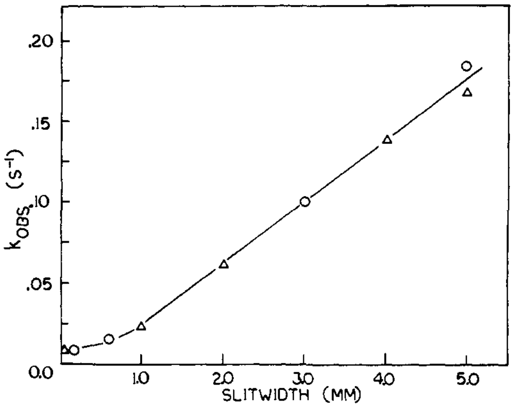
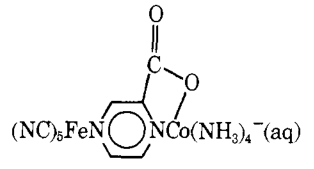


Figure 1. Specific rate of electron transfer in B vs. spectrophotometer slit width: [Co_{total}] = 1.0×10^{-3} M, [Fe_{total}] = 1.0×10^{-5} M. 24 °C, pH 6.5, μ = 0.15 M ($LiClO_4$). Triangles denote added ascorbic acid (5×10^{-4} M).



B

cm). B is characterized by its close similarity in spectrum with A. For B, λ_{max} 630 ± 10 nm, ϵ_{max} $(9 \pm 1) \times 10^3$ M^{-1} cm^{-1}. Decay of the absorption due to B is a first-order process described by rate plots that are linear over at least three half-lives.[8] Aqueous cobalt(II) and an iron(III)-containing product, presumably the 2-pyrazinecarboxylate complex of pentacyanoferrate(III) ion, are the products of the reaction.

We find that k_{obsd}, the first-order specific rate of disappearance of B is approximately a linear function of the optical slit width employed in the stopped-flow instrument. This dependence is shown in Figure 1. The bandwidth of the spectrophotometer (3 nm/mm) is inside the charge-transfer envelope even at the widest slit setting used (5 mm). Also, the rate of reaction at a given slit width is relatively independent of wavelength in the range 615-640 nm. Therefore the increase in k_{obsd} given in Figure 1 is ascribed to an increase in light intensity, I_0, entering the observation cuvette. At narrow slitwidth (0.10-0.15 mm) k_{obsd} reaches a constant value, 0.012 s^{-1}, the specific rate of the dark reaction (k_{th}). Reaction conditions were 24 °C, μ = 0.15 M ($LiClO_4$), pH 6.5 (phosphate buffer).

To determine ϕ_{et}, the quantum yield for photoredox decomposition of the intermediates, it is necessary to find I_0. This was accomplished by measuring the rate of photolysis of aqueous hexaureachromium(III) ioin the stopped-flow cuvette under the same physical conditions employed in studying the precursor complexes. At 620 nm, 5.0 mm slitwidth, I_0 was $(4.2 \pm 0.4) \times 10^{15}$ quanta cm^{-3} s^{-1} ($(1.4 \pm 0.13) \times 10^{-8}$ einsteins cm^{-2} s^{-1}). The wavelength 620 nm was chosen because it corresponds to an absorbance peak of the primary actinometer[9] and is near the absorbance maxima of A and B.

By working at very low initial concentrations of Fe(II) (1.0×10^{-5} M after dilution) it could be ensured that the total optical absorbance was always 0.1 or less and that the light intensity throughout the cuvette was therefore close to I_0. ϕ_{et} could then be calcted using eq 2.[10]

$$\phi_{et} = k_l/(2.303 \times 10^3 I_0 \epsilon) \qquad (2)$$

For B, ϕ_{et} equals 0.9 ± 0.15, computed using k_l and ϵ values that are, respectively, 0.17 ± 0.01 s^{-1} and $6.1 \pm 0.3 \times 10^3$ M^{-1} cm^{-1}. k_l was found at 5.0 mm slitwidth using the equation $k_l = k_{obsd} - 0.012$ s^{-1}. ϵ_{620} was measured directly at 5.0 mm slitwidth.

For A, k_{th} was not detected. Therefore k_l was considered equal to k_{obsd} (4.1×10^{-3} s^{-1}, 24 °C, 5.0 mm slitwidth). The values of I_0 and ϵ at 5.0 mm slitwidth in this case were $(1.1 \pm 0.1) \times 10^{-8}$ einsteins cm^{-2} s^{-1} and $(8.4 \pm 0.3) \times 10^3$ M^{-1} cm^{-1}. Substitution in eq 2 yields $\phi_{et} = (2.0 \pm 0.3) \times 10^{-2}$.

The difference in the photoreactivities of A and B can be rationalized if the mechanism in each case involves an excited state in which iron(III) is linked to cobalt(III) via a short-lived, bridging pyrazine radical. In the species formed by MLCT excitation of B, the tetraamminecobalt(III) moiety evidently is sufficiently reactive to oxidize the bridging radical after virtually every excitation event. From the radiative lifetime estimated for a $Fe^{II}(d) \rightarrow pyrazine(\pi^*)$ excited state,[11] the lower limit for photoinduced electron transfer to tetraamminecobalt(III) would be ca. 10^9 s^{-1}. The low quantum yield in the case of A indicates that the bis(ethylenediamine)cobalt(III) oxidant is considerably less reactive in competing for the electron, just as A is thermally unreactive compared to B.

In Figure 1 the value of k_{th} is 0.012 ± 0.001 s^{-1}. This value is larger than those found previously for thermal intramolecular electron transfer between $Fe(CN)_5{}^{3-}$ and $Co(NH_3)_5{}^{3+}$ mediated by 4,4′-bipyridine (2.6×10^{-3} s^{-1})[3a] or by 4-pyridine carboxylate (1.8×10^{-4} s^{-1}),[3b] yet much smaller than k_{obsd} for intramolecular electron transfer between Co(III) and Ru(II) bridged by 4-pyridine carboxylate (ca. 200 s^{-1}).[2]

Acknowledgments are made to the National Science Foundation (Grant MPS75-098-7 and an Energy Related Traineeship for D.A.P.) and to the University of Missouri foa Summer Faculty Research Fellowship (J.M.M.).

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Received May 19, 1976

The Remarkable Alcoholysis Reaction and Structure of *trans*-Bis(α-chlorovinyl)bis(dimethylphenylphosphine)platinum(II)

Sir:

Although simple vinyl halides are known to be highly unreactive in solvolytic processes,[1] α-chlorovinylplatinum(II)

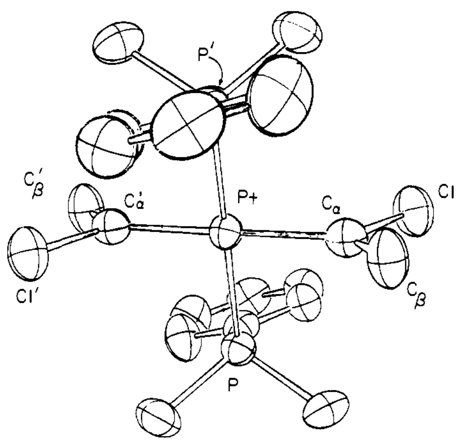


Figure 1. An ORTEP view of **1** viewed almost perpendicular to the coordination plane of platinum. Atom ellipsoids represent equiprobability surfaces of thermal displacement and contain 50% of the probability distribution.

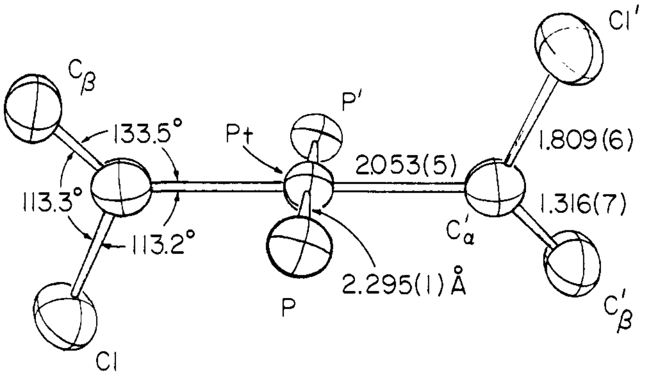


Figure 2. An ORTEP view of **1** including important bond angles and bond distances.

complexes have recently been found to react readily with alcohols at room temperature to give cationic alkoxy-carbene complexes.[2] Even in the less ionizing solvents chloroform, dichloromethane, and benzene, α-chlorovinylplatinum(II) compounds are labile toward the reversible elimination of HCl as shown in the sequence 1.[3]

We wish now to report the structural characterization of *trans*-Pt(CCl=CH$_2$)$_2$(PMe$_2$Ph)$_2$, I, and its reaction with

$$\underset{\text{I}}{trans\text{-Pt(CCl=CH}_2)_2\text{L}_2} \rightleftarrows \underset{\text{II}}{trans\text{-Pt(CCl=CH}_2)(\text{C}\equiv\text{CH})\text{L}_2} + \text{HCl}$$

$$\underset{\text{II}}{trans\text{-Pt(CCl=CH}_2)(\text{C}\equiv\text{CH})\text{L}_2} \rightleftarrows \underset{\text{III}}{trans\text{-Pt(C}\equiv\text{CH})_2\text{L}_2} + \text{HCl} \quad (1)$$

$$2\text{II} \rightleftarrows \text{I} + \text{III};\ K \cong 1;\ \text{where L} = \text{PMe}_2\text{Ph}$$

methanol. These findings provide considerable insight into the remarkable lability of the PtCCl=CH$_2$ moiety.

trans-Pt(CCl=CH$_2$)$_2$(PMe$_2$Ph)$_2$, I, was prepared by treating *trans*-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$, III, with anhydrous HCl (2 equiv) in benzene. I is a white crystalline solid which melts with effervescence at 130 °C to yield acetylene and *trans*-PtCl(CCl=CH$_2$)(PMe$_2$Ph)$_2$. The ^{1}H NMR spectrum of I shows[4] the presence of *trans*-phosphine ligands and β-vinylic protons.

Crystals of I grown from benzene were found to be monoclinic, space group $P2_1/c$, with cell constants a = 9.039 (2) Å, b = 6.322 (1) Å, c = 19.415 (4) Å, and β = 91.91 (2)°, and contain two molecules per unit cell. The intensity data were collected with an automated Syntex diffractometer using the ω-2θ scan method; 3250 independent reflection intensities were measured using monochromatized Mo Kα radiation. After correction for absorption ($\mu r \sim 7$), the solution of the structure proceeded by routine Patterson-Fourier methods and was refined by full-matrix least squares to a final R[5] index of 0.063 and weighted R_w[6] = 0.072.

Figure 1 shows the molecule (excluding hydrogen atoms) in its entirety. Figure 2 gives a view slightly above the P-Pt-P axis with bonding parameters of interest. The phosphine phenyl groups and vinylic chlorine atoms are directed above and below the coordination plant of platinum. The platinum atoms reside on centers of symmetry and thus the coordination plane about platinum is rigorously planar. With the P-Pt-C$_\alpha$ angle equal to 87.85°, the coordination geometry is nearly ideal.

The C$_\alpha$-C$_\beta$ bond distance is normal for a carbon-carbon double bond but the C$_\alpha$-Cl distance and the interatomic angles about C$_\alpha$ are quite unusual.[7] Vinyl chloride is reported to have a C-Cl bond length of 1.728 (7) Å[8] and the similar bond in 2-chloropropene is 1.727 Å.[9] The average C-Cl bond distance in (η^2-C$_2$Cl$_4$)Pt(PPh$_3$)$_2$ is 1.75 (3) Å.[10] The significantly

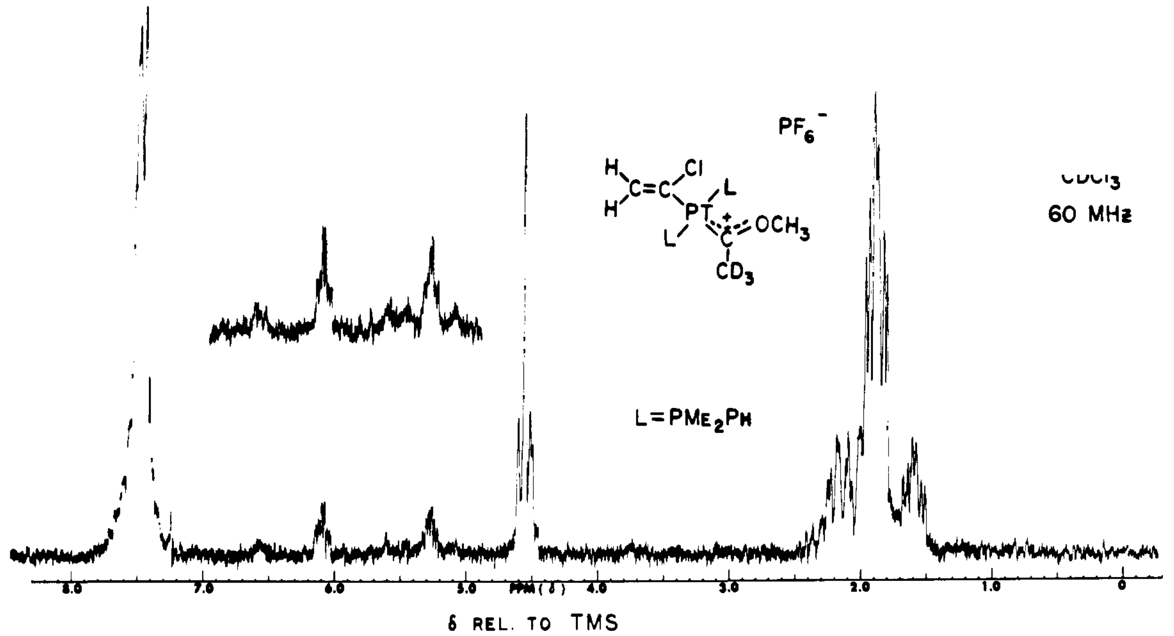
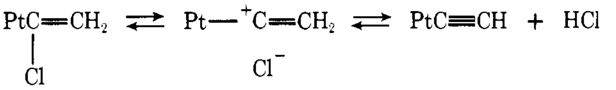


Figure 3. ^{1}H NMR spectrum of IV-PF$_6$ recorded in CDCl$_3$ solution at 60 MHz and 40 °C. See ref 13 for assignments.

longer C_α-Cl bond distance in I, 1.809 (6) Å, is similar to the C_{sp^3}-Cl bond distance found in *tert*-butyl chloride, 1.828 (5) Å,[11] 1.807 (4) Å.[12] Furthermore, the observed Pt-C_α-Cl bond angle is smaller than expected while the Pt-C_α-C_β angle is expanded toward linearity, in opposition to what would be expected from steric considerations. See paragraph at end of paper regarding supplementary material.

I dissolves in methanol to give *trans*-$[Pt(CCl{=}CH_2)(COMe(Me))(PMe_2Ph)_2]^+Cl^-$, IV-Cl, which in the presence of $AgPF_6$ (1 equiv) gives a stable hexafluorophosphate salt, IV-PF_6, as a white crystalline compound, mp 117-118 °C, $\nu_{str}(CCl{=}CH_2)$ 1570 cm^{-1}. Analogous reactions in MeOD lead to IV-Cl and IV-PF_6 in which the vinylic protons of the Pt-CCl=CH_2 moiety are *not* exchanged with deuterium atoms of the solvent. This is clearly evident from the ^1H NMR spectrum of IV-PF_6 which is shown in Figure 3. In particular the gem coupling of the vinylic protons is maintained.[13]

Detailed studies[14] of the elimination of HCl from *trans*-$PtX(CCl{=}CH_2)(PMe_2Ph)_2$ in benzene and dichloromethane, where X = CCl=CH_2, -C≡CH, and -Cl, are consistent with sequence 2.



$$\underset{\displaystyle Cl}{PtC}{=}CH_2 \rightleftarrows \underset{\displaystyle Cl^-}{Pt{-}^+C{=}CH_2} \rightleftarrows PtC{\equiv}CH + HCl \quad (2)$$

The present work also supports 2: the long C_α-Cl bond distance and the large Pt-C_α-C_β angle in I are suggestive of a facile C_α-Cl heterolysis reaction. The observation that I reacts with MeOD to give IV-Cl/PF_6, in which reaction occurs at only one α-chlorovinyl ligand of I, indicates that the reactivity of the α-chlorovinyl ligand is very sensitive to the nature of the $[L_2PtX]$ moiety to which it is bonded. It is reasonable to suppose that C_α-Cl heterolysis in IV-PF_6 is suppressed both by the positive charge on platinum and by the presence of the π-acceptor carbene ligand in the trans-position. At present we can only speculate on the relative importance of these factors. However, further work is in progress including a structural characterization of IV-PF_6.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant MPS 73-05016) for support of this work.

Supplementary Material Available: A listing of bond distances and bond angles (1 page). Ordering information is given on any current masthead page.

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(5) $R = \sum \lvert F_o - F_c \rvert / \sum \lvert F_o \rvert$.
(6) $R_w = (\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4)^{1/2}$.
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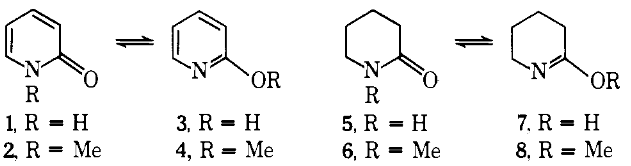
Application of Ion Cyclotron Resonance Spectroscopic Gas-Phase Basicities to the Study of Tautomeric Equilibria[1]

Sir:

Prototropic equilibria are sensitive to solvent and phase: their study is of considerable significance theoretically and experimentally.[2] Many spectroscopic and other methods are available for the study of such equilibria and quantitative data can be obtained provided detectable quantities (usually >5%) of both tautomers exist. However, the study of highly biased equilibria usually needs the basicity method, which depends on utilizing the relative pK_a values of suitable models (usually methyl derivatives) of each tautomer, cf. eq 1.[2] Unfortunately, simple application of the basicity method is restricted to aqueous solutions, although in conjunction with heat of solution data estimates of K_T can be made for equilibria in other solvents.[3]



1, R = H
2, R = Me
3, R = H
4, R = Me
5, R = H
6, R = Me
7, R = H
8, R = Me

$$pK_T = pK(1) - pK(3) \approx pK(2) - pK(4) \qquad (1)$$

Recently Beak[4] has shown by uv and ir spectroscopy that 2- and 4-hydroxypyridine and some related compounds exist predominantly in the hydroxy form in the gas phase. For 2-hydroxypyridine (**1** ⇌ **3**) he obtained $\Delta H°$ = 0.3 ± 0.4 kcal mol^{-1} in favor of the hydroxy form **3**; for the related tetrahydro derivatives **5** ⇌ **7**, $\Delta H°$ is not determined directly, as the equilibrium content of **7** is not detectable, but using $\Delta H°$ for the equilibria[5] of the methyl derivatives **2** ⇌ **4** and **6** ⇌ **8**, he estimated $\Delta H°$ (**5** ⇌ **7**) as ca. 7 kcal mol^{-1} in favor of the oxo form **5**.

We wish to point out that gas-phase proton affinities, determined by pulsed ion cyclotron resonance (ICR) thermal proton transfer equilibria,[6,7] offer a unique complementary approach. Data for the model compounds are collected in Table I: this indicates that **4** is more basic than **2** by $\Delta H°$ = 2.1 kcal mol^{-1}. However, the effect of O-methylation on the basicity of **3** is probably greater than the effect of N-methylation on the basicity of **1**. Thus, comparing $H_2O \rightarrow MeOH \rightarrow Me_2O$ with $NH_3 \rightarrow MeNH_2 \rightarrow Me_2NH$ indicates a differential effect on proton affinity (O > N) of 2.8 and 1.6 kcal mol^{-1} for the first and second methylations, respectively.[8] Comparison of ICR gas-phase basicities obtained in the present work with