330, 270
$C_6H_5P(CH_2CH_2CN)_2$ (PhCEP)	72–73	white	−23.8	3.20[e] (1.98)[f]	136	2235, 2255	700, 675, 620, 520, 492, 427, 380, 360, 300
$(C_6H_5)_2PCH_2CH_2CN$ (Ph_2CEP)	64	pale yellow	−17.6	(2.51)[f]	141	2240	695, 635, 615, 545, 510, 480, 472, 400, 370, 320

[a] In °C. [b] Relative to 85% H_3PO_4. [c] Reference 25. [d] In cm^{-1}. [e] Reference 5. [f] Calculated from equations given in ref 6.

Table II. Physical and Infrared Data for L_2PtX_2 Complexes

				analysis[a]								
				% C		% H						
L	X	color	mp[b]	calcd	found	calcd	found	ν_{CN}[f]	ν_{PtP}[f]	ν_{PtX}[f]	geom[g]	other vib[f] (700–200 cm^{-1})
CEP	Cl	yellow	174–176	33.14	33.01	3.71	3.82	2240	283, 365	305, 273	cis	660, 525, 512, 505, 330
									408	345	trans	
	Br	yellow	192–194	30.51[c]	30.40	3.81[c]	3.42	2240	408	308	trans	700, 670, 565, 520, 500, 435, 385
	I	yellow	206–208	25.88	25.74	2.90	2.88	2245	402	170	trans	700, 670, 570, 520, 500, 440, 390, 370, 290
PhCEP	Cl	white	236–238	41.27	41.32	3.75	3.79	2250	390, no[g]	314, 288	cis	695, 650, 615, 580, 565, 530, 520, 491, 475, 460, 395
	Br	white	182–184	37.44[c]	37.17	3.72[c]	3.66	2250	390, no	300, 266	cis	645, 580, 565, 535, 517, 492, 480, 462, 390
	I	yellow	200–204	32.70	32.93	2.97	3.03	2250	317	197	trans	650, 620, 560, 515, 492, 465, 385, 295
Ph_2CEP	Cl	yellow	175–176	46.71[d]	46.82	4.02[d]	3.87	2235	485, 422	315, 292	cis	690, 615, 540, 522, 500, 470, 455, 440, 380, 335
	Br	yellow	192–196	43.48[e]	43.88	3.62[e]	3.82	2230	472, 447	no, 298	cis	691, 642, 615, 524, 510, 485, 345
	I	yellow	133–135	38.85	39.08	3.04	3.14	2230	445	no	trans	693, 640, 615, 550, 522, 507, 483, 470, 340

[a] In each case, the presence or absence of solvent has been verified by ^1H NMR spectroscopy. [b] In °C. [c] Calculated for $L_2PtX_2\cdot EtOH$. [d] Calculated for $L_2PtX_2\cdot 1.5H_2O$. [e] Calculated for $L_2PtX_2\cdot 0.5EtOH$. [f] in cm^{-1}. [g] As determined by ^{31}P NMR spectroscopy. [h] no = not observed.

L_2PtX_2 complexes in which coordination is through phosphorus. The characteristic IR nitrile band ν_{CN} (Table II) occurs at or near the values observed for the free ligands, indicating the absence of coordination of the nitrile group.[24]

The phosphorus chemical shifts for the free ligands (Table I) correlate with their basicities moving upfield with an increase in the number of cyanoethyl groups and a decrease in basicity ($\delta(^{31}P) = 7.37pK_a - 36.87$; $r^2 = 0.90$). The steric size of these ligands, as measured by the Tolman cone angle,[25] increases with an increase in the number of phenyl groups. The π-acceptor abilities[7] of these ligands should follow the order CEP > PhCEP > Ph_2CEP. A measure of the donor ability toward platinum(II), the coordination chemical shift ($\Delta\delta(^{31}P)$) indicates (Table II) that the donor ability decreases in the order CEP > Ph_2CEP > PhCEP. This suggests that both steric effects and π-acceptor properties of the ligands are important.

Of the nine complexes herein reported, only $(CEP)_2PtCl_2$ has been previously described.[9] The infrared bands (Table II) were assigned with the aid of earlier work[26-30] and by comparison of the spectra of the ligands and complexes. The geometries of the complexes in solution were determined by ^{31}P NMR spectroscopy, and it was assumed that for these normally inert platinum(II) complexes the solution and solid-state geometries are the same in most cases (vide infra). As is typical[31,32] for $(R_3P)_2PtX_2$ complexes, the magnitude of the platinum–phosphorus coupling constant is an indication of geometry. Cis complexes typically have $^1J_{PtP} > 3000$ Hz, while trans complexes have $^1J_{PtP} < 2400$ Hz. With the exception of $(CEP)_2PtCl_2$, all the complexes form exclusively one isomer in solution. This eliminates the ambiguities associated with assigning the geometry solely on the basis of infrared spectroscopy. For example, Walton and Whyman[9] as-

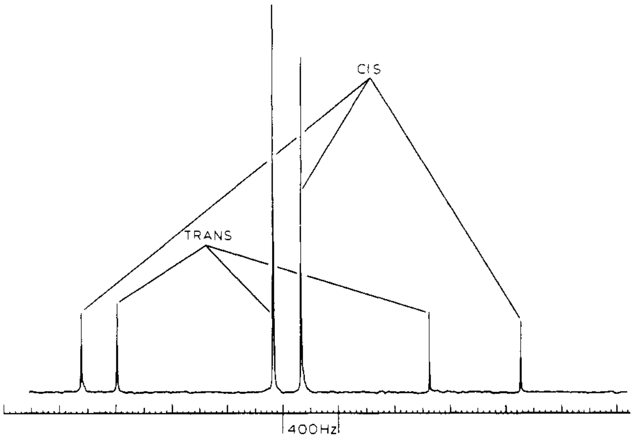

Figure 1. 40.26-MHz $^{31}P\{^1H\}$ NMR spectrum of $(CEP)_2PtCl_2$ in Me_2SO at 298 K.

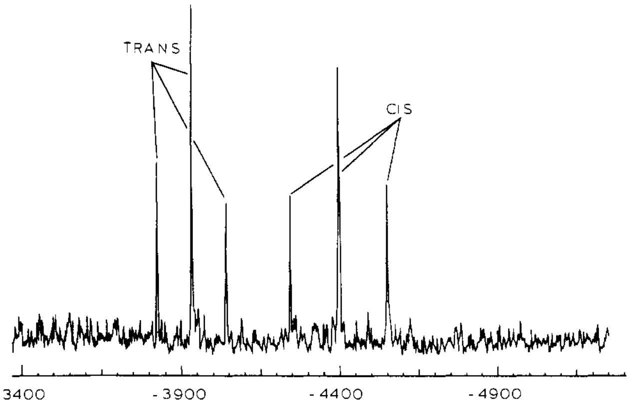

Figure 2. 21.30-MHz $^{195}Pt\{^1H\}$ NMR spectrum of $(CEP)_2PtCl_2$ in Me_2SO at 298 K.

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Table III. $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR Spectral Data for L_2PtX_2

L	X	$\delta(^{31}P)^a$	$\Delta\delta(^{31}P)^b$	$\delta(^{195}Pt)^c$	$^1J_{PtP}{}^d$	geom
CEP	Cl	4.84	30.34	−4408	3489	cis
	Cl	10.47	35.97	−3918	2476	trans
	Br	6.30	31.80	−4494	2407	trans
	I	−0.42	25.08	−5323	2344	trans
PhCEP	Cl	0.30	24.10	−4368	3560	cis
	Br	0.06	23.86	−4866	3521	cis
	I	−0.48	23.32	−5609	2395	trans
Ph₂CEP	Cl	7.51	25.11	−4388	3662	cis
	Br	7.81	25.91		3574	cis
	I	1.75	19.35	−5664	2451	trans

[a] Relative to 85% H_3PO_4. [b] $\Delta\delta(^{31}P) = \delta(^{31}P)$ complex − $\delta(^{31}P)$ ligand. [c] Relative to H_2PtCl_6 at 21.4 MHz. [d] In hertz.

signed $(CEP)_2PtCl_2$ the trans geometry on the basis of their observation of only one ν_{PtCl} vibration in its low-frequency infrared spectrum. We have synthesized this complex by another route, and although its infrared spectrum is identical with that reported[9] by Walton and Whyman, its ^{31}P NMR spectrum shows two resonances with associated satellites (Figure 1). One resonance has a $^1J_{PtP}$ of 3489 Hz and the other a $^1J_{PtP}$ of 2476 Hz, indicating a mixture of cis and trans isomers. In its ^{195}Pt NMR spectrum (Figure 2) two triplets are observed, further indicating two species, each containing two equivalent phosphine ligands. Further discussion of the significance of this data appears later in this paper.

Several observations appear noteworthy in the ^{31}P and ^{195}Pt NMR data (Table III). Although there is little variation in the ^{31}P chemical shifts of the complexes, the coordination chemical shifts show that the donor ability of these ligands toward platinum(II) does not parallel their donor ability toward a proton (pK_a's; vide supra). The donor ability order CEP > Ph₂CEP > PhCEP as determined from $\Delta\delta(^{31}P)$ does not correlate with the magnitude of the platinum–phosphorus coupling constants, $^1J_{PtP}$, which should also be a measure of the donor ability. The coupling constants suggest the order Ph₂CEP > PhCEP > CEP, but it should be recognized that these coupling constants are a function of s-electron density in the bond[33] and as such are essentially insensitive to π-bonding. This further suggests that π-bonding is important for CEP, as it shows the largest coordination chemical shift and smallest platinum–phosphorus coupling constant. Since the σ- and π-bonding are synergistic, this is the result that might be anticipated for significant π-acceptance.

The ^{31}P coordination chemical shift is influenced by the halide increasing in the order Cl > Br > I and correlates linearly with the platinum–phosphorus coupling constant within each ligand group. For the trans CEP complexes the correlation equation is $^1J_{PtP} = 11.84(\Delta\delta(^{31}P)) + 2042$ ($r^2 = 0.99$). There are only two data points for the other two ligands. This decrease in $^1J_{PtP}$ with an increase in the mass of the halide in $(R_3P)_2PtX_2$ complexes has previously been noted.[20] The platinum-195 chemical shifts also correlate with $\Delta\delta(^{31}P)$ and $^1J_{PtP}$. Generally, as $\delta(^{195}Pt)$ moves upfield, both $\Delta\delta(^{31}P)$ and $^1J_{PtP}$ decrease for constant geometry. The upfield shift of $\delta(^{195}Pt)$ with increasing mass of the halide bound to platinum appears to be a general phenomenon.[14,34]

The $^{13}C\{^1H\}$ NMR data for the ligands and their complexes are presented in Table IV. As has been noted for platinum alkylphosphine complexes,[35,36] the α- and β-carbon resonances move upfield upon coordination. This effect attenuates with increasing distance from phosphorus along an alkyl chain. As a result, the cyano carbon resonance varies by less than 1 ppm throughout this series of complexes, which is also consistent with the absence of nitrile coordination. The line shapes of the phenyl carbon resonances are indicative[37] of geometry, but those of the alkyl carbon resonances are not. However, for $(CEP)_2PtCl_2$ two sets of resonances were observed for each carbon in concert with the ^{31}P and ^{195}Pt NMR data, indicative of the presence of two isomers in solution. For the $(PhCEP)_2PtCl_2$ complex, the CN carbon resonance was a five-line multiplet, allowing the determination[37] of $^2J_{PP} = 17.1$ Hz, which is a value typical of *cis*-$(R_3P)_2PtX_2$ complexes.[20]

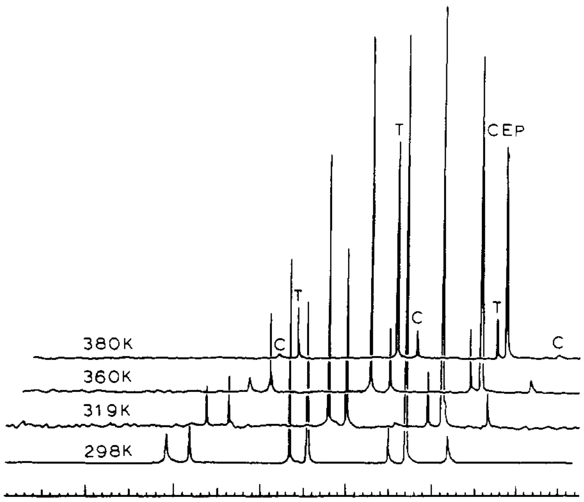

Figure 3. Temperature dependence of the 40.26-MHz $^{31}P\{^1H\}$ NMR spectrum of $(CEP)_2PtCl_2$ + CEP in Me₂SO. Least-squares analysis of a plot of ln K_{eq} vs. T^{-1} yields $\Delta H_{eq} = 4.0 \pm 0.5$ kcal mol⁻¹, $\Delta S_{eq} = 12.7 \pm 1$ eu, and $\Delta G_{302} = -0.3 \pm 0.5$ kcal mol⁻¹ for *cis*-$L_2PtCl_2 \rightleftharpoons$ *trans*-L_2PtCl_2.

Proton NMR data are not reported for these complexes because at 100 MHz only one broad resonance, which overlaps with the residual Me₂SO-d_5 solvent resonance, is observed for the methylene protons.

Catalysis of Geometrical Isomerization by Added Phosphine. The tris(2-cyanoethyl)phosphine complexes and phenylbis(2-cyanoethyl)phosphine complexes are insoluble or only very slightly soluble in typical organic solvents. The only solvent suitable for spectroscopy of low-abundance or low-susceptibility nuclei proved to be Me₂SO-d_6. This limited our studies, since low-temperature observation was prohibited by the high freezing point of Me₂SO. Complexes of diphenyl(2-cyanoethyl)phosphine proved to be sufficiently soluble in CDCl₃ to allow for NMR studies in this solvent.

As has been noted, only dichlorobis(tris(2-cyanoethyl)phosphine)platinum(II) is present in solution as a mixture of cis and trans isomers. The ratio of trans to cis isomers is sample-dependent, as the isolated solid material is a mixture of isomers whose relative amounts depend upon the time taken in the preparation of the complex and the rate at which equilibrium is attained. The amount of the cis isomer increases with an increase in reaction time, suggesting that the trans isomer is the kinetic product.

Addition of excess phosphine to solutions of $Pt(CEP)_2Cl_2$ results in a rapid shift of the trans to cis ratio to equilibrium. This equilibrium is temperature-dependent, as shown in Figure 3. A plot of ln K_{eq}(trans/cis) vs. inverse temperature allows calculation of the thermodynamic parameters for the isomerization. The cis isomer is seen to be the thermodynamically more stable isomer. The increase in entropy upon isomerization from cis to trans is due to formation of the less highly solvated trans isomer, which has no dipole moment.[37] As might be expected, this reaction is temperature-dependent in the absence of added phosphine; however, it now becomes extremely slow, taking days to reach the same equilibrium position as in the presence of excess ligand as a catalyst. The bromide and iodide complexes of tris(2-cyanoethyl)phosphine are formed exclusively as the trans isomers, and heating solutions of them for several hours in Me₂SO at 373 K

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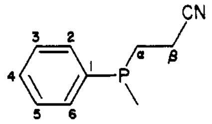
Table IV. Carbon-13 NMR Data for $(Ph_{3-n}(CEP)_n)_2PtX_2$ (n = 1–3) and Free Ligands



		$\delta(^{13}C)$, $\lvert {}^nJ_{PC} + {}^{n+2}J_{PC}\rvert$, mult[a]						
L	X	C_α	C_β	CN	C_1	$C_{2,6}$	$C_{3,5}$	C_4
CEP	free	20.54, 15.8, d	13.14, 19.5, d	120.78, 11.0, d				
	Cl[b]	16.32, no, m	11.44, no, m	119.40, no, m				
		18.96, no, m	12.28, no, m	119.74, no, m				
	Br	17.96, 34.2, d	12.06, 21.9, t	120.01, 15.8, m				
	I	21.86, no, m	12.52, no, m	119.81, no, m				
PhCEP	free	24.20, 15.9, d	14.40, 22.1, d	118.9, 12.2, d	133.68, no, m	132.59, 20.7, d	129.81, 40.38, d	129.10, no, s
	Cl	19.60, 39.1, m	12.23, 29.3, t	119.01[c]	125.95, 63.4, d	131.1, 9.8, t	128.96, 9.8, t	131.9, 0, s
	Br	21.02, 39.1, m	12.74, no, m	119.72, no, m	no	131.37, no, m	129.47, no, m	132.24, no, s
	I	23.42, 35.4, m	12.69, no, m	119.43, no, m	129.56, 0, s	132.88, 12.2, t	128.54, 13.0, t	131.32, 0, s
Ph_2CEP	free	23.93, 14.7, d	13.86, 23.2, d	119.4, 0, s	136.24, 13.6, d	132.42, 19.5, d	128.74, 15.8, d	128.7, 0, s
	Cl	23.76, no, m	13.47, no, m	119.23, no, m	126.2, 0, s	132.93, 9.8, m	128.54, 9.9, t	131.41, 0, s
	I	28.36, 29.0, m	13.50, 0, s	118.32, no, m	129.15, 0, s	133.78, 10.9, t	128.46, 10.9, t	131.24, 0, s

[a] J is in hertz; no = not observable or not assignable; s = singlet; d = doublet; t = triplet; m = multiplet. Habib et al. (Habib, M.; Trujillo, H.; Alexander, A.; Storhoff, B. N. *Inorg. Chem.* **1985**, *24*, 2344) report data for Ph_2CEP and its L_2PdX_2 complexes where X = Cl or Br. [b] Cis isomer data on top; trans on bottom. [c] Five-line multiplet analyzed and simulated to yield ${}^3J_{PC}$ = 17.3 Hz, ${}^5J_{PC}$ = 0.9 Hz, and ${}^2J_{PP}$ = 17.1 Hz.

Table V. $^{31}P\{^1H\}$ NMR Spectral Data for $[Ph_2CEP]_3PtX_3$ at 223 K

X	$\delta(^{31}P)$[a]	$^2J_{PP}$	$^1J_{PtP}$	$\delta(^{31}P)$[a]	$^1J_{PtP}$
Cl	8.93, d	22	2526	−4.30, t	3960
Br	8.69, d	22	2220	−5.39, t	3954

[a] d = doublet; t = triplet.

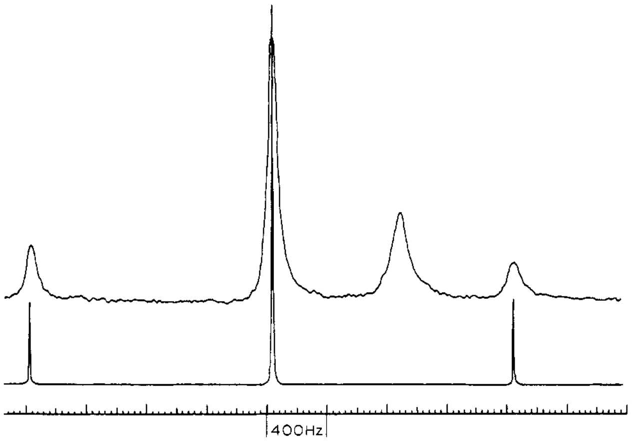


Figure 4. 40.26-MHz $^{31}P\{^1H\}$ NMR spectra of $(PhCEP)_2PtCl_2$ in Me_2SO at 298 K (lower) and a 1:1 molar ratio of $(PhCEP)_2PtCl_2$ and PhCEP in Me_2SO at 298 K (upper).

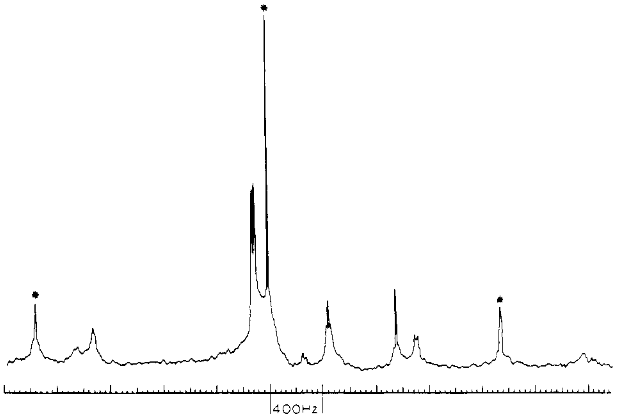


Figure 5. 40.26-MHz $^{31}P\{^1H\}$ NMR spectrum of a 1:1 molar ratio of $(PhCEP)_2PtCl_2$ and PhCEP in $CDCl_3$ at 223 K. Resonances marked with an asterisk are due to $(PhCEP)_2PtCl_2$.

Table VI. Conductivity Data for Solutions of (Cyanoethyl)phosphine Platinum(II) Complexes with Added Ligand (1:1 Molar Ratio)

$$L_2PtX_2 + L \rightleftharpoons L_3PtX_2$$

L	X	Λ_M,[a] Ω^{-1} cm^2 mol^{-1}	L	X	Λ_M,[a] Ω^{-1} cm^2 mol^{-1}
CEP	Cl	2.3	Ph_2CEP	Cl	3.1
	Br	2.4		Br	2.8
	I	2.5		I	3.7
PhCEP	Cl	2.6	$[Ph_4P]NO_3$[b]		80.4
	Br	2.8	$[Et_4N][Ph_3PNiBr_3]$[c]		75.7
	I	2.9			

[a] All solutions are 1×10^{-3} M in nitromethane. [b] Ugo, R.; et al. *J. Chem. Soc. A* **1966**, 1185. [c] Cotton, F. A.; et al. *J. Am. Chem. Soc.* **1961**, *83*, 344.

showed no evidence of formation of the cis isomer by ^{31}P NMR spectroscopy. Thus, the heavier halides stabilize the trans isomer.

Addition of excess phosphine to solutions of all three platinum complexes of phenylbis(2-cyanoethyl)phosphine results in ^{31}P NMR spectra exhibiting broad resonances due to intermediate exchange at 303 K, as exemplified in Figure 4. As low-temperature studies were impossible, no further experiments on these complexes were attempted.

Solutions of dihalobis(diphenyl(2-cyanoethyl)phosphine)platinum(II) in $CHCl_3$ that contain excess phosphine have ^{31}P NMR spectra that display resonances resulting from the four-coordinate complex and free ligand, X = Cl or I, or broad resonances, X = Br, due to intermediate exchange. Cooling these solutions to 233 K results in several distinct changes.

For X = Cl or Br, several new resonances appear at low temperature. A doublet downfield of the resonance for the four-coordinate complex and an upfield triplet in the ratio of 2:1 with their associated platinum satellites are observed (Figure 5, Table V). This A_2X spin system is consistent with that observed for a variety of pentacoordinate species[20] as well as with the four-coordinate ionic $[L_3PtX]X$ complex. The magnitudes of the platinum–phosphorus coupling constants tell us that the triplet arises from a unique phosphine trans to a halide while the multiplicity and phosphorus–phosphorus coupling constant place it cis to two equivalent phosphines. Warming these solutions to 233 K causes all the resonances to broaden. For X = I, the $^{31}P\{^1H\}$ NMR spectrum showed resonances due only to $(Ph_2CEP)_2PtI_2$ and Ph_2CEP at 223 K. The molar conductivities of these complexes were measured in nitromethane and are listed in Table VI. All the complexes are nonelectrolytes in this solvent, suggesting that ionic species are not formed in solution. If ionic species are not formed in nitromethane, a polar solvent, it is also unlikely that they would be formed in either Me_2SO or $CHCl_3$.

The equilibrium constants for the formation of the pentacoordinate species are 0.83 for the chloride complex and 0.69 for the bromide complex. These values are lower than those found for the phenyldivinylphosphine[38] or 1-phenyl-3,4-dimethylphosphole complexes.[20] However, the values for the diphenyl(2-cyanoethyl)phosphine complexes are not particularly reliable since, due to their low solubility, precipitate was forming at low temperature during the NMR data acquisition.

There is a definite geometric aspect to ligand-exchange reactions of platinum phosphine complexes. For all the complexes studied herein, as well as other complexes previously studied,[20] if the trans isomer is thermodynamically more stable than the cis isomer, then the complex does not form pentacoordinate species with added ligand or isomerize to the cis isomer at elevated temperatures. If, as in the case of $(CEP)_2PtCl_2$, the cis isomer is only slightly thermodynamically more stable, then at higher temperatures the increase in entropy is sufficient to favor the trans isomer. However, if the trans isomer is slightly thermodynamically more stable than the cis isomer, then an increase in the entropy contribution to the free energy renders the isomerization to the cis isomer even less favorable.

The formation of pentacoordinate species also has a geometrical aspect. Both the dichlorotris(diphenyl(2-cyanoethyl)phosphine)platinum(II) and dibromotris(diphenyl(2-cyanoethyl)phosphine)platinum(II) complexes, herein shown to be pentacoordinate, when rewarmed to room temperature, re-form the respective cis isomer with no evidence of the trans isomer.

Thus, when the pentacoordinate species is sufficiently stable to be observed, only an equilibrium between *cis*-L_2PtX_2 and L_3PtX_2 is observed. In contrast, when *cis*- and *trans*-L_2PtX_2 have similar thermodynamic stabilities, cis–trans isomerization is observed and the pentacoordinate species become a transition state for the geometrical isomerization, and L_3PtX_2 is not spectroscopically observable. Combining the results of all the studies to date concerning L_3PtX_2 pentacoordinate platinum complexes suggests that ligand steric effects are dominant over electronic effects in stabilizing pentacoordinate complexes. Thus, when the neutral ligand L is sterically small, *cis*-L_2PtX_2 is uniformly thermodynamically more stable than the trans complexes. In this case, upon addition of excess L to a solution of *cis*-L_2PtX_2, the pentacoordinate L_3PtX_2 is detectable at low temperature. If the neutral ligand is slightly larger, then *cis*-L_2PtX_2 and *trans*-L_2PtX_2 have similar thermodynamic stabilities, and the reversible cis to trans geometrical isomerization is catalyzed by L, but no L_3PtX_2 pentacoordinate complexes may be spectroscopically observed. When L is still larger, the *trans*-L_2PtX_2 complexes increase in thermodynamic stability and the *cis*-L_2PtX_2 complex may be kinetically trapped by virtue of its synthesis. Then excess L catalyzes the unidirectional cis–trans isomerization, and again no pentacoordinate L_3PtX_2 complexes can be detected.

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Registry No. *cis*-$(CEP)_2PtCl_2$, 100838-88-8; *trans*-$(CEP)_2PtCl_2$, 20699-88-1; *trans*-$(CEP)_2PtBr_2$, 101166-31-8; *trans*-$(CEP)_2PtI_2$, 101166-32-9; *cis*-$(PhCEP)_2PtCl_2$, 101166-33-0; *cis*-$(PhCEP)_2PtBr_2$, 101166-34-1; *trans*-$(PhCEP)_2PtI_2$, 101166-35-2; *cis*-$(Ph_2CEP)_2PtCl_2$, 101166-36-3; *cis*-$(Ph_2CEP)_2PtBr$, 101166-37-4; *trans*-$(Ph_2CEP)_2PtI_2$, 101166-38-5; $[Ph_2CEP]_3PtCl_2$, 101166-39-6; $[Ph_2CEP]_3PtBr_2$, 101166-40-9; dichlorobis(benzonitrile)platinum(II), 14873-63-3.

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Kinetics of Aquation of Potentially Strained Chromium(III) Complexes Containing Tetradentate Macrocyclic Ligands

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The rate constants for the hydrolysis of *cis*- and *trans*-$\{CrLCl_2]^+$ where L is cyclen (I) or isocyclam (III) have been determined in 0.1 M acid solution and have been compared with similar chromium(III) complexes containing other tetradentate ligands. The rate constants for the first aquation reaction have the following order (25 °C): *cis*-cyclen (7.6×10^{-2} s^{-1}) > *cis*-isocyclam (8.6×10^{-4} s^{-1}) > *cis*-cyclam (2.5×10^{-5} s^{-1})[4] and *trans*-isocyclam (5 s^{-1}) > *trans*-cyclam (2×10^{-8} s^{-1}).[4] The ratio of the rate constants for the aquation of *cis*-$[Cr(cyclen)Cl_2]Cl{\cdot}H_2O$ to *cis*-$\{Cr(cyclam)Cl_2]Cl$ is 3040 to 1, while the ratio of rate constants for *cis*-$\{Cr(isocyclam)Cl_2]Cl$ to *cis*-$[Cr(cyclam)Cl_2]Cl$ is 34.4 to 1. However, the ratio of rate constants for *trans*-$\{Cr(isocyclam)Cl_2]Cl$ to *trans*-$[Cr(cyclam)Cl_2]Cl$ is approximately 4×10^7 to 1. The relative rates of reactions have been interpreted in terms of the bond strain imposed by the macrocycles and steric factors.

Introduction

Macrocyclic ligands bonded to first-row transition-metal ions are usually kinetically inert with respect to dissociation of the macrocyclic ligand from the metal ion.[1] As a result, six-coordinate chromium(III) and cobalt(III) complexes containing a tetradentate macrocyclic ligand will have only two sites that are susceptible to substitution by relatively weak nucleophiles such as water. The reactivity of these two sites is expected to be influenced by the nature of the macrocycle.

Busch and Hung[2] have shown that the rates of the first aquation of $[CoLCl_2]^+$ (L is a neutral tetraaza cyclic ligand) are parallel to the bond strain imposed by the macrocycle. Cobalt(III) complexes usually undergo substitution reactions by a D mechanism while chromium(III) complexes undergo substitution reactions by an A mechanism.[3] At present there have been no systematic studies comparing how various macrocyclic ligands can influence the rates of aquation of $[CrLCl_2]^+$.

Campi, Ferguson, and Tobe[4] have obtained kinetic data for the aquation of the *cis*- and *trans*-$[Cr(cyclam)Cl_2]^+$. We have prepared and characterized chromium(III) complexes containing a 12- and 15-membered saturated tetraaza cyclic ligands (I, II) and an unsymmetrical 14-membered saturated tetraaza cyclic ligand

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[4] Campi, E.; Ferguson, J.; Tobe, M. L. *Inorg. Chem.* **1970**, *9*, 1781.

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