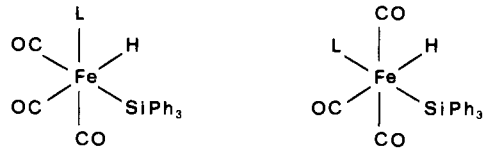
coupling constants). The proton, bonded to the phosphorus atom, was not found in the NMR spectrum; this behavior is common to these phosphonium salts.[9]

The hydrido ligand band in the complexes $[Fe(CO)_4(H)SiPh_3]$, I, and II, shows τ_H shifts to higher field by increasing the number of phosphine ligands (Table I); this is in agreement with the increase of electronic density of the iron atom which shields the proton.

The reactivity of $[Fe(CO)_4(H)SiPh_3]$ with the phosphine ligands shows that the paths of reaction are different according to the ligand basicity. With very basic phosphine ligands (PEt_3 in apolar solvents) $[Fe(CO)_4(H)SiPh_3]$ reacts as an acid and gives the ionic complexes III. The reaction mechanism of the less basic ligands is shown in Scheme I.

The effect of the CO pressure and of the ligand L concentration on the $[Fe(CO)_4L]/[Fe(CO)_3L_2]$ ratio (Figures 1 and 2) is in accord with Scheme I. When L = 1,2-bis(diphenylphosphino)ethane, the intermediate I, formed in the first step of the reaction, gives by chelation the disubstituted complex II without elimination of $HSiPh_3$; in the presence of carbon monoxide the substitution of this ligand is unpaired and the formation of $[Fe(CO)_3PPh_2CH_2CH_2PPh_2]$[10] with elimination of $HSiPh_3$ is observed.

The first step of Scheme I is an equilibrium reaction and indicates that the dissociation of an Fe–CO bond is an easy process at room temperature. Therefore the substitution of a CO with an alkene in the catalytic hydrosilylation does not need photochemical activation. On the other hand the insertion of an alkene in the metal–H bond and the subsequent elimination of the hydrosilylated olefin are very fast reactions[11] and do not need photochemical activation. On the basis of the present results the strong trans effect of the hydrido ligand[12] gives a substituted derivative of A structure. The trans position of the alkene and of the hydrido ligand prevents the insertion reaction. Therefore the photochemical action should isomerize the A structure into the C structures and allow the insertion



C

of an alkene in the Fe–H bond, activating the catalytic process. Photochemical isomerization of octahedral complexes is very common in the literature;[13] in particular photochemical cis ⇌ trans isomerizations are observed for $M(CO)_4X_2$ and $M(CO)_2L_2X_2$ complexes[14] (M = Fe, Ru, Os; L = phosphine ligands; X = halogens).

Summary

The reaction between $[Fe(CO)_4(H)SiPh_3]$ and different nucleophiles L (L = CO, PPh_3, $AsPh_3$, $SbPh_3$, $PPh_2CH_2CH_2PPh_2$, or $P(C_2H_5)_3$) has been studied. The structure of the complex $[Fe(CO)_3(H)(SiPh_3)PPh_3]$ (I) is assigned on the basis of spectroscopic evidence; the complexes $[Fe(CO)_2(H)(SiPh_3)PPh_2CH_2CH_2PPh_2]$ (II) and $[Fe(CO)_4SiPh_3]^-[HP(C_2H_5)_3]^+$ (III) are isolated and characterized. A reaction mechanism is proposed on the basis of the reaction product and of the effect of the basicity and concentration of L.

Acknowledgment. Thanks are expressed to Dr. G. Reichenbach for useful discussion. This work was supported in part by the National Research Council of Italy (CNR).

Registry No. I, 81802-57-5; II, 81802-58-6; III, 81845-35-4; $Fe(CO)_4HSiPh_3$, 33361-69-2; $Fe(CO)_3(H)(SiPh_3)AsPh_3$, 81802-59-7; $Fe(CO)_3(H)(SiPh_3)SbPh_3$, 81802-60-0; $Fe(CO)_2(PPh_2CH_2PPh_2)PPh_3$, 81802-61-1; $Fe(CO)_4PPh_3$, 35679-07-3; $Fe(CO)_3(PPh_3)_2$, 21255-52-7; $Fe(CO)_4AsPh_3$, 35644-25-8; $Fe(CO)_4SbPh_3$, 35917-16-9; $Fe(CO)_3(AsPh_3)_2$, 20516-72-7; $Fe(CO)_3(SbPh_3)_2$, 20516-73-8.

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Nuclear Magnetic Resonance Studies of the Solution Chemistry of Metal Complexes. 18. Complexation of Palladium(II) by Glycyl-L-histidine and Glycyl-L-histidylglycine

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Metal-induced ionization of hydrogen from amide (peptide) nitrogens with subsequent metal binding to the deprotonated nitrogens is a characteristic feature in the complexation of palladium(II) by small peptides.[1-4] Thus, at neutral pH, dipeptide ligands such as glycylglycine generally react with Pd(II) to form planar complexes with the metal coordinated at the amino and deprotonated peptide nitrogens and the carboxylate oxygen. Tripeptide ligands form planar complexes, with Pd(II) coordinated at the amino group, two deprotonated peptide nitrogens, and the carboxylate group.

The complexation of Pd(II) by the dipeptide glycyl-L-histidine (Gly-His) is thought to deviate from this general pattern.[1] The Gly-His complex of Pd(II) is presumed to have a structure similar to that of the Gly-His complex of Cu(II), which has been shown by X-ray crystallographic analysis to be approximately square planar with the copper coordinated by the amino nitrogen, the deprotonated peptide nitrogen, and the imidazole 1-nitrogen of one dipeptide ligand and the carboxylate group of another.[5,6]

In the present paper, we describe the results of ^1H NMR and potentiometric studies of the complexation of Pd(II) by Gly-His and Gly-His-Gly. In order to elucidate the mode of binding in these complexes, we have included in this study ^1H NMR measurements on the hydrogens of the peptide groups.

Experimental Section

Gly-His and Gly-His-Gly were used as received from Sigma Chemical Co. K_2PdCl_4 was obtained from Alfa Inorganics.

Potentiometric titrations were performed at 25 °C on solutions containing 0.005 M peptide, 0.005 M K_2PdCl_4, and 0.154 M NaCl. The pH was measured with a Fisher Model 620 pH meter equipped with a Fisher microcombination electrode. The pH meter was calibrated with pH 4.00, 7.00, and 10.00 buffers.

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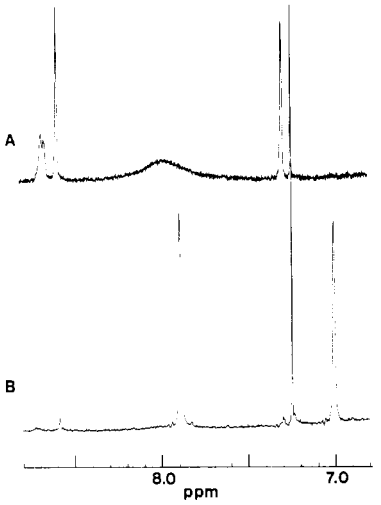


Figure 1. High-frequency regions of the 400-MHz ^1H NMR spectra of (A) 0.030 M Gly-His in H_2O solution at pH 2.20 and (B) 0.030 M Gly-His plus 0.030 M K_2PdCl_4 in H_2O solution at pH 2.06. Both solutions contain 0.154 M NaCl.

^1H NMR spectra were obtained on Bruker WH-200/DS and WH-400/DS spectrometers. Spectra were measured for D_2O and for H_2O solutions of the free ligands in 0.154 M NaCl and for solutions of the ligands plus an equimolar concentration of K_2PdCl_4 in 0.154 M NaCl. Spectra of D_2O solutions were measured by the pulsed Fourier transform method. Chemical shifts were measured relative to internal *tert*-butyl alcohol (1.230 ppm vs. DSS). The rapid-scan cross-correlation method[7] was used to obtain spectra of the 6.5–9.5-ppm region for the H_2O solutions. Chemical shifts were measured relative to $CHCl_3$ in an external capillary (7.244 ppm vs. DSS). Susceptibility changes as the solution pH was varied were shown to be small, and no corrections were made.

Results and Discussion

Glycyl-L-histidine. The titration of a solution containing 0.005 M Gly-His and 0.005 M K_2PdCl_4 with NaOH yields an end point near pH 6 after the addition of 2 equiv of base. Since Gly-His has only a single acidic hydrogen which is titrated with a pK_A of 8.25,[8] and since Pd(II) does not bind OH^- until pH > 8 in solutions of dipeptides,[4] this indicates complexation of Pd(II) by Gly-His with the displacement of two acidic hydrogens. Martin and co-workers[1,2] have shown these to be the ammonium and peptide hydrogens. To elucidate the mode of binding in the complex, we measured ^1H NMR spectra for Gly-His free in solution and in solutions containing equimolar K_2PdCl_4.

Figure 1A shows the 6.5–9.5-ppm region of the spectrum, measured by the rapid-scan cross-correlation method,[7] of a pH 2.20 solution of 0.030 M Gly-His. Of particular interest is the doublet at 8.67 ppm for the peptide proton. The other resonances are for the C2–H (8.588 ppm) and C4–H (7.297 ppm) protons of the imidazole ring, the ammonium protons (8.0 ppm), and $CHCl_3$ (7.244 ppm) in an external capillary. As the pH of the solution is increased, the doublet for the peptide proton shifts to lower frequency, and in the pH 6–8 region, it broadens and disappears due to exchange with solvent protons.

In contrast, when the solution contains an equimolar amount of K_2PdCl_4, the spectrum consists of two sets of resonances at very low pH. One set has chemical shifts identical with those observed for the solution of free Gly-His. The second set is for complexed Gly-His and consists of resonances for only the imidazole C2–H and C4–H protons. As the pH is increased, the relative intensity of the resonances for free Gly-His decreases until at pH 2.2 they are no longer observable. Figure 1B shows the spectrum obtained at pH 2.06. The absence of a resonance for the peptide hydrogen provides direct evidence that, by pH 2.2, all of the Gly-His is complexed, with the peptide nitrogen deprotonated and bonded to the Pd(II). Additional evidence is provided by the 0.36-ppm shift of the resonance for the proton on the α-carbon of the histidine residue to lower frequency. These results indicate the pK_A for Pd(II)-induced deprotonation of the peptide nitrogen to be <1.5, which is somewhat lower than observed by Wilson and Martin for simple peptides.[1]

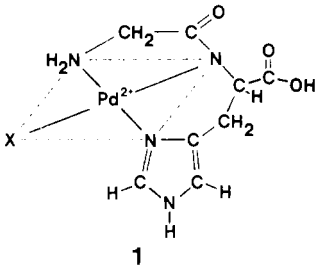
Table I. Coupling Constants[a] and Rotamer Populations

compd	pD	J_{AX}[b]	J_{BX}	t[c]	g[c]	h[c]
Gly-His	5.15	5.0	8.0	51	24	25
Pd(II)-(Gly-His)	5.07	4.0	3.7	12	15	73
Gly-His-Gly	6.62	6.4	7.4	46	37	17
Pd(II)-(Gly-His-Gly)	6.00	3.9	3.7	12	14	74

[a] For coupling between the two nonequivalent methylene protons and the methine proton of the His $CHCH_2$ spin system. [b] A was assigned to the higher frequency resonance in the AB pattern for the methylene protons.[4] [c] In percent; calculated with the methodology developed in ref 4.

The large change in the chemical shift of the resonances for the imidazole C2–H and C4–H protons upon complexation indicates binding to the imidazole ring. The change for the C2–H resonance is considerably larger than that for the C4–H resonance, consistent with binding to the imidazole 1-nitrogen, as found in the Cu(II) complex.[5,6] Molecular models show that the amino nitrogen, the deprotonated peptide nitrogen, and the imidazole 1-nitrogen of rotamer h in Figure 2 can simultaneously occupy three of the four coordination positions around square-planar Pd(II). From the coupling constants for the histidine $CHCH_2$ spin system, rotamer h is calculated[4] to have a population of 73% as compared to 25% for the free ligand at the same pD (Table I).

As the pD of a D_2O solution of the Pd(II)–Gly-His complex is increased from 1 to 6.5, the resonances for the proton on the α-carbon of the histidine residue and the C2–H and C4–H protons of the imidazole ring shift to lower frequency by 0.33, 0.05, and 0.10 ppm, respectively, indicating titration of an acidic group in the complex. Over this same pD region, the carboxylic acid group of the free ligand is titrated, causing low-frequency shifts for these same resonances of 0.33, 0.05, and 0.07 ppm, respectively. Thus, in the complex that forms at low pH, Pd(II) is bonded to the amino, deprotonated peptide, and imidazole 1-nitrogens, with the carboxylate group protonated (structure **1**). Presumably the fourth coordination



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position is occupied by either D_2O (H_2O) or Cl^-.[4] From the pH dependence of the chemical shift for the C4–H resonance in the correlation spectra measured for complexed and free Gly-His in H_2O solution, the pK_A values of the carboxylic acid groups of complexed and free Gly-His are calculated[9] to be 3.9 and 2.7, respectively.

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(10) AB patterns were observed for the Gly methylene protons in all the spectra of both free and Pd(II)-complexed Gly-His and Gly-His-Gly.

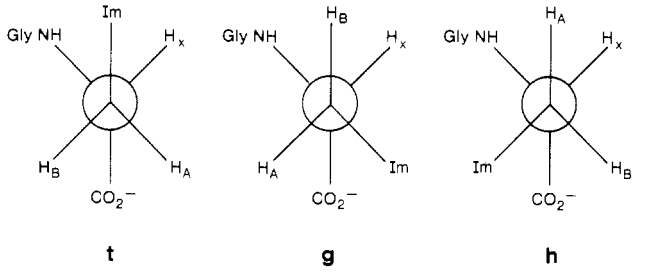


Figure 2. Staggered rotamers along the C_α–C_β bond of the histidine residue of Gly-His.

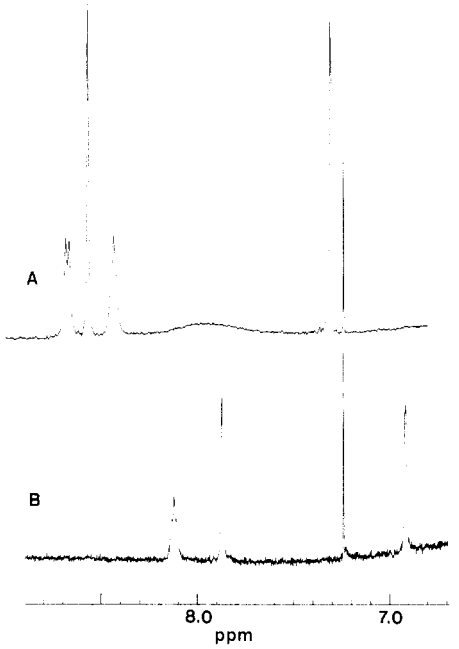


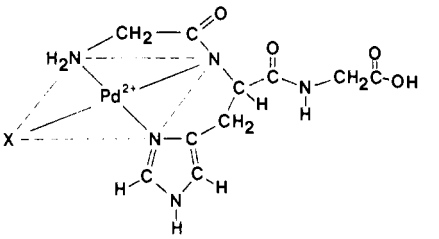
Figure 3. High-frequency regions of the 400-MHz ^1H NMR spectra of (A) 0.030 M Gly-His-Gly in H_2O solution at pH 2.91 and (B) 0.030 M Gly-His-Gly plus 0.030 M K_2PdCl_4 in H_2O solution at pH 2.98. Both solutions contain 0.154 M NaCl.

At pD above 6.9, additional resonances that are quite broad appear in the spectrum, indicating a change in the nature of the complex. It has not been possible to characterize the high-pH complexes from the NMR data.

Glycyl-L-histidylglycine. The titration curve for a solution containing 0.005 M K_2PdCl_4 and 0.005 M Gly-His-Gly does not show a sharp end point as observed in the analogous experiment with Gly-His. The solution pH is 2.5 initially, 3.5 after the addition of 1 equiv of base, 5.0 after the addition of 2 equiv, and 9.5 after the addition of 3 equiv.

The peptide proton region of the ^1H NMR spectrum of a pH 2.91 solution of Gly-His-Gly is shown in Figure 3A. The doublet at 8.72 ppm is due to the proton on the histidyl peptide nitrogen, and the unresolved triplet at 8.48 ppm is due to the glycine peptide proton. The resonances at 8.58, 7.31, and 7.244 ppm are due to the histidyl C2–H and C4–H protons and external $CHCl_3$, respectively. The same region for a pH 2.98 solution containing equimolar K_2PdCl_4 is shown in Figure 3B. The absence of the doublet for the histidyl peptide proton indicates Pd(II) binding to the deprotonated histidyl peptide nitrogen. The triplet at 8.12 ppm indicates the glycine peptide nitrogen is still protonated. This triplet is observed up to pH 6. As we found for Gly-His, the C2–H and C4–H resonances of Gly-His-Gly experience a large shift to lower frequency upon complexation, consistent with binding of Pd(II) to the imidazole 1-nitrogen. The coupling constants for the histidyl $CHCH_2$ spin system (Table I) indicate the population of conformation h (Figure 2) to be 74% for the complexed ligand.

The methylene protons of the glycine residue of Pd(II)-complexed Gly-His-Gly give an AB pattern[9] that shifts 0.30 ppm to lower frequency as the pD is increased from 1.5 to 7, indicating titration of the carboxylic acid group in the complex. Above pH 7, additional resonances that are quite broad appear in the spectra, indicating a change in the complex. The above data indicate that Pd(II) is bonded to the amino, deprotonated histidyl peptide, and imidazole 1-nitrogens while the glycine peptide nitrogen and the carboxylate group are protonated in the complex that forms at low pH (structure **2**). As the pH



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is increased, the carboxylic acid is titrated with the total consumption of 2 equiv of base at pH 5. The triplet for the glycine peptide proton (Figure 3) of both free and complexed Gly-His-Gly also shifts to lower frequency as the carboxylic acid is titrated from which pK_A values of 3.7 and 3.0 were calculated[9] for the complexed and free ligand.

In conclusion, this study has shown that the imidazole 1-nitrogen of histidine in peptides is a strong binding site for Pd(II). In the Gly-His complex, Pd(II) binds to the amino, deprotonated peptide, and imidazole 1-nitrogens, while the carboxylic acid group is free. In contrast, simple dipeptides bind Pd(II) through the amino and deprotonated peptide nitrogens and the carboxylate group. In the Gly-His-Gly complex, Pd(II) also binds to the amino nitrogen, deprotonated peptide nitrogen, and imidazole 1-nitrogen donor set, in preference to binding to the amino nitrogen, two deprotonated peptide nitrogens, and the carboxylate oxygen as is the case with other tripeptides. The strength of the complexes formed with the amino nitrogen, deprotonated peptide nitrogen, and imidazole 1-nitrogen donor set is further indicated by the complete formation of the complexes by pH 2.2, a somewhat lower pH than for Pd(II) complexes of simple peptides.

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Registry No. Gly-His, 2489-13-6; Gly-His-Gly, 7758-33-0; Pd, 7440-05-3.

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Kinetic Investigation of the Equilibrium between Mono- and Bis(1,10-phenanthroline)copper(I) in Aqueous and Sodium Dodecyl Sulfate Solution

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As part of our continuing investigation of the oxidation of $Cu(phen)_2^+$ by inorganic reagents in micellar solution[1,2] we

