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Displacement of Dienes from Planar Complexes. 1. Reaction of (1,5-Cyclooctadiene)dichloropalladium(II) with 2,2'-Bipyridyl

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Received October 31, 1975 AIC50788O

A kinetic study on the reaction between (1,5-cyclooctadiene)dichloropalladium(II) and 2,2'-bipyridyl (bpy) in methanol, leading to Pd(bpy)Cl$_2$, is reported. The observed kinetic law of the process is

$$k_{\text{obsd}} = \left\{\frac{Kk_1}{K + [\text{Cl}^-]}\right\}[\text{bpy}] + \frac{Kk_2}{K + [\text{Cl}^-]}$$

which suggests that the chloride ions are first substituted and that the dipositive complex [Pd(COD)(bpy]$^{2+}$ (COD = 1,5-cyclooctadiene) is formed as an intermediate. The stage of the reaction leading from [Pd(COD)(bpy)]$^{2+}$ to Pd(bpy)Cl$_2$ was independently investigated following the reaction of [Pd(C$_8$H$_{12}$OCH$_3$)(bpy)]$^+$ with H$^+$ and Cl$^-$ in methanol. The experimental results are interpreted considering the formation, during the course of this reaction, of unreactive five-coordinated [Pd(COD)(bpy)Cl]$^+$ in equilibrium with the reactive four-coordinated species [Pd(COD)(bpy)]$^{2+}$.

Introduction

Ligand substitution reactions in coordination compounds occur with a variety of mechanisms, depending on the nature of the reagents, the solvent, and the coordination number. The behavior of d^8 transition metal complexes such as those of Rh$^{\text{I}}$, Pt$^{\text{II}}$, Pd$^{\text{II}}$, and Au$^{\text{III}}$ appears to be simple, in the sense that the substrates generally undergo a bimolecular substitution with transition states in which both the entering and the leaving groups are bonded to the metal.

Kinetic studies of the displacement of polydentate ligands from d^8 transition metal compounds have also been reported in the recent literature.[1-6]

Generally the mechanism involves opening of the chelate ring, followed by competition between ring closure and displacement of the ligand. Therefore simple kinetic expressions are not common even if any single mechanistic path must obviously be consistent with those known for substitutions of unidentate groups.[7]

In this context it was interesting to investigate the displacement of some diolefins from palladium(II) compounds such as Pd(diene)Cl$_2$, (diene = 1,5-cyclooctadiene, dicyclopentadiene, norbornadiene). In the wake of some of our previous results[8,9] we anticipate that the presence of a strong trans-labilizing ligand in the complex, such as a diolefin, should allow the chloride ions to undergo an easier substitution.

The aim of the work is then to investigate the effect of the charge of the complex on the stability of metal–diolefin bonds in palladium(II) compounds and the susceptibility of the coordinated dienes to undergo nucleophilic attack as related to the structure of the diolefin and the formal charge of the metal.

This paper reports a kinetic study of the reaction

$$\text{Pd(COD)Cl}_2 + \text{bpy} \rightarrow \text{Pd(bpy)Cl}_2 + \text{COD}$$

(COD = 1,5-cyclooctadiene; bpy = 2,2'-bipyridyl) in 95% aqueous methanol. Results related to other diene complexes will be described in forthcoming papers.

Experimental Section

Preparation of Compounds. Pd(COD)Cl$_2$[10] and Pd(bpy)Cl$_2$[11] were prepared as reported in the literature. Pd(bpy)Br$_2$ was prepared by treating K$_2$PdBr$_4$[12] with 2,2'-bipyridyl in methanol. Pd(bpy)X$_2$ complexes (X = Cl, Br) were also obtained by treating Pd(COD)X$_2$ with 2,2'-bipyridyl or [Pd(C$_8$H$_{12}$OCH$_3$)(bpy)]PF$_6$ with HX under the same kinetic conditions.

(5-Methoxycyclooctenyl)(bipyridyl)palladium(II) Hexafluorophosphate, [Pd(C$_8$H$_{12}$OCH$_3$)(bpy)]PF$_6$. A 142-mg sample of Pd(COD)Cl$_2$ (0.5 mmol) in CH$_3$OH was treated, under stirring, with 169 mg of AgNO$_3$ (1 mmol). AgCl was filtered off and 78 mg of 2,2'-bipyridyl was added to the yellow solution. After addition of excess of NH$_4$PF$_6$, white needles slowly precipitated and were washed several times with CH$_3$OH.

The ir spectrum of this compound shows a very strong band at 1070 cm^{-1} due to the C–O–CH$_3$ grouping and other bands respectively at 1595, 1605, and 765 cm^{-1} due to the coordinated bipyridyl.[13] A broad band centered at 830 cm^{-1} can be attributed to the PF$_6^-$ anion.[14] The value of Λ_M for a 5×10^{-4} M acetone solution of this salt is 150 Ω^{-1} cm^2 mol^{-1} thus confirming that the compound is a uni-univalent electrolyte. Anal. Calcd for PdC$_{19}$H$_{23}$ON$_2$PF$_6$: C, 41.73; H, 4.2; N, 5.12. Found: C, 41.5; H, 4.1; N, 5.2.

(Cyclooctadiene)(bipyridyl)palladium(II) Bisperchlorate, [Pd(C$_8$H$_{12}$)(bpy)](ClO$_4$)$_2$. A suspension of 70 mg of [Pd(C$_8$H$_{12}$OCH$_3$)(bpy)]ClO$_4$ was treated with an excess of HClO$_4$ in CH$_2$Cl$_2$. The green-yellow product formed was washed several times with acetone.

Its ir spectrum shows a broad band centered at 1080 cm^{-1} due to the ClO$_4^-$ anion whereas other bands at 1600 and 770 cm^{-1} can be attributed to the presence of bipyridyl. The value of Λ_M for a 2.49×10^{-4} M acetone solution of this salt is 294 Ω^{-1} cm^2 mol^{-1} thus confirming that the complex is a bi-univalent electrolyte. Anal. Calcd for PdC$_{18}$H$_{20}$N$_2$Cl$_2$O$_8$: C, 37.95; H, 3.53; O, 22.46; N, 4.91. Found: C, 38.04, H, 3.64; O, 22.43; N, 5.05.

Kinetics. Separate solutions of the complex and reagents were prepared in methanol containing 5% by volume of water. The concentrations of chloride or bromide and proton ions were determined by standard titrimetric methods. The ionic strength was maintained constant at 0.5 M. The reagent solutions were separately brought to reaction temperature and then mixed in the thermostated cell of an OPTICA CF4R double-beam recording spectrophotometer; the kinetics were followed by observing absorption changes in the ultraviolet region of the spectrum. Any single kinetic run was carried out with concentrations of halide and H$^+$ large enough to provide pseudo-first-order conditions. The concentration of palladium(II) complexes, in the reaction mixture, was in the range 1×10^{-4}–2.5×10^{-4} M. Fresh solutions of the complexes were always used.

Pseudo-first-order rate constants, k_{obsd} (s^{-1}), were calculated from slopes of linear plots of ln $(A_\infty - A_t)$ vs. time (A is the optical density).

Results and Discussion

The reaction

$$\text{Pd(COD)Cl}_2 + 2,2'\text{-bpy} \xrightarrow{\text{H}^+,\ \text{Cl}^-} \text{Pd(bpy)Cl}_2 + \text{COD} \qquad (1)$$

proceeds rapidly and smoothly to completion in 95% aqueous methanol at 25 °C in the presence of hydrochloric acid and lithium chloride.

Preliminary results suggested that the rate of olefin displacement by Cl$^-$ from Pd(COD)Cl$_2$ is very slow and does not affect the reaction of the same complex with 2,2'-bipyridyl.

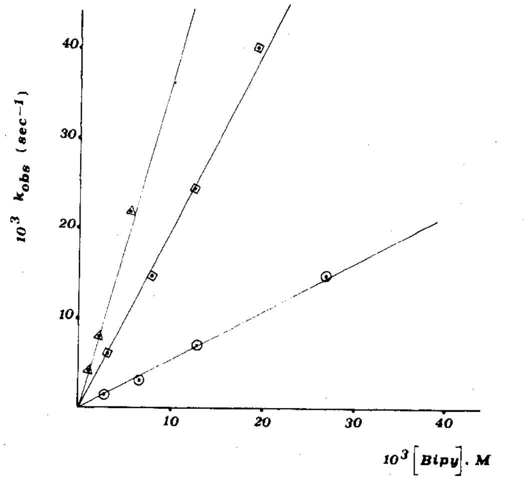


Figure 1. Plot of k_{obsd} (s^{-1}) values against the analytical concentration of bpy at $[Cl^-] = 0.5$ M and variable hydrogen ion concentrations: △, $[H^+] = 4.94 \times 10^{-2}$ M; ◻, $[H^+] = 10^{-1}$ M; ⊙, $[H^+] = 3.05 \times 10^{-1}$ M.

The course of reaction 1 was followed at λ 350 nm and only one stage was detected. At lower wavelengths it was impossible to follow any kinetics because of the large absorption of bipyridyl. However, when $Pd(COD)Cl_2$ and bpy were allowed to react in a 1:1 ratio, $Pd(bpy)Cl_2$ was detected, as final product, from two characteristic bands between 300 and 310 nm.

Kinetic runs were carried out at seven different chloride concentrations and at three hydrogen ion concentrations. Within each set of runs $[Cl^-]$ and $[H^+]$ were kept constant as the analytical concentration of bipyridyl was changed. Pseudo-first-order conditions, with respect to the bipyridyl, were provided by adding a large excess of ligand. In acid media the main species is $bpyH^+$. We found, in fact, that the absorbance and the shape of the ultraviolet spectrum of a methanol solution containing a 10^{-4} M concentration of bipyridyl do not change, between 400 and 220 nm, when the hydrogen ion concentration ranges from 10^{-3} to 5×10^{-1} M. The absorption maxima (~240 and ~300 nm) and the extinction coefficient at 300 nm (1.65×10^4) are also very close to those observed for aqueous solution of $bpyH^+$.[15] The equilibrium to be accounted for in the experimental conditions used is

$$bpyH^+ \rightleftarrows bpy + H^+ \tag{2}$$

which lies far to the left. Although in all cases the concentration of free 2,2′-bipyridyl was smaller than that of the substrate, it was kept constant all during the course of the reaction by the rapid acid equilibrium (2).

In the absence of pK_a values for the base employed in aqueous methanol, we have been forced to use the pK_a value of 4.43, determined in aqueous solutions.[16] This assumption appears to be quite reasonable since it has been found, on the basis of potentiometric determinations, that the basic strength of amines in water is a reliable index of their base strength in aprotic solvents.[17] This should be also true for methanol, which has a greater similarity to water than to nonprotolytic solvents.

Results reported in the recent literature show that the reactivity of bipyridyl solutions toward transition metal complexes could be complicated because both free (bpy) and protonated ($bpyH^+$) species are potential reagents.[11,18] Therefore we tried, first of all, to establish if one or both of the species involved in equilibrium 2 were reagents in reaction 1.

Each set of values of the observed rate constants at $[Cl^-] = 0.5$ M and variable $[H^+]$, at a given proton concentration, gives good straight lines when plotted against the analytical concentration of 2,2′-bipyridyl as shown in Figure 1. The slopes of these plots, *r*, exhibit a linear dependence on the reciprocal of $[H^+]$ with zero intercept (Figure 2). On the basis of these findings and according to equilibrium 2 we conclude that $bpyH^+$ is not a reactive species.

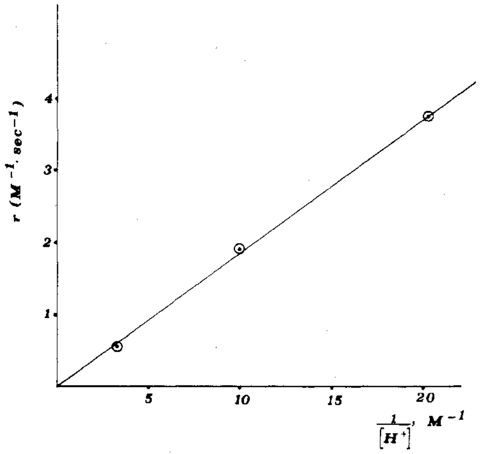
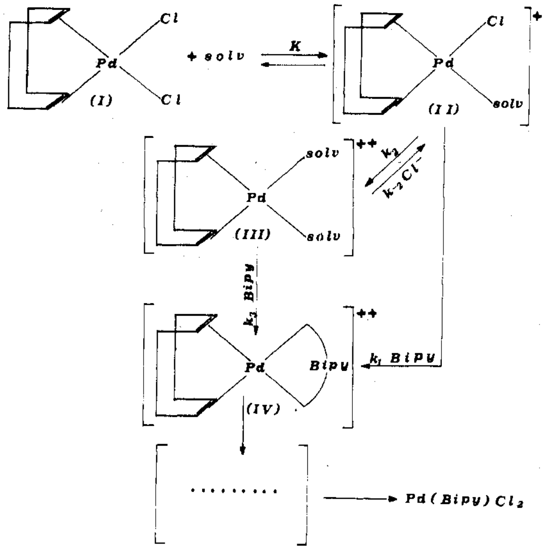


Figure 2. Linear dependence of the slopes of the plots of k_{obsd} (s^{-1}) values against the analytical concentration of bpy, *r*, on $1/[H^+]$ at $[Cl^-] = 0.5$ M.

Scheme I



Experimental rate constants at $[H^+] = 0.5$ M and variable $[Cl^-]$ show a different behavior when plotted against the concentration of free bipyridyl. At higher $[Cl^-]$ no intercept was observed, whereas at lower $[Cl^-]$ well-defined intercepts can be detected (Figure 3). Furthermore gradients of all plots, *s*, depend on the chloride concentration and their inverse, $1/s$, exhibit the linear dependence with a definite intercept, shown in Figure 4, when reported against $[Cl^-]$.

These results indicate an overall rate law of the form

$$k_{obsd} = \left\{\frac{a}{b + c[Cl^-]}\right\}[bpy] + d \tag{3}$$

where *d* is a term dependent on $[Cl^-]$. A reasonable mechanism accounting for these results is shown in Scheme I.

Since only one stage can be detected at λ 350 nm, it may reasonably be assumed either that the step leading from the intermediate IV to $Pd(bpy)Cl_2$ is a fast one or alternatively that, at the wavelength used, no absorption change accompanies this reaction. In any case we can discuss our results as referring to the formation of the intermediate IV, and the

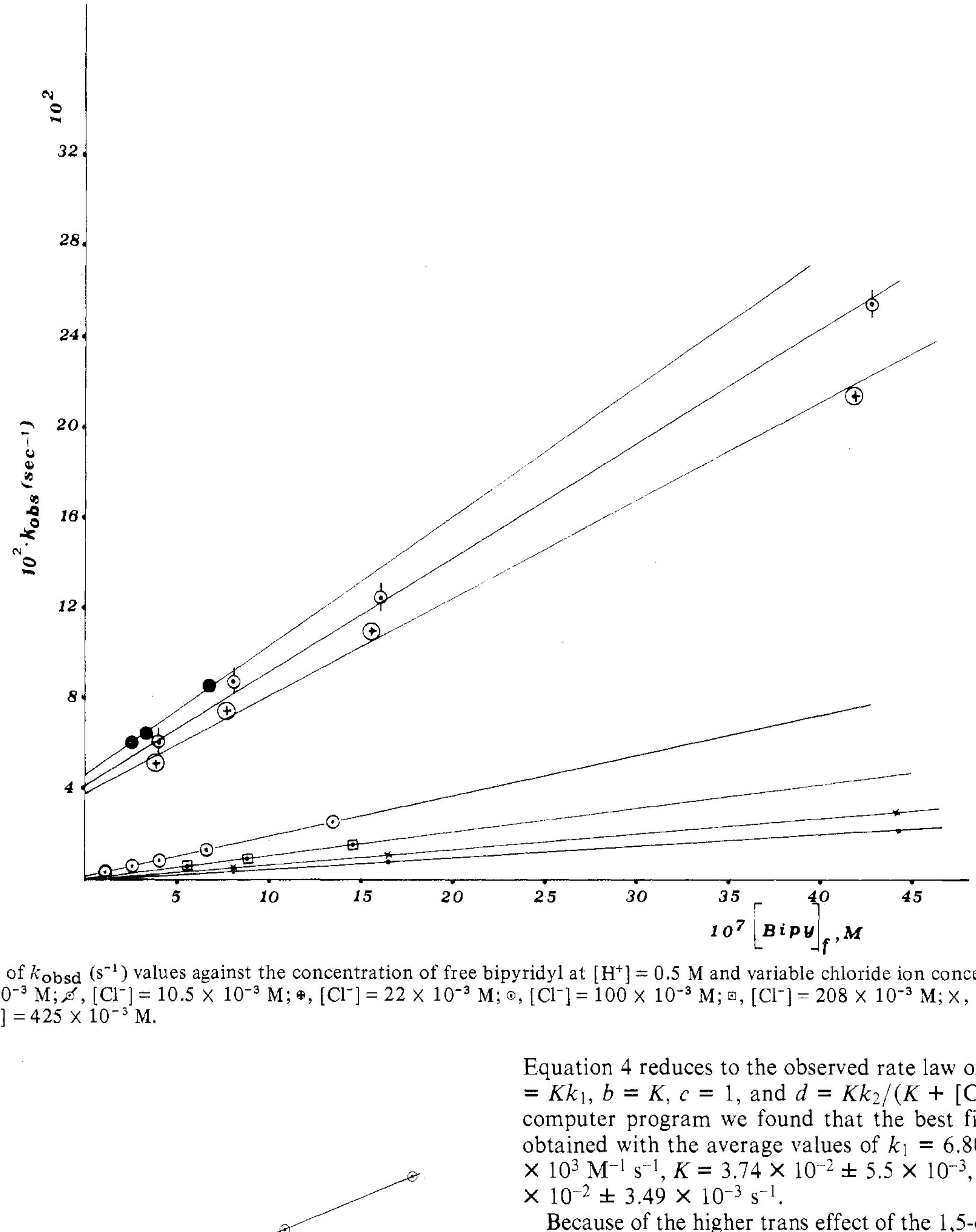


Figure 3. Plot of k_{obsd} (s^{-1}) values against the concentration of free bipyridyl at $[H^+] = 0.5$ M and variable chloride ion concentrations: ●, $[Cl^-] = 5.4 \times 10^{-3}$ M; ⌀, $[Cl^-] = 10.5 \times 10^{-3}$ M; ⊕, $[Cl^-] = 22 \times 10^{-3}$ M; ⊙, $[Cl^-] = 100 \times 10^{-3}$ M; ⊡, $[Cl^-] = 208 \times 10^{-3}$ M; ×, $[Cl^-] = 315 \times 10^{-3}$ M; ·, $[Cl^-] = 425 \times 10^{-3}$ M.

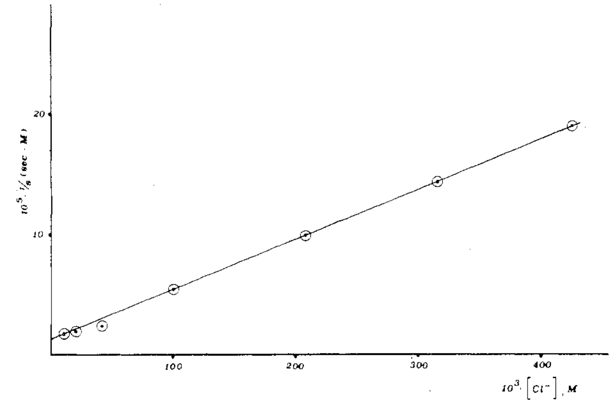


Figure 4. Dependence of the reverse of the slopes of the plots of k_{obsd} (s^{-1}) values against the concentration of free bipyridyl, $1/s$, on $[Cl^-]$ at $[H^+] = 0.5$ M.

derived rate law, at lower $[Cl^-]$ if $k_{-2}[Cl^-] << k_3[bpy]$, takes the form

$$k_{obsd} = \left\{\frac{Kk_1}{K + [Cl^-]}\right\}[bpy] + \frac{Kk_2}{K + [Cl^-]} \tag{4}$$

At higher chloride concentrations the term $k_{-2}[Cl^-]$ becomes more important and the last term of eq 4 becomes negligible. Under these conditions the rate law is the first term of eq 4. Equation 4 reduces to the observed rate law of eq 3 where $a = Kk_1$, $b = K$, $c = 1$, and $d = Kk_2/(K + [Cl^-])$. Using a computer program we found that the best fit of eq 4 was obtained with the average values of $k_1 = 6.80 \times 10^4 \pm 6.7 \times 10^3$ M^{-1} s^{-1}, $K = 3.74 \times 10^{-2} \pm 5.5 \times 10^{-3}$, and $k_2 = 5.55 \times 10^{-2} \pm 3.49 \times 10^{-3}$ s^{-1}.

Because of the higher trans effect of the 1,5-cyclooctadiene in comparison to that of the chloride, it can be considered that in $Pd(COD)Cl_2$ the chloride ions are the most labile.[8,9] The mechanism in Scheme I involves an extensive solvation of the diene complex I leading to the intermediate II. This undergoes a bimolecular substitution of the solvent by 2,2′-bipyridyl, followed by a fast chelation in the cis position to give $[Pd(COD)(bpy)]^{2+}$. This intermediate further reacts and $Pd(bpy)Cl_2$ is formed as final product. The term, independent of [bpy], represents the route of the reaction through intermediate III. A second-order kinetic pattern, relative to the k_1 term, results from the solvolysis of the palladium substrate being faster than the subsequent reaction of the solvated species with the entering nucleophile. This is at variance with the customary behavior of d^8 complexes toward nucleophilic displacements, where solvolysis is the rate-determining step of the solvent-assisted reaction pathway.[7] However this may be due to the fact that bpy is a poor reagent.[11]

Although we did not observe any reactivity of the species $Pd(COD)Cl_2$ toward bipyridyl, we cannot exclude its occurrence. We should think that the extensive solvation of the starting complex coupled with the high reactivity of the in-

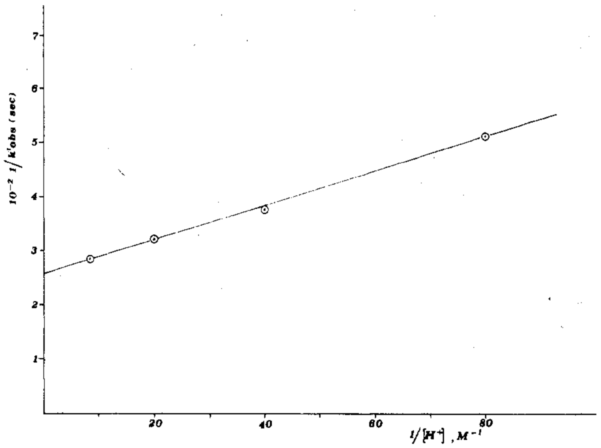


Figure 5. Plot of $1/k'_{\mathrm{obsd}}$ (s) values against $1/[\mathrm{H}^+]$ for reaction 5; $[\mathrm{Cl}^-] = 10^{-2}$ M.

termediate (II), which reflects the lability of the solvent as a leaving group, precludes any possibility of its experimental determination.

The value of k_1 is greater than the analogous second-order rate constant for displacement of chloride by bipyridyl in $\mathrm{PdCl_4}^{2-}$ ($k_1 = 37\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ at 5 °C).[11] This is not unexpected considering the high trans-labilizing power of the diolefin.

Assuming the validity of the mechanism shown in Scheme I, we have kinetic evidence for a novel positively charged palladium(II) complex, $[\mathrm{Pd(COD)(bipy)}]^{2+}$. We could isolate it, as a perchlorate salt, and independent experiments showed that, in methanol solutions, the equilibrium was rapidly established as

$$[\mathrm{Pd(C_8H_{12}OCH_3)(bpy)}]^+ + \mathrm{H}^+ \rightleftarrows [\mathrm{Pd(C_8H_{12})(bpy)}]^{2+} + \mathrm{CH_3OH}$$

Thus, in order to study the stage of the reaction leading from the intermediate IV to $\mathrm{Pd(bpy)Cl_2}$, we carried out a kinetic investigation on the reaction

$$[\mathrm{C_8H_{12}OCH_3)Pd(bpy)}]^+ + \mathrm{H}^+ + \mathrm{Cl}^- \rightarrow \mathrm{Pd(bpy)Cl_2} + \mathrm{COD} + \mathrm{CH_3OH} \qquad (5)$$

in 95% aqueous methanol.

The absorption change during the course of reaction 5 is practically negligible in the range 400–320 nm. However between 310 and 300 nm there is a sufficient spectral variation to allow kinetic calculations to be done. Final spectra, in this region, show two bands characteristic of $\mathrm{Pd(bpy)Cl_2}$.

Reaction 5 proceeds through only one stage and does not occur in the presence of Cl^- only; however, it goes to completion if H^+ is also present.

The plot of $1/k'_{\mathrm{obsd}}$ (s) values against $1/[\mathrm{H}^+]$, where k'_{obsd} are the experimental rate constants for reaction 5 at $[\mathrm{Cl}^-] = 10^{-2}$ M and variable concentrations of H^+, is shown in Figure 5. Experimental rate data at two different constant concentrations of hydrogen ion and variable $[\mathrm{Cl}^-]$ are plotted against $[\mathrm{Cl}^-]$ in Figure 6, giving an irregular plot suggesting a prior increase of the rate with $[\mathrm{Cl}^-]$ and a subsequent decrease at higher chloride concentrations.

In order to explain these results we propose the mechanism given in Scheme II.

Since no intermediates could be detected in the course of the reaction and if we introduce a simplification by applying the steady-step approximation to the species D, the following kinetic expression can be derived from Scheme II

$$k'_{\mathrm{obsd}} = \frac{(k_3 + k_2)k_1K[\mathrm{H}^+][\mathrm{Cl}^-]}{k_{-1}K[\mathrm{H}^+] + (k_{-1}K' + k_2 + k_3)K[\mathrm{Cl}^-][\mathrm{H}^+] + K'K(k_2 + k_3)[\mathrm{H}^+][\mathrm{Cl}^-]^2 + (k_2 + k_3)[\mathrm{Cl}^-] + k_{-1}} \qquad (6)$$

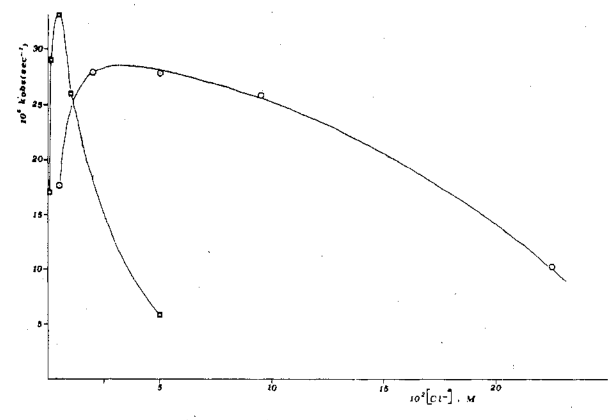
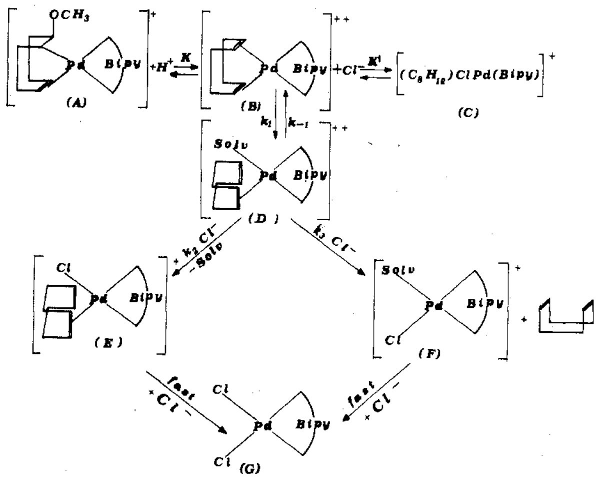


Figure 6. Plots of k'_{obsd} (s^{-1}) values against $[\mathrm{Cl}^-]$ for reaction 5: ○, $[\mathrm{H}^+] = 2.5 \times 10^{-2}$ M; □, $[\mathrm{H}^+] = 2.05 \times 10^{-1}$ M.

Scheme II



This equation accounts for the dependence of the rate values on $[\mathrm{H}^+]$ at constant chloride concentration.

The shape of the plots of k'_{obsd} against $[\mathrm{Cl}^-]$ at constant $[\mathrm{H}^+]$ in Figure 6 should reflect the different weight of all of the terms in eq 6 with increasing chloride concentration. Interestingly the shift of the plot in Figure 6 with the increase of the hydrogen ion concentration parallels the shift of the equilibrium $\mathrm{H}^+ + \mathrm{A} \rightleftarrows \mathrm{B}$ toward the diene form.

Since A, in Scheme II, is an unreactive species toward Cl^- and if we consider the dependence of the rate on $[\mathrm{H}^+]$ in Figure 6, we can reasonably assume that the diene complex B can react forming the intermediate D. This may react selectively via two paths depending on $[\mathrm{Cl}^-]$, and E and F species may be obtained. Fast reactions lead, then, to the final product $\mathrm{Pd(bpy)Cl_2}$. The reduction of the rate at higher $[\mathrm{Cl}^-]$ is thought to depend on the formation of an unreactive chloro complex C via a fast preequilibrium.

We have spectrophotometric evidence which suggests a rapid interaction of species B with Cl^-. When, in fact, complex A is dissolved in acid media, there is a change of the ultraviolet spectrum, since the equilibrium $\mathrm{A} + \mathrm{H}^+ \rightleftharpoons \mathrm{B}$ is rapidly established in solution. (On the other hand, complex B was isolated as a perchlorate salt when $[\mathrm{Pd(C_8H_{12}OCH_3)(bpy)}]\mathrm{ClO_4}$ was allowed to react in methylene chloride with $\mathrm{HClO_4}$.) No more spectral variation is observed above $[\mathrm{H}^+] = 0.1$ N indicating that in these conditions the equilibrium is shifted toward B. Furthermore when Cl^- is added to an acid solution containing B and a 0.1 N concentration of H^+, a rapid and consistent variation of the spectrum is still observed indicating an interaction of complex B with the chloride ion (Figure 7). The subsequent slow reaction leads to $\mathrm{Pd(bpy)Cl_2}$. However on the basis of these findings we cannot say if the

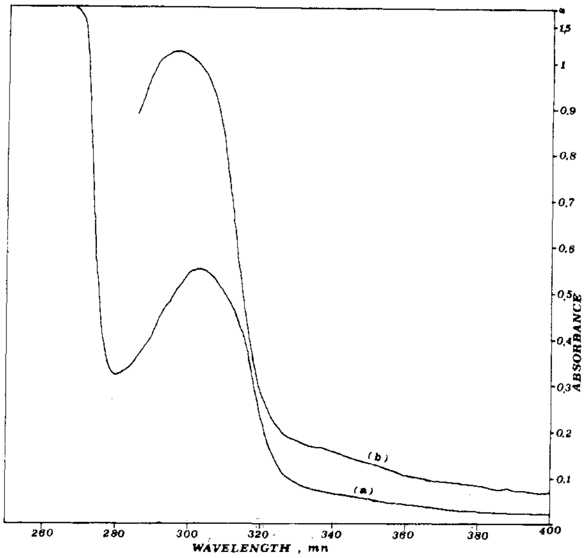


Figure 7. Uv spectra (a) of a methanol solution of a 3 × 10^{-5} M concentration of $[(C_8H_{12}OCH_3)Pd(bpy)]^+$ in 0.1 N $HClO_4$ and (b) of a methanol solution of the same concentration of the complex dissolved in 0.1 N $HClO_4$ containing an excess of Cl^-.

halide attack occurs at the palladium center or at the coordinated double bond of B.

Five-coordinated palladium(II) complexes are very well-known and their formation is likely to be favored by poorly electronegative ligands.

Complexes of the type $[PdL_4X]^+$ [19] (L = N,N′-disubstituted thio- and selenoureas; X = halogen) or $[Pd(L\text{-}L)_2X]^+$ [20] (L-L = $Ph_2AsCH_2CH_2AsPh_2$; X = halogen) have been obtained and equilibrium constant studies[21] on the system

$$[Pd(L\text{-}L)_2]^{2+} + X^- \rightleftarrows [Pd(L\text{-}L)_2X]^+$$

show that the trend to their formation parallels the polarizability of the ligand X^-. π bonding also favors five-coordination.

Chloropalladation of unsaturated organic substrates is, on the other hand, an important reaction in organopalladium chemistry. Additions of Pd–Cl to allenes,[22] olefins,[23] acetylenes,[24] methylcyclopropanes,[25] dicyclopropylmethane,[26] spiropentane,[27] and conjugated dienes[28] have been reported. It is generally believed that cis addition of Pd–Cl to the unsaturated substrates occurs in nonpolar solvents when an excess of halide is absent. Many catalytic processes[23,29] and exchange and isomerization reactions[30] are thought to proceed via σ-bonded chloro complexes.

The susceptibility of a coordinated olefin to react with a nucleophile seems to depend on the basicity of the ligand. Complexes of the type (diene)MX_2 (diene = cyclooctadiene, norbornadiene, dicyclopentadiene; M = Pd, Pt; X = Cl, Br, I) readily undergo, in fact, nucleophilic attack, at the coordinated olefin, by the conjugate bases of alcohols,[31] keto esters,[32] malonic esters,[32] β-diketones,[33] carboxylic acids,[34] and amines[35] to give complexes containing enyl type ligands. Many of these compounds have been shown to regenerate the complexes (diene)MX_2 on treatment with hydrohalic acids, HX, without any substitution of the basic group, bonded to the organic moiety, by X^-.

Since all of our attempts to isolate any intermediate of reaction 5 were unsuccessful, we carried out additional kinetic experiments on the reaction

$$[(C_8H_{12}OCH_3)Pd(bpy)]^+ + H^+ + Br^- \rightarrow Pd(bpy)Br_2 + COD + CH_3OH \qquad (7)$$

Plots of k_{obsd} against the halide concentrations, in Figure 8, allow a comparison of the kinetic results relative to the reaction

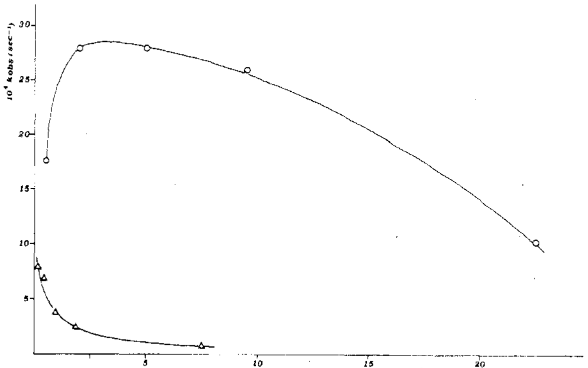


Figure 8. Comparison of the plots of k_{obsd} (s^{-1}) values against $[X^-]$ at $[H^+] = 2.5 \times 10^{-2}$: ○, $X^- = Cl^-$; △, $X^- = Br^-$.

of $[(C_8H_{12}OCH_3)Pd(bpy)]^+$ with Cl^- and Br^- at $[H^+] = 2.5 \times 10^{-2}$ M. It is already known that the bromide ion is better than the chloride in nucleophilic substitutions of square-planar complexes[7] and therefore the lower reactivity of Br^- in comparison to that of Cl^- and the different shapes of the plots reported in Figure 6 would suggest that the value of the equilibrium constant K' in Scheme II is higher for bromide than for chloride. This order parallels the polarizability of the ligands and supports the hypothesis that an unreactive five-coordinated compound is formed by interaction of complex B with the halide ions at least in a predominant way.

Kinetic evidences for the accumulation of a reactive five-coordinated reaction intermediate in nucleophilic substitutions of Rh(I) complexes[36] have been reported and similarly complexes of the type $Pt(C_2H_4)(L\text{-}L)Cl_2$ (L-L = 2,2′-bipyridyl, 1,10-phenanthroline, *N,N,N′,N′*-tetramethylethylenediamine, *N,N′*-dicyclopropylbiacetyl diimine, *N,N′*-di-*p*-tolylbiacetyl diimine, and *N,N′*-di-*p*-tolylacenaphthenequinone diimne) have been obtained.[37]

Conversely, if our considerations are correct, we present, in this paper, the first evidences suggesting the formation of an unreactive five-coordinated complex, as intermediate, in substitution reactions of square-planar complexes.

We recall, in this regard, that the stability of metal–olefin complexes depends on the oxidation state of the metal and its effective nuclear charge. When, in fact, the positive charge of the complex increases, the π bonding from the metal to the olefin will decrease and the replacement of the olefin becomes easier. In this particular case the favorable geometry of the chelated 1,5-cyclooctadiene further contributes also to stabilize the five-coordinated complex.

Accordingly the path leading to the substitution of the olefin by the halide either could be controlled by the solvent or could be a dissociative one.

Evidence supporting a dissociative mechanism in square-planar complexes reactions is now increasing in the literature. Thus, isomerization reactions of *cis*-$[PtL_2RCl]$ (L = triethylphosphine, R = aryl group) proceeds through a three-coordinated intermediate[38,39] and similarly insertion reactions of olefin into the Pt–H bond of *trans*-$[Pt(PEt_3)_2H(NO_3)]$ are thought to proceed through a three-coordinate species.[40]

Finally we observe that the path for displacement of the diene involves competition between ring closure and displacement of the ligand. A similar mechanism was also proposed for the displacement of 1,5-cyclooctadiene from $Mo(CO)_4(C_8H_{12})$.[41]

Acknowledgment. We thank the Italian CNR for its financial support and Professor G. Ricca for all computer calculations.

Registry No. $[Pd(C_8H_{12}OCH_3)(bpy)]PF_6$, 59301-92-7; $[Pd(C_8H_{12})(bpy)](ClO_4)_2$, 59350-31-1; $Pd(COD)Cl_2$, 12107-56-1; 2,-

2′-bpy, 366-18-7; [$Pd(C_8H_{12}OCH_3)(bpy)]ClO_4$, 59301-93-8; Cl^-, 16887-00-6; Br^-, 24959-67-9.

Supplementary Material Available: Listings of specific kinetic data used to estimate kinetic constants reported in the paper (7 pages). Ordering information is given on any current masthead page.

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Relationship between the Singlet–Triplet Splitting and the Cu–O–Cu Bridge Angle in Hydroxo-Bridged Copper Dimers

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Received March 4, 1976 AIC60170U

Magnetic susceptibility and structural data for two additional di-μ-hydroxo-bridged copper(II) complexes are now available. The new data support the linear correlation between the singlet–triplet splitting, $2J$, and the Cu–O–Cu bridge angle which has been observed. Magnetic susceptibility data for $[Cu(bpy)OH]_2(ClO_4)_2$ (bpy = 2,2′-bipyridine), for $[Cu(tmen)OH]_2(ClO_4)_2$ (tmen = *N,N,N′,N′*-tetramethylethylenediamine), and for one complex for which there are no structural data, $[Cu(tmpd)OH]_2(ClO_4)_2$ (tmpd = *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine), yield $2J$ values of 93, −360, and 130 cm^{-1}, respectively. The complexes exhibit triplet-state EPR spectra, and the infrared spectra have been analyzed in terms of the coordination of the perchlorate ion.

Introduction

An extensive study of the structural and magnetic properties of di-μ-hydroxo-copper(II) dimers has yielded a linear correlative relationship between the Cu–O–Cu bridge angle and the exchange parameter $2J$.[1-4] The latter is defined by the Hamiltonian

$$H = -2J\Sigma\vec{S}_1\cdot\vec{S}_2$$

The systems that have been investigated have the general formula $(CuLOH)_2^{2+}$, where L is the bidentate ligand 2,2′-bipyridine (bpy), 2-(2-dimethylaminoethyl)pyridine (dmaep), 2-(2-ethylaminoethyl)pyridine (eaep), *N,N,N′,N′*-tetraethylethylenediamine (teen), or *N,N,N′,N′*-tetramethylethylenediamine (tmen). The $2J$ values that have been observed in the series range from +172 to −509 cm^{-1}, and the Cu–O–Cu angles range from 95.6 to 104.1°. Since structural data for two additional members of the series, $[Cu(bpy)OH]_2(ClO_4)_2$[5] and $[Cu(tmen)OH]_2(ClO_4)_2$,[6] have become available recently, it was of interest to compare their exchange coupling constants with the angles at the bridging oxygen atoms. This comparison is reported here. In addition, the magnetic properties of di-μ-hydroxo-bis(*N,N,N′,N′*-tetramethyl-*o*-phenylenediamine)dicopper(II) perchlorate, $[Cu(tmpd)OH]_2(ClO_4)_2$, have been determined, and the properties of this compound are described herein.

Experimental Section

Di-μ-hydroxo-bis(*N,N,N′,N′*-tetramethyl-*o*-phenylenediamine)dicopper(II) perchlorate was prepared by adding *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine to a solution of hydrated copper(II) perchlorate dissolved in the minimum amount of water. The dark