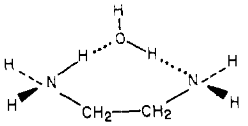
rotomeric ligand isomers upon complex formation rates,[6] we now suggest that the threefold lower formation rate constant observed for Hen^+ relative to $tmen^+$ is explainable in the terms that a significant fraction of the Hen^+ species is intramolecularly hydrogen bonded[13] (in a "gauche-in" conformation[6]) and is thus unreactive toward the metal ion.

One might suspect that internal hydrogen bonding would affect the protonation rate constants of the ligand, as has been found in comparing salicylic acid to phenol,[33] and might thus be reflected in abnormal protonation equilibrium constants. However, in the case of salicylic acid the proton is shared directly between two atoms of the same molecule, whereas in the case of Hen^+ the proton may be shared *via* a bridging water molecule



Such an arrangement would not affect the protonation rate constant since, as Eigen has pointed out,[32] the proton has direct access to the defect proton in the bulk solvent *via* the proton-jump mechanism.

Thus, we do not imply that either the process of rupturing an intramolecular hydrogen bond or the final loss of the proton from the ligand itself has any influence upon the rate of Ni(II) reaction with Hen^+. Rather, the existence of intramolecular hydrogen bonding shifts the conformational equilibria of the Hen^+ species such that, at any specific time, a smaller fraction of the protonated ligand is in a conformation favorable for coordinate bond formation to the metal ion.[6]

Conclusions

The formation rate constant for unprotonated ethylenediamine reacting with $Ni(H_2O)_6^{2+}$ is found to be about 200 times larger than would be anticipated on the basis of a normal dissociative mechanism. In attributing this enhancement to outer-sphere *intermolecular* hydrogen bonding between a donor atom of the ligand and a coordinated water molecule in terms of the internal conjugate base (ICB) effect, it is inferred that the principal accelerating factor is an increase in the outer-sphere equilibrium constant, K_{os}, as the result of a decrease in the rate constant for the diffusion of the two reactants apart, k_{-0}.

In the case of the monoprotonated ligand species, an apparent retardation in the formation rate constant is attributed to the influence of *intramolecular* hydrogen bonding in decreasing the fraction of ligand which is in a reactive conformation.

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Registry No. Ni^{2+}, 14701-22-5; ethylenediamine, 107-15-3.

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The Relative Stabilities of Some Platinum(II) Carbonyl Complexes

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Equilibrium constants, K_{eq}, for the reaction $(n\text{-}C_4H_9)_4N^+[(CO)PtCl_2(X)]^- + 4\text{-Zpy} \rightleftharpoons (n\text{-}C_4H_9)_4NX + (CO)PtCl_2(4\text{-Zpy})$, where X = Cl, Br, or I and 4-Zpy is a 4-substituted pyridine with Z = $COCH_3$, CO_2CH_3, H, C_2H_5, CH_3, or $C(CH_3)_3$, were determined in chloroform solution by infrared measurements of the CO bands. As expected, the more electron releasing Z is, the larger K_{eq} is, independent of X; the effect of changing Z is much greater than that of changing X.

Introduction

We have shown earlier[1] that if the infrared spectra of the complexes 1,3-dichloro-2-carbonyl-4-(4-Z-pyridine)platinum(II), $(CO)PtCl_2(4\text{-Zpy})$, are determined in acetonitrile (or acetone) solution using KBr cells, the solvent dissolves sufficient bromide ion to displace the pyridine, and a mixture of two carbonyl species is produced, giving rise to two readily distinguishable CO bands in the ir spectrum. We have also reported earlier[1] that the relative intensity of the two bands in acetone depends on the nature of Z; the more electron withdrawing Z is, the greater is the intensity (concentration) of the bromide complex. This displacement reaction seemed to us to merit separate investigation.

We wish to report now the results of a limited study on the equilibrium competition between bromide (and other halides) and 4-substituted pyridines (4-Zpy) for a site on the platinum in the reaction

$$[(n\text{-}C_4H_9)_4N]^+\underset{\mathbf{1}}{[(OC)PtCl_2(X)]^-} + 4\text{-Zpy} \rightleftharpoons (n\text{-}C_4H_9)_4NX + \underset{\mathbf{2}}{(OC)PtCl_2(4\text{-Zpy})} \qquad (1)$$

where X = Cl, Br, or I and Z = $C(CH_3)_3$, CH_3, C_2H_5, H, CO_2CH_3, or $COCH_3$. These equilibrium studies on carbonyl complexes of Pt(II) complement those previously reported

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on olefin complexes[2,3] and silver(I)-pyridine complexes[4] in aqueous media.

Experimental Section

Infrared spectra were obtained using a Beckman IR-12 spectrophotometer. All solvents were reagent or spectral grade and were dried over molecular sieves. The chloroform was chromatographed over neutral, activity grade 1 alumina to remove ethanol. All pyridines were purified by vacuum distillation just prior to use. The tetraalkylammonium salts were dried for at least 1 week over P_4O_{10} *in vacuo*, prior to use. The carbonyl stretching frequencies were determined at ambient machine temperature in KBr cells. The values of the extinction coefficient at ν_{max} were used to calculate concentration. Melting points were determined using a Melt-Temp apparatus.

Preparation of Complexes. Tetra-*n*-butylammonium Trichlorocarbonylplatinate(II). To 0.436 g (1.1 mmol) of Ziese's salt, $K(C_2H_4)PtCl_3$, dissolved in 10 ml of acetone, there was added with stirring 1.01 g (3.6 mmol) of $(n\text{-}C_4H_9)_4NCl$. The precipitate of KCl formed immediately. After 10 min the precipitated KCl was removed by centrifugation. The supernatant liquid was decanted and its volume was reduced by evaporation *in vacuo*. The precipitate which appeared on addition of hexane was filtered and washed with cold ether. The resulting solid was then dissolved in 10 ml of $CHCl_3$ and CO was bubbled into the solution for 10 min. The complex was precipitated by addition of hexane and was recrystallized from chloroform-hexane, mp 126-127°; ν_{CO} 2101 cm^{-1}. *Anal.*[5] Calcd for $C_{17}H_{36}Cl_3NOPt$: C, 35.69; H, 6.34. Found: C, 35.59; H, 6.44.

Tetra-*n*-butylammonium 1,3-Dichloro-2-bromo-4-carbonylplatinate(II). To 0.107 g (0.30 mmol) of *trans*-$(C_2H_4)PtCl_2(p\text{-}NCC_5H_4N)$ dissolved in 10 ml of $CHCl_3$, there was added with stirring 0.238 g (0.7 mmol) of $(n\text{-}C_4H_9)_4NBr$. After 10 min the ethylene complex was precipitated by addition of ether; it was then filtered and dried *in vacuo*. The resulting solid was dissolved in 10 ml of $CHCl_3$ and CO bubbled into the solution for 10 min. The color changed from yellow to light yellow. The carbonyl complex was precipitated by addition of hexane and was recrystallized from chloroform-hexane; mp 120-121°; ν_{CO} 2096 cm^{-1}. *Anal.* Calcd for $C_{17}H_{36}Cl_2BrNOPt$: C, 33.13; H, 5.89. Found: C, 31.95; H, 5.73.

Tetra-*n*-butylammonium 1,3-Dichloro-2-iodo-4-carbonylplatinate(II). This complex was prepared by the previously known method;[1] mp 107-109°; ν_{CO} 2091 cm^{-1}.

Spectrophotometric Determination of Equilibrium Constants. Approximately 10 mg of pure $(n\text{-}C_4H_9)_4N^+[(CO)PtCl_2(X)]^-$ was carefully weighed and the carbonyl salt was dissolved in approximately 6×10^{-2} *M* $CHCl_3$ solution of pyridine. After standing for several hours the infrared spectra were determined between the regions 2000 and 2300 cm^{-1}. The equilibrium constant *K* for eq 1 is

$$K_{eq} = \frac{[(n\text{-}C_4H_9)_4NX][(OC)PtCl_2(4\text{-}Zpy)]}{[(n\text{-}C_4H_9)_4N^+[(OC)PtCl_2(X)]^-][4\text{-}Zpy]} \qquad (2)$$

Equation 2 reduces to

$$K_{eq} = \frac{[[A]_0 - [A]]^2}{[A] - [[4\text{-}Zpy]_0 - [A]]}$$

where [A] is the equilibrium concentration of the carbonyl salt evaluated from the Beer-Lambert expression, $[A]_0$ is the initial molal concentration of the carbonyl salt, and $[4\text{-}Zpy]_0$ is the initial molal concentration of the substituted pyridine ligand.

Results and Discussion

The equilibrium constants obtained for eq 1 are shown in Table I. The substituents at the 4 position of the pyridines have the effect expected, based on the electronic effect that these substituents have on the basicity of the pyridine. The results also show that, unexpectedly, K_{eq} is much more dependent on the nature of Z than on X; variation of Z can produce as much as a 100-fold change in K_{eq} while a variation in X produces only a twofold change. Although the effect of changing X is small with any particular pyridine, there is an apparent anomalous order of the relative stabilities of the halides I > Cl > Br, the usual order of stabilities for Pt(II) complexes being I > Br > Cl. The differences we have found, although very small, are real and may be due to superposition of opposing effects.[6]

Table I. Equilibrium Constants[a] for the Reaction $(n\text{-}C_4H_9)_4N[(CO)PtCl_2(X)] + 4\text{-}Zpy \rightleftharpoons (n\text{-}C_4H_9)_4NX + (OC)PtCl_2(4\text{-}Zpy)$

X	Z	K_{eq}	X	Z	K_{eq}
Cl	$COCH_3$	0.031 ± 0.005	Br	C_2H_5	1.1 ± 0.1
Cl	CO_2CH_3	0.060 ± 0.025	Br	CH_3	1.2 ± 0.1[b]
Cl	H	0.25 ± 0.05	Br	$C(CH_3)_3$	2.4 ± 0.2
Cl	C_2H_5	0.90 ± 0.08	I	$COCH_3$	0.012 ± 0.009
Cl	CH_3	1.3 ± 0.1	I	H	0.14 ± 0.02
Cl	$C(CH_3)_3$	1.6 ± 0.1	I	C_2H_5	0.53 ± 0.06
Br	$COCH_3$	0.043 ± 0.009	I	CH_3	0.61 ± 0.01
Br	H	0.32 ± 0.06	I	$C(CH_3)_3$	1.3 ± 0.7

[a] Each data point represents at least four determinations. [b] The equilibrium approached from the right-hand side gave 1.1 ± 0.1.

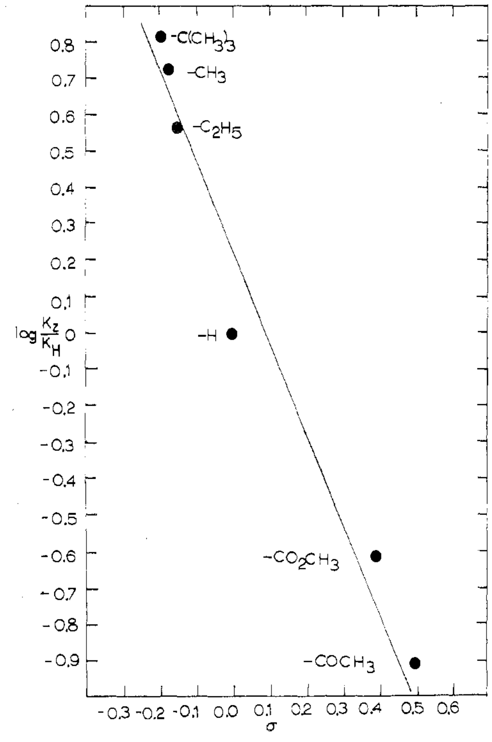

Figure 1. Hammett plot for the equilibrium reaction $(n\text{-}C_4H_9)_4N^+[(OC)PtCl_3]^- + 4\text{-}Zpy \rightleftharpoons (n\text{-}C_4H_9)_4NCl + (OC)PtCl_2(4\text{-}Zpy)$.

When the equilibrium constants K_Z (X = Cl) in eq 2 are divided by K_H (Z = H) and the log of this ratio plotted against σ values[7], Figure 1, a nearly linear Hammett relationship is obtained. The large negative slope ($\rho = -2.4$) indicates that the nucleophilic substitution reaction is very sensitive to electrical effects at the nitrogen atom. The plot when X = Br ($\rho = -2.3$) and I ($\rho = -2.6$) also showed a good linear relationship[8].

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Registry No. $(n\text{-}C_4H_9)_4N[(CO)PtCl_3]$, 34964-16-4; $(n\text{-}C_4H_9)_4N[(CO)PtCl_2Br]$, 51157-48-3; $(n\text{-}C_4H_9)_4N[(CO)PtCl_2I]$, 38626-17-4; $(OC)PtCl_2(4\text{-}pyCOCH_3)$, 20064-58-8; $(OC)PtCl_2(4\text{-}pyCO_2CH_3)$, 20064-59-9; $(OC)PtCl_2(py)$, 51261-84-8; $(OC)PtCl_2(4\text{-}pyC_2H_5)$, 51157-49-4; $(OC)PtCl_2(4\text{-}pyCH_3)$, 20064-55-5; $(OC)PtCl_2[4\text{-}py\text{-}C(CH_3)_3]$, 51157-50-7; py, 110-86-1; 4-pyCH$_3$, 108-89-4.

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Five-Coordinate Methylplatinum(II)-Acetylene Complexes Stabilized by Tridentate Poly(pyrazolyl)borate Ligands

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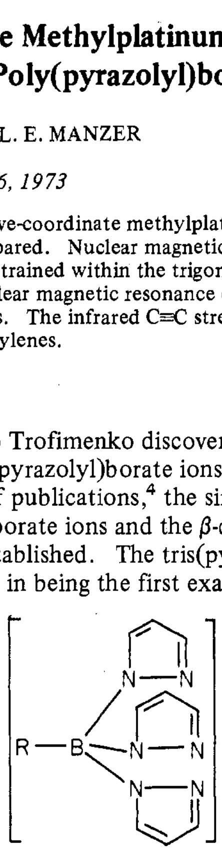
A variety of five-coordinate methylplatinum(II)-acetylene complexes stabilized by tridentate poly(pyrazolyl)borate ligands have been prepared. Nuclear magnetic resonance studies indicate that the complexes are trigonal bipyramidal with the acetylene constrained within the trigonal plane of the platinum and two equatorial pyrazolyl nitrogen atoms. Double-resonance nuclear magnetic resonance experiments have allowed assignment of all the 3-H, 4-H, and 5-H resonances of the pyrazolyl rings. The infrared C≡C stretching frequencies are discussed in relation to the bonding and chemistry of coordinated acetylenes.

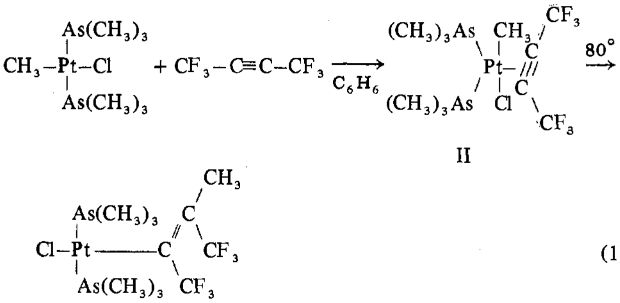
Introduction

Several years ago Trofimenko discovered a new class of ligands,[2] the poly(pyrazolyl)borate ions[3] $[R_nB(pz)_{4-n}]$, and in a number of publications,[4] the similarities between the bis(pyrazolyl)borate ions and the β-diketonate ions, as ligands, were established. The tris(pyrazolyl)borate ions, I, are unique, in being the first examples of uninegative, tridentate ligands of C_{3v} symmetry and form a number of complexes analogous to their well-known cyclopentadienyl counterparts. Although structurally similar, the tris(pyrazolyl)borate complexes are generally much more stable than the cyclopentadienyl compounds. For example, Cu(CO)[HB(pz)$_3$][5] is air and heat stable while Cu(CO)(π-C$_5$H$_5$)[6] is thermally unstable and air sensitive.



I

Five-coordinate complexes of platinum(II) are sufficiently rare[7-14] that the possibility of stabilizing such species using a tridentate poly(pyrazolyl)borate ligand was worth exploring. In particular, we were interested in the formation of five-coordinate olefin and acetylene complexes which have been postulated as intermediates in the transition metal catalyzed polymerization and hydrogenation of olefins and acetylenes[13-21]. For example, *trans*-Pt(CH$_3$)ClL$_2$ (L = tertiary phosphine, arsine, or stibine) reacts with an excess of perfluorobut-2-yne to give 1:1 adducts,[14] II (eq 1). The structure of the five-coordinate adduct, II,



II

$$\mathrm{CH_3Pt(Cl)[As(CH_3)_3]_2 + CF_3C{\equiv}CCF_3 \xrightarrow{C_6H_6} Pt(CH_3)Cl(CF_3C{\equiv}CCF_3)[As(CH_3)_3]_2 \ (II) \xrightarrow{80^\circ} ClPt[C(CF_3){=}C(CF_3)CH_3][As(CH_3)_3]_2} \quad (1)$$

has been determined by a three-dimensional X-ray analysis, confirming the trigonal-bipyramidal configuration.[22] Insertion of the platinum methyl group into the C≡C bond occurs at 80° to give the vinylplatinum(II) complex.[16]

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[1] To whom correspondence should be addressed.

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