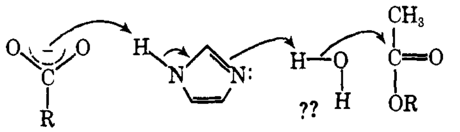
tions either as a nucleophile or as a general base with water as nucleophile (eq 4). The question of water



(4)

involvement has been investigated but a clear answer is not yet possible.

Enzymatic active sites may resemble dipolar aprotic solvents such as acetonitrile with small amounts of water present. The amide structure of the peptide backbone is certainly dipolar and crystallography has demonstrated variable amounts of water in active sites. Consequently, the medium we have studied appears to be a plausible model for the effective medium of an active site. It is striking that k_2' is predominant in this medium at $[C_6H_5CO_2^-]$ approximately 4×10^{-3} M and [IM] approximately 0.1 M and that catalysis by benzoate ions and imidazole is much more effective than benzoate ion alone or imidazole alone. Therefore, catalysis by carboxylate ion and imidazole is a very powerful mode of catalysis even in the absence of the binding, orientation, and proximity effects which are important in enzymatic catalysis.

The effectiveness of this mode of catalysis also has important implications for biochemical evolution. The evolution of proteins as biological catalysts imposes certain limitations on the solvent properties of active sites. To the extent that it is true that active sites must resemble the medium we have investigated, the proton relay mechanism (eq 4) appears to be a particularly effective catalytic mechanism that would have been readily selected in the course of evolution when carboxylate, imidazole, and hydroxyl groups were available as functional groups of proteins.

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Formation and Oxidative Addition Reactions of Five-Coordinate Iridium(I) Complexes

Sir:

While oxidative addition reactions of covalent molecules such as H_2 to low-spin d^8 complexes (notably to iridium(I) complexes of the type $Ir(CO)L_2X$, where L = phosphine or arsine and X = halide) have received considerable attention,[1-5] the reactivity patterns associated with variation of the ligands in such complexes are not yet well understood. Such ligand variations (as well as related variations in ligand concentrations and solvent properties) are especially significant when they are accompanied by changes in the coordination number of the d^8 complex from four to five. We wish to communicate the results of studies which reveal some new effects of this type and which contribute to an understanding of them.

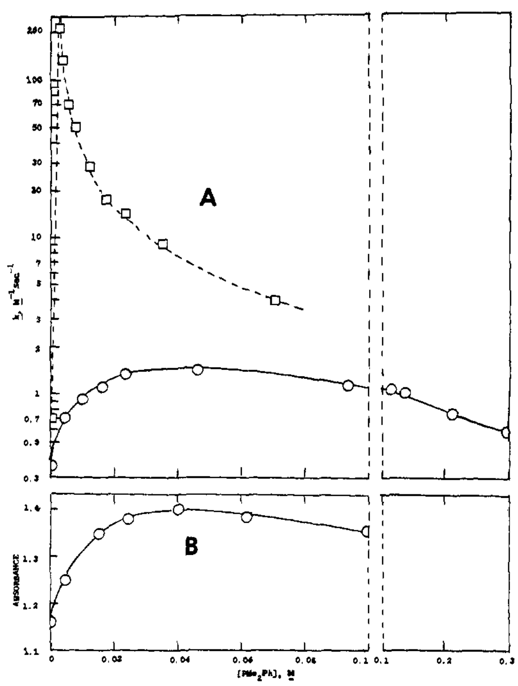

Figure 1. (A) Effect of excess PMe_2Ph on the rate of reaction of $Ir(CO)(PMe_2Ph)_2Cl$ with H_2 at 25°: ○, in chlorobenzene; □, in dimethylformamide. (B) Absorbance change at 362 nm accompanying the addition of PMe_2Ph to a 5.35×10^{-4} M solution of $Ir(CO)(PMe_2Ph)_2Cl$ in chlorobenzene.

Contrary to the behavior of the well-known compound $Ir(CO)(PPh_3)_2Cl$[3,4] which, in solution, is unaffected by the addition of excess PPh_3, we have found that the addition of low concentrations of excess PMe_2Ph (up to 0.04 M) to chlorobenzene solutions of the analogous complex $Ir(CO)(PMe_2Ph)_2Cl$ (**1**) results initially in the reversible association reaction described by eq 1, leading to the formation of the five-coordinate complex, $Ir(CO)(PMe_2Ph)_3Cl$ (**2**).

$$\underset{\mathbf{1}}{Ir(CO)(PMe_2Ph)_2Cl} + PMe_2Ph \underset{}{\overset{K}{\rightleftarrows}} \underset{\mathbf{2}}{Ir(CO)(PMe_2Ph)_3Cl} \quad (1)$$

Evidence for this equilibrium is provided by the following observations: (1) the spectral changes accompanying the addition of up to 0.04 M PMe_2Ph, corresponding to the disappearance of the 377-nm band of **1** and to increases in absorbance at wavelengths below an isosbestic point at 365 nm and above another isosbestic at 394 nm; (2) the isolation from solutions containing excess PMe_2Ph of the pure solid compound $Ir(CO)(PMe_2Ph)_3Cl$ which has been fully characterized spectrally and by elemental analysis (ν_{CO} = 1885 *vs.* 1960 cm^{-1} for **1**) and whose structure is now being determined by X-ray diffraction; (3) the increased rate of reaction with H_2 accompanying the addition of up to 0.04 M PMe_2Ph. The reaction with H_2 under these conditions yields the previously characterized complex,[6] $Ir(CO)(PMe_2Ph)_3H_2^+$, in accord with eq 2. The spectral and reactivity changes, both depicted in Figure 1, parallel each other and quantitatively fit the equilibrium described by eq 1 yielding the values 2×10^{-2} M^{-1} for the equilibrium constant K and

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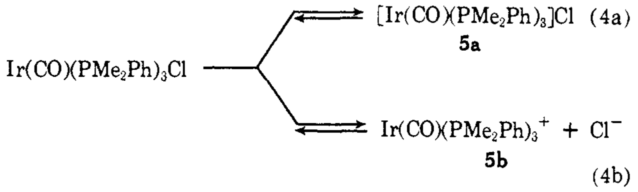
1.8 M^{-1} sec^{-1} for the apparent rate constant (k) of the reaction of **2** with H_2 (compared with 0.35 M^{-1} sec^{-1} for the corresponding reaction of **1** to form $\mathrm{Ir(CO)(PMe_2Ph)_2ClH_2}$).[7]

$$\mathrm{Ir(CO)(PMe_2Ph)_3Cl + H_2 \xrightarrow{k} \underset{\mathbf{3}}{[Ir(CO)(PMe_2Ph)_3H_2]Cl}} \qquad (2)$$

Increasing the $\mathrm{PMe_2Ph}$ concentration above 0.04 M resulted in parallel decreases (also depicted in Figure 1) in the absorbance due to **2**, as well as in the reactivity toward H_2. Both of these trends correspond to inverse dependencies on the $\mathrm{PMe_2Ph}$ concentration which are consistent with the coordination of another $\mathrm{PMe_2Ph}$ ligand, in accord with eq 3, to form the pentacoordinate complex, $\mathrm{Ir(CO)(PMe_2Ph)_4^+}$ (**4**) (salts of which have previously been prepared and characterized),[8] which apparently is unreactive toward H_2.

$$\mathrm{Ir(CO)(PMe_2Ph)_3Cl + PMe_2Ph \rightleftharpoons \underset{\mathbf{4}}{[Ir(CO)(PMe_2Ph)_4]Cl}} \qquad (3)$$

The apparently enhanced reactivity of $\mathrm{Ir(CO)(PMe_2Ph)_3Cl}$ toward H_2 [compared with that of $\mathrm{Ir(CO)(PMe_2Ph)_2Cl}$] is somewhat surprising since five-coordinate d^8 complexes are usually considered to be intrinsically unreactive toward substrates such as H_2 and to oxidatively add such substrates through mechanisms involving prior dissociation to reactive four-coordinate derivatives.[9,10] Accordingly, we are inclined to attribute the enhanced reactivity to a small amount of the highly reactive ionic species, $\mathrm{Ir(CO)(PMe_2Ph)_3^+}$, presumably present as undissociated ion pairs, $\mathrm{[Ir(CO)(PMe_2Ph)_3]Cl}$ (compositionally identical with, and hence kinetically indistinguishable from, **1** with which they are in equilibrium through eq 4a) since dissociation into free ions (eq 4b) seems unlikely in a relatively nonpolar solvent such as chlorobenzene. Our failure to observe any inhibition due to a "common ion" effect when excess chloride was added as [n-$\mathrm{Bu_4N}$]Cl also argues against such dissociation.



$$\mathrm{Ir(CO)(PMe_2Ph)_3Cl \rightleftharpoons \underset{\mathbf{5a}}{[Ir(CO)(PMe_2Ph)_3]Cl}} \qquad (4a)$$

$$\mathrm{Ir(CO)(PMe_2Ph)_3Cl \rightleftharpoons \underset{\mathbf{5b}}{Ir(CO)(PMe_2Ph)_3^+} + Cl^-} \qquad (4b)$$

A reasonable expectation based on the above interpretation is that, because of enhanced stabilization of the reactive ionic species **5a** and **5b**, the rate enhancement accompanying the addition of $\mathrm{PMe_2Ph}$ to **1** *should be more pronounced and should occur at lower* $\mathrm{PMe_2Ph}$ *concentrations in more polar solvents.* As shown in Figure 1, this expectation is fully borne out by a comparison of dimethylformamide (DMF) and chlorobenzene as solvents. Addition of excess $\mathrm{PMe_2Ph}$ to **1** in DMF resulted in an increase in the rate constant for reaction with H_2 to a value of $>2 \times 10^2$ M^{-1} sec^{-1} at *ca.* 2×10^{-3} M $\mathrm{PMe_2Ph}$, compared with a maximum value of 1.4 M^{-1} sec^{-1} at *ca.* 4×10^{-2} M $\mathrm{PMe_2Ph}$ in chlorobenzene. The decrease in reactivity at higher $\mathrm{PMe_2Ph}$ in DMF is attributable to the equilibrium depicted by eq 5, analogous to that proposed for chlorobenzene (eq 3), but involving instead the *free* (reactive) $\mathrm{IrCO(PMe_2Ph)_3^+}$ and (unreactive) $\mathrm{IrCO(PMe_2Ph)_4^+}$ ions. This is supported (i) by the observation that the behavior in this region was independent of the nature of the anion (*i.e.*, of whether $\mathrm{Ir(CO)(PMe_2Ph)_2Cl}$ or $\mathrm{Ir(CO)(PMe_2Ph)_2Br}$ was used) and unaffected by the addition of a foreign halide salt, *e.g.*, up to 0.1 M [n-$\mathrm{Bu_4N}$]Br and (ii) by previously reported evidence from conductivity measurements that addition of excess $\mathrm{PMe_2Ph}$ to $\mathrm{Ir(CO)(PMe_2Ph)_2Cl}$ in ethanol–benzene (19:1, v/v) solution results in the formation of dissociated $\mathrm{Ir(CO)L_4^+}$ and $\mathrm{Cl^-}$ ions.[11] Since solvent effects for the oxidative addition of H_2 are typically small,[12] we are inclined to attribute the much higher rate enhancement observed in DMF, compared to chlorobenzene, to a higher concentration of the reactive species (**5a** and/or **5b**) (*i.e.*, to the fact that equilibrium 4b lies farther to the right in DMF than does equilibrium 4a in chlorobenzene) rather than to an intrinsically higher reactivity.

$$\mathrm{Ir(CO)(PMe_2Ph)_3^+ + PMe_2Ph \rightleftharpoons Ir(CO)(PMe_2Ph)_4^+} \qquad (5)$$

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[7] We have confirmed that the second-order rate law, $-d[H_2]/dt = k[Ir^I][H_2]$, previously established for the reaction of H_2 with $\mathrm{Ir(CO)(PPh_3)_2Cl}$, applies also to these systems. The kinetic measurements were made by following the reactions spectrophotometrically. Typical initial concentrations were 1×10^{-4} M $\mathrm{Ir^I}$ and 2.5×10^{-3} M H_2.

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Effect of a Single Thymine Photodimer on the Oligodeoxythymidylate–Polydeoxyadenylate Interaction[1]

Sir:

The presence of cyclobutyl-type pyrimidine dimers[2] in DNA produces local distortion of its secondary structure. Evidence for this includes lowering of melting temperature (T_m) and increased reactivity with formaldehyde resulting from uv irradiation of DNA.[3] More specific evidence has been derived from detailed analysis[4] of the action of the 5′ → 3′ exonuclease activity of *Escherichia coli* DNA polymerase in excision and repair of thymine photodimer regions in DNA. The postulated extent of hydrogen-bond disruption includes the photodimer, with its two opposing adenines in the complementary strand, and at least one

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