the vanadate to a sizable extent, the peptide group attains a key position, and chelate formation through the additional use of the amino and/or carboxylate groups is likely to occur. Since N-protected dipeptides and also H-val-asp-OH (with a sterically demanding isopropyl group in the vicinity of the amino function) do not coordinate, the N-terminal end appears to participate. Considering the peptide linkage, potential candidates for vanadate coordination are the carbonyl oxygen and the amide nitrogen. Although the lone pair of the latter takes part in double bonding to the adjacent carbonyl carbon, there are strong arguments for its invovlement in complex formation, arising from the observation that H-gly-pro-OH and H-gly-sar-OH (with a tertiary amide function in the peptide linkage) do not undergo complex formation.

In conclusion, we have shown, using ^{51}V NMR spectroscopy, that vanadate forms complexes with dipeptides at physiological pH, which may model vanadium binding sites in proteins. The complexes that are mononuclear at least in the case of H-gly-asp-OH, although comparatively weak, are stronger by 1-2 orders of magnitude than thosse which have been documented with oxalate and lactate.[18] The peptide function and the N-terminal amino group are involved in coordination (C″ in Chart I), but appropriate side-chain functions of the C-terminal amino acid, such as a hydroxyl group, may also participate. The low-field shift of the ^{51}V resonance relative to the vanadates and also relative to various complexes with hydroxy carboxylates[18,26] is in accord with at least one nitrogen in the first coordination sphere.[14,15] Similar downfield shifts have been reported for the vanadate complexes formed with tris(hydroxymethyl)aminomethane[27] and several derivatives of ethanolamine,[19] for which N-O coordination has been proposed.

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Registry No. gly, 56-40-6; asp, 56-84-8; ser, 56-45-1; Z-gly-glu, 3916-39-0; Z-glu-tyr, 988-75-0; val-asp, 20556-16-5; gly-pro, 704-15-4; gly-sar, 29816-01-1; $H_2VO_4^-$, 34786-97-5; $H_2V_2O_7^{2-}$, 103884-11-3; $V_4O_{12}^{4-}$, 12379-27-0; $V_5O_{15}^{5-}$, 78197-82-7; V, 7440-62-2.

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Displacement of Carbon-Bonded Chloranilate from the $[Pd(C\text{-}CA)Cl_2]^{2-}$ Ion by Hydrochloric Acid

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Although the susceptibility of alkylpalladium(II) compounds toward decomposition in acidic media is well documented,[1-6] kinetic studies of palladium-carbon bond cleavage induced by hydrogen ion have not been carried out. We recently initiated synthetic and mechanistic studies of palladium(II) compounds with hydroxyquinone ligands in order to systematically examine the dynamics of Pd-C bond-making and bond-breaking reactions in systems that do not exhibit complicating side reactions such as mixed alkane/olefin generation coupled with partial reduction of Pd(II) to Pd(0).[7] Thus, the dichloro(chloranilato)palladate(II) ion, originally prepared and structurally characterized by Krasochka et al.,[8] contains chloranilate (CA^{2-}) bonded as a bent, bis(carbanion) donor (Figure 1) rather than as a conventional π-complex (π-CA^{2-}) of the quinonoid 2,5-dioxo-3,6-dichloro-1,4-benzoquinone resonance form. We previously reported that carbon-bonded chloranilate (C-CA^{2-}) in $[Pd(C\text{-}CA)Cl_2]^{2-}$ is retained upon the extraction of chloride ion by $AgNO_3$ in acetonitrile to give $[Pd(C\text{-}CA)(CH_3CN)_2]$, which accepts triphenylphosphine readily with accompanying linkage isomerization, generating $[Pd(\pi\text{-}CA)(PPh_3)_2]$.[7]

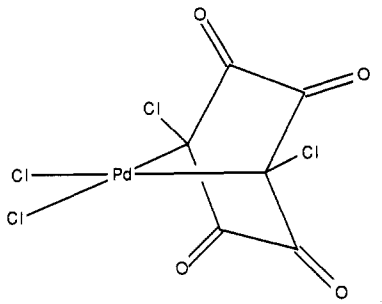

Figure 1. Structure of the $[Pd(C\text{-}CA)Cl_2]^{2-}$ ion in $K_2[Pd(CA)Cl_2]\cdot 4H_2O$, adapted from ref 8. Pd-C bond lengths are 2.02 and 2.07 Å, and the bend angle of chloranilate in the boat conformation is 46.0°.

During the investigation of $K_2[Pd(C\text{-}CA)Cl_2]$ as a precursor to other (chloranilato)palladium(II) compounds, it was noted that the complex slowly decomposes in aqueous HCl, affording $PdCl_4^{2-}$ and unionized chloranilic acid (H_2CA) as the sole products (eq 1). In contrast, the complex loses chloride and ultimately decays

$$[Pd(C\text{-}CA)Cl_2]^{2-} + 2Cl^- + 2H^+ \rightarrow PdCl_4^{2-} + H_2CA \quad (1)$$

to palladium metal in neutral or basic aqueous solutions that do not contain excess chloride ion. As part of our continuing mechanistic studies of Pd-C bond cleavage reactions, we report here kinetic measurements on the protonolysis reaction (1) at 50 °C. Of particular interest is the question of whether both the incoming nucleophile and electrophile participate in the rate-determining step.

Experimental Section

$K_2[Pd(C\text{-}CA)Cl_2]\cdot 0.5H_2O$ was prepared and characterized as previously described.[7] Standardized HCl and $HClO_4$ solutions were used in conjunction with NaCl to determine the hydrogen and chloride ion dependences of observed pseudo-first-order protonolysis rate constants (k_{obsd}) at a constant ionic strength of 1.0 M. Decay of freshly prepared $[Pd(C\text{-}CA)Cl_2]^{2-}$ solutions (50 μM) in a 1 cm path length cell thermostated at 50.0 ± 0.2 °C was monitored by using the 260-nm absorbance decrease (Perkin-Elmer Lambda 5 spectrophotometer) associated with reaction 1. Reported k_{obsd} values, derived from the linear least-squares slopes of $\ln(A_t - A_\infty)$ vs time plots, are the average of at least five trials.

Results and Discussion

In acidic chloride media, the release of carbon-bonded chloranilate from $[Pd(C\text{-}CA)Cl_2]^{2-}$ proceeds quantitatively according to the stoichiometry of eq 1. Ultraviolet peaks of the reactant[7] at 236 nm (ϵ 2.2 × 10^4 M^{-1} cm^{-1}), 264 nm (ϵ 1.8 × 10^4 M^{-1} cm^{-1}), and 312 nm (ϵ 1.5 × 10^4 M^{-1} cm^{-1}) are replaced by the intense 222- and 300-nm bands characteristic of $PdCl_4^{2-}$ and H_2CA, respectively, with four well-defined isosbestic points at 234, 280, 311, and 430 nm. Considering these isosbestic points and the fact that the equilibrium UV spectrum agrees well with that calculated from the sum of $PdCl_4^{2-}$ and H_2CA absorbances, it may be

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Table I. Observed Rate Constants for Dichloro(chloranilato-*C*)palladate(II) Decay to Tetrachloropalladate(II) and Chloranilic Acid in Aqueous Solution[a]

$[H^+]$, M	$[Cl^-]$, M	10^2k_{obsd}, s^{-1}	$[H^+]$, M	$[Cl^-]$, M	10^2k_{obsd}, s^{-1}
0.10	1.00	0.339	0.90	1.00	1.86
0.20	1.00	0.465	1.00	1.00	2.35
0.25	1.00	0.667	1.00	0.10	0.466
0.40	1.00	0.772	1.00	0.25	0.800
0.50	1.00	0.956	1.00	0.40	1.06
0.60	1.00	1.34	1.00	0.60	1.50
0.70	1.00	1.45	1.00	0.75	1.84
0.75	1.00	1.52	1.00	0.90	2.17
0.80	1.00	1.59			

[a] 50.0 ± 0.2 °C I = 1.0 M (HCl, NaCl, $HClO_4$); $[[Pd(C\text{-}CA)Cl_2]^{2-}]_0$ = 50 μM. Uncertainty in rate constants is estimated at ±2%.

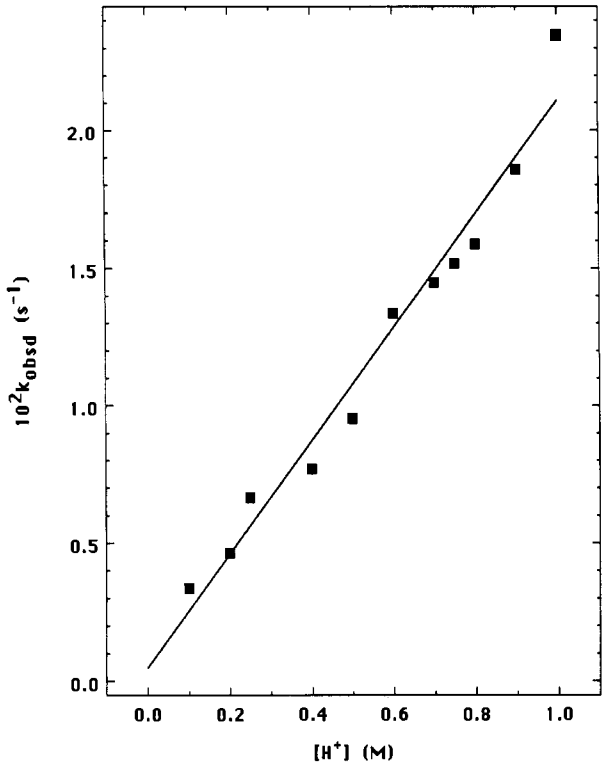

Figure 2. Plot illustrating the hydrogen ion dependence of the chloranilate displacement rate at constant chloride concentration (1.0 M, HCl/NaCl) (I = 1.0 M, 50.0 °C).

concluded that there is not an appreciable buildup of an absorbing intermediate in the displacement of CA^{2-} from $[Pd(C\text{-}CA)Cl_2]^{2-}$ by hydrochloric acid.

First-order analytical plots based on the 260-nm absorbance decrease were found to be linear over greater than 4 half-lives in 50 °C determinations of k_{obsd} as a function of hydrogen ion and chloride ion concentrations. Observed rate constants are presented in Table I, and plots of k_{obsd} vs $[H^+]$ and $[Cl^-]$ are illustrated in Figures 2 and 3, respectively. When $[Cl^-]$ was held constant at 1.0 M, k_{obsd} correlated linearly with $[H^+]$, giving an intercept within experimental error of zero. At fixed $[H^+]$ = 1.0 M, a k_{obsd} vs $[Cl^-]$ plot was also found to be linear, but the nonzero intercept indicates the presence of parallel protonolysis pathways, zeroth and first order in chloride ion. A nonlinear least-squares fit (method of steepest descent) of all kinetic data to the rate law of eq 2 was successful, generating $k_1 = (3 \pm 1) \times 10^{-3}$ M^{-1} s^{-1}

$$k_{obsd} = k_1[H^+] + k_2[H^+][Cl^-] \quad (2)$$

and $k_2 = (1.9 \pm 0.1) \times 10^{-2}$ M^{-2} s^{-1}. The Cl^--dependent term carries between 39% and 86% of the substitution reaction in the 0.1–1.0 M chloride ion concentration range examined. It should be noted that k_{obsd} at $[H^+] = [Cl^-] = 1.0$ M is reproducibly anomalous, falling substantially above the least-squares line defined

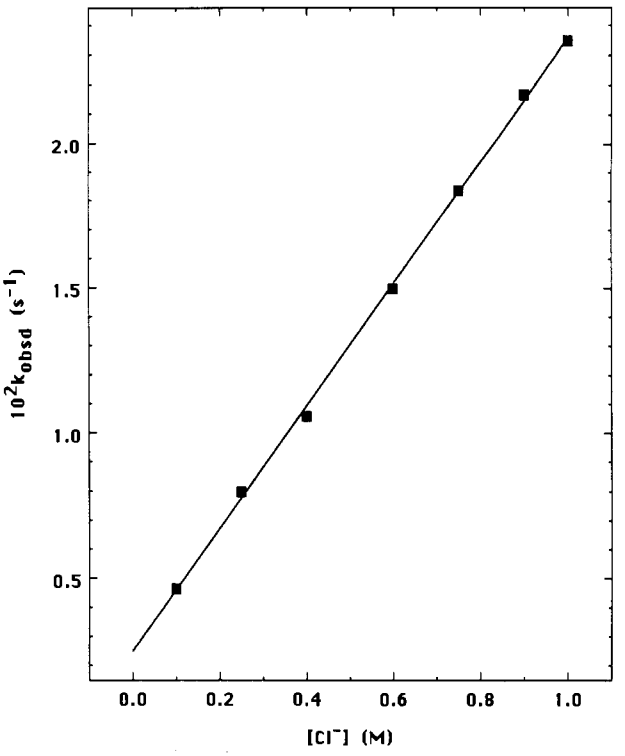

Figure 3. Plot illustrating the chloride ion dependence of the chloranilate displacement rate at constant hydrogen ion concentration (1.0 M, HCl/$HClO_4$) (I = 1.0 M, 50.0 °C).

by the H^+-dependence data (Figure 2, HCl/NaCl medium) but squarely on the analogous Cl^--dependence correlation (Figure 3, HCl/$HClO_4$ medium).

Palladium(II) ligand substitution reactions typically mimic those of analogous platinum(II) complexes but proceed at rates ca. 10^5 times larger. Both associative and dissociative components influence Pd(II) substitution dynamics involving five-coordinate intermediates,[9-15] and pathways in which the solvent initially displaces the leaving group contribute more effectively than in Pt(II) ligand-exchange reactions.[16] Considering the sensitivity of palladium(II) complexation rates to the conformations of diene incoming groups,[17] the slowness of chloranilate protonolysis from $[Pd(C\text{-}CA)Cl_2]^{2-}$ even at 50 °C suggests considerable stability of the bent resonance form, coordinated as a dicarbanion.

The rate law of eq 2 is identical with that reported for the protonolysis reactions of a single alkyl ligand from trans-$[PtCl(CH_3)(PEt_3)_2]$ ($k_1 = 1.78 \times 10^{-2}$ M^{-1} s^{-1}, $k_2 = 3.0$ M^{-2} s^{-1}; 40 °C)[18] and *trans*-$[PtH(CH_2CN)(PEt_3)_2]$ ($k_1 = 1.79 \times 10^{-3}$ M^{-1} s^{-1}, $k_2 = 3.39 \times 10^{-2}$ M^{-2} s^{-1}; 40 °C)[19] and also applies to the rate of H–D exchange in *trans*-$[PtHCl(PEt_3)_2]$.[20] In contrast, the displacement rate of an aryl group from *cis*- or *trans*-$[Pt(C_6H_5)_2(PEt_3)_2]$ by HCl is simply first order in hydrogen ion, exhibiting no dependence on the concentration of the chloride incoming group.[21] In the case of the Pt(II)–alkyl protonolysis

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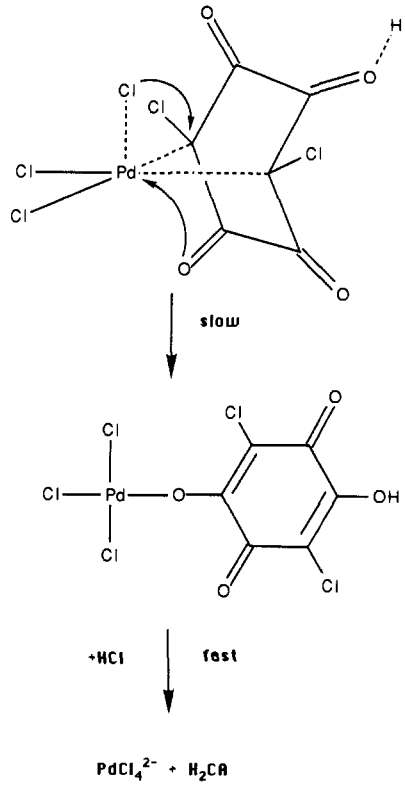

Figure 4. Proposed mechanism of the k_2 pathway for displacement of carbon-bonded chloranilate from $[Pd(C\text{-}CA)Cl_2]^{2-}$ by hydrochloric acid.

reactions, rate law 2 may result from concerted electrophilic and nucleophilic attacks by H^+ and Cl^- on the Pt–C bond or alternatively from the intermediacy of a Pt(IV) complex generated by oxidative addition of HCl; RH would then follow from a rapid reductive elimination process.[21]

Considering the rarity of Pd(IV)–alkyl complexes,[22,23] the documentation of oxidative-addition processes for Pd(0) but not Pd(II),[24] and the lack of a precedent for a Pd(IV)–hydride species, it is extremely unlikely that the k_2 pathway for protonolysis of $[Pd(C\text{-}CA)Cl_2]^{2-}$ reflects oxidative addition of HCl in the rate-determining step. A more straightforward mechanistic hypothesis (Figure 4) invokes rate-limiting Pd–C bond breaking facilitated by the attack of an axially bound nucleophile, coupled with protonation of a carbonyl oxygen atom to promote its conversion to a phenolic –OH group as $C\text{-}CA^{2-}$ is transformed into the *p*-quinone form of HCA^-. On this basis, the k_1 pathway is readily understood in terms of H_2O replacing Cl^- as the activating nucleophile; taking $[H_2O]$ as ca. 55.5 M, the third-order rate constant corresponding to H_2O-assisted chloranilate protonolysis (k_1') is calculated to be 5×10^{-5} M^{-2} s^{-1} and $k_2(Cl^-)/k_1'(H_2O) = 4 \times 10^2$, in accord with the expected reactivity advantage for the softer nucleophile. Although the proposed $PdCl_3(HCA)^{2-}$ intermediate appears reasonable, rate-determining proton attack at a Pd–C bond, resulting in the immediate release of chloranilate from the first coordination sphere of palladium, cannot be ruled out.

The present findings on the displacement of carbon-bonded chloranilate provide an interesting contrast to mechanistic studies of $Pd(acac)_2$ protonolysis in hydrochloric acid, yielding $Pd(acac)Cl_2^-$ and Hacac products.[25] In the case of acac displacement from $Pd(acac)_2$ at constant $[H^+]$, a two-term rate expression of the form $k_{obsd} = k' + k''[Cl^-]$ pertains, in agreement with our results on $[Pd(C\text{-}CA)Cl_2]^{2-}$, but k_{obsd} approaches a saturation limit with increasing $[H^+]$ instead of following a simple first-order dependence. Pearson and Johnson attribute this saturation behavior to the protonation of a monodentate acetylacetonate moiety generated by chloride ion induced ring opening.[25] Such protonation evidently retards reclosure of the acac chelate ring, promoting the second Pd–O bond cleavage reaction that leads to $Pd(acac)Cl_2^-$ and free Hacac. The first-order hydrogen ion dependence of reaction 1 rules out the formation of a half-opened chloranilate chelate species analogous to [Pd(acac)(acacH)Cl] in the protonolysis pathway but is entirely consistent with the partial protonation of a weakly basic carbonyl group of the $C\text{-}CA^{2-}$ ligand.

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Registry No. $K_2[Pd(C\text{-}CA)Cl_2]$, 115185-75-6.

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Iron(IV) Phthalocyanines. Mössbauer Spectral Studies of (μ-Carbido)(phthalocyaninato)iron(IV) and of Its Axially Ligated and Oxidized ($Pc^{\bullet+}$ π Cation Radical) Derivatives

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We have recently described the electronic features of μ-bridged iron phthalocyanine complexes of type $(FePc)_2X$, where $X = O^{2-}$ or N^{3-}, and showed that Mössbauer spectroscopy was a particularly useful technique for assigning formal oxidation states and spin states to iron in these compounds.[1-5] In the μ-oxo compounds the isomer shift (δ) and quadrupole splitting (ΔE_Q) were indicative of $S = {}^5/_2$ Fe(III) centers in both of the crystalline isomers μ-oxo(**1**) and μ-oxo(**2**), and it was possible to distinguish different geometric features in the two isomers from differences in the size of ΔE_Q.[1,2] Some novel six-coordinate Lewis-base adducts of type $(LFePc)_2O$, where L = pyridine, imidazole, etc., were assigned as low-spin ($S = {}^1/_2$) Fe(III) centers from consideration of the Mössbauer and magnetic susceptibility data.[3] The δ value for the μ-nitrido complex $(FePc)_2N$ was observed to be close to zero and thereby indicative of considerable iron(IV) character.[4,5] We now describe the Mössbauer features of the μ-carbido complex $(FePc)_2C$ and of a range of its six-coordinate Lewis-base adducts and oxidized derivatives. Carbido complexes of transition metals are still generally not widely established. The porphyrin analogue $(FeTPP)_2C$ is one notable example of this interesting class of compounds, and its Mössbauer parameters are included here for comparison.[6-8] A well-established set of Mössbauer parameters for Fe^{IV} macrocycles, especially those containing the Pc(1–) cation radical ligand, are also useful for comparison with the values reported for Fe^{IV}-heme proteins such as peroxidases.[7,8]

The syntheses and spectral and structural features of the present compounds will be described in detail elsewhere. While the present paper was being written, a short note on the synthesis and preliminary structural features of $(FePc)_2C$ was published by Rossi et al.,[9] but no data on Mössbauer spectra or magnetic moments were reported.

Experimental Section

The syntheses and properties of the complexes are described in detail elsewhere.[10]

Mössbauer spectral measurements and line-shape-fitting routines were carried out as described previously.[1-4] Isomer shifts are quoted relative to α-Fe.

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