Contribution from the Instituto de Química, Universidade Federal do Ceará, Ceará, Brazil, and the Instituto de Química, Universidade de Sao Paulo, Sao Paulo, Brazil

Transamination and Amine-Exchange Reactions in the System Iron(II)–Sodium Pyruvate–Aminomethylpyridine. I. Stoichiometry and Reaction Products[1a]

MARIA ISAURA DIÓGENES HOLANDA, P. KRUMHOLZ,[1b] and HELENA LI CHUM*

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The reaction between 2-aminomethylpyridine, sodium pyruvate, and iron(II) (stoichiometry 4:2:1) yields as major products bis[2-(2'-pyridylmethyleneaminomethyl)pyridine]iron(II), $Fe(PP)_2^{2+}$ (85%), and α-alanine (75%). The reaction proceeds via the formation of an iron(II) complex of a Schiff base derived from 2-aminomethylpyridine and pyruvate, which then undergoes an intramolecular transamination forming a complex of the isomeric Schiff base derived from pyridine-2-carboxaldehyde and α-alanine. The latter complex exchanges the amino acid residue for the 2-aminomethylpyridine, such that $Fe(PP)_2^{2+}$ is formed and α-alanine is liberated. The proposed intermediate derived from pyridine-2-carboxaldehyde and the amino acid was also prepared and shown to exchange the α-alanine residue for 2-aminomethylpyridine, thus confirming the proposed reaction mechanism.

Introduction

The important role of metal ions in transamination[2] reactions involving pyruvic acid and amino acids was proposed by Mix and co-workers.[3,4] These authors attributed the copper ion catalysis in these transamination reactions to the formation of a Schiff base–copper complex, (COOC(R)=NC(HR')-COO)Cu. The migration of C=N and of the proton would lead to the formation of the isomeric Schiff base (OOCC-(RH)N=C(R')COO)Me. Leussing and co-workers[5-8] were able to detect the presence of these intermediate Schiff base complexes in several systems, confirming Mix's assumptions.[2-4]

Amine-exchange reactions involving coordinate imine functions have been reviewed by Lindoy[9] and found to occur in a series of bidentate Schiff base ligands.[10,11] Recently, a very interesting example of diamine exchange in nitrogen–oxygen donor macrocyclic ligands was reported.[12] In these reactions amine exchange is observed only when the exchanging amine is more basic than the amine used to form the imine complex. The reactions seem to be equilibrium controlled, and the presence of a large excess of the exchanging amine favors the reaction.

In this paper we report that by allowing iron(II), 2-aminomethylpyridine, and sodium pyruvate to react, in very mild conditions, a low-spin iron(II) complex of a terimine[13] ligand and α-alanine are obtained through a sequence of transamination and amine-exchange reactions. These types of reactions are of interest because they occur in biologically important systems[14] where the formation of Schiff bases can be involved and frequently also coordination of the imine grouping to metal ions.[11]

Experimental Section

Reagents and Equipment. All chemicals were reagent grade unless otherwise noted, Sodium pyruvate (Merck or Sigma) was dried over P_2O_5 to constant weight before use and tested for the presence of the dimer.[15] Sodium glyoxylate was prepared from glyoxylic acid (Fluka) according to a procedure described by Metzler et al.[16] Pyridine-2-carboxaldehyde (Aldrich, Fluka) and 2-aminomethylpyridine (Aldrich) were vacuum distilled before use and kept at 0 °C. Aqueous iron(II) chloride solutions were prepared by dissolving $FeCl_2 \cdot 4H_2O$ (Baker) in acid solution and filtering, and powder iron was added to the filtrate, kept under N_2 in a Schlenk tube. Iron(II) sulfate (Baker) was also used. DL-α-Alanine (Nutritional Biochemicals Corp.) was used without further purification.

The following visible–uv absorption spectrophotometers were used: Hitachi Perkin-Elmer Coleman 124, Hitachi Perkin-Elmer 129, and Zeiss DMR-10.

* To whom correspondence should be addressed at the Department of Chemistry, Colorado State University, Fort Collins, Colo. 80523.

The ^1H NMR spectra were recorded using Varian T-60 and XL-100 spectrometers. A Beckman 120 C amino acids analyzer was used to identify α-alanine.

Stoichiometry. The stoichiometry of the reaction between iron(II), sodium pyruvate, and 2-aminomethylpyridine was studied spectrophotometrically by recording the visible absorption spectra of aqueous solutions in several proportions. A typical experiment is described. In a Schlenk tube (8 ml) 1 ml of aqueous $FeSO_4$ (4×10^{-2} M) was added to an aqueous solution of sodium pyruvate of adequate concentration. Then, 2-aminomethylpyridine was added to a final volume of 4 ml. The reaction mixture was kept at 30 °C under N_2. At appropriate time intervals, samples of 0.5 ml of this solution were diluted to 50 ml with 0.01 M succinic acid solution for measuring the absorption spectra.

Rate Measurements. Under N_2, aqueous solutions of $FeSO_4$ (0.015–0.03 M) containing sodium pyruvate and 2-aminomethylpyridine in several proportions were prepared and transferred to capillary spectrophotometric cells (0.26-mm optical path) according to procedures described earlier.[17] Absorbance of the solutions was measured between 400 and 600 nm in 90 s on a previously reported spectrophotometer,[18] at 22 ± 2 °C.

Bis[2-(2'-pyridylmethyleneaminomethyl)pyridine]iron(II) Perchlorate, $Fe(PP)_2(ClO_4)_2$, from Pyridine-2-carboxaldehyde, 2-Aminomethylpyridine, and Iron(II). The complex was prepared by modification[19] of the procedure reported by Lions and Martin.[20]

Bis[2-(2'-pyridylmethyleneaminomethyl)pyridine]iron(II) Perchlorate, $Fe(PP)_2(ClO_4)_2$, from 2-Aminomethylpyridine, Sodium Pyruvate, and Iron(II). To a solution containing 0.28 g (1 mmol) of $FeSO_4 \cdot 7H_2O$ and 0.22 g (2 mmol) of sodium pyruvate in 80 ml of deaerated water, at 30 °C, 0.52 ml (5 mmol) of 2-aminomethylpyridine was added. After 2 h at 30 °C 6 ml of 1 N acetic acid was added. After slow addition of 10 ml of 0.4 M $NaClO_4$ at room temperature, the mixture was kept at 0 °C for 2 h. The crystalline perchlorate salt was filtered off and washed with cold 0.04 N $NaClO_4$ and water. The complex (0.55 g, 85% yield based on total iron) was dried over P_2O_5 in vacuo. Anal. Calcd for $FeC_{24}N_6H_{22}Cl_2O_8$: Fe, 8.60; C, 44.40; H, 3.42; N, 12.95. Found: Fe, 8.59; C, 45.20; H, 3.60; N, 12.91.

Isolation and Identification of α-Alanine. α-Alanine was isolated and identified in the filtrate of the synthesis of $Fe(PP)_2(ClO_4)_2$ from 2-aminomethylpyridine, sodium pyruvate, and iron(II), described above. The filtrate was passed through a cation-exchange column containing Dowex 50W-X8 resin. The amino acid was eluted with 150 ml of 2 N ammonia solution and 50 ml of water. The eluate was dried in vacuo and extracted three times with ethanol. The solid residue was dissolved in water and filtered off, and the filtrate was dried in vacuo, to obtain 0.15 g of a solid. Through an amino acids analyzer it was shown that this solid contained 90% of α-alanine; that represents 75% yield of alanine from the reaction between iron(II), sodium pyruvate, and 2-aminomethylpyridine. No other amino acids were detected.

Bis(pyridine-2-carboxaldehyde α-alanilimine)iron(II). To a deaerated aqueous solution containing 0.36 g of DL-α-alanine (4 mmol)

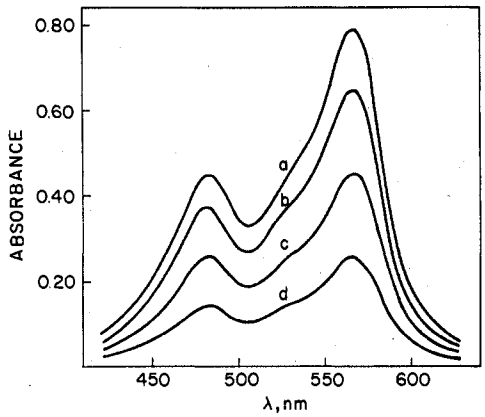


Figure 1. Visible absorption spectra of solutions containing iron(II), sodium pyruvate (PYR), and 2-aminomethylpyridine (AMP) after 1:100 dilution in 0.01 M succinic acid. [Fe(II)] = 1.0×10^{-2} M; [AMP] = 5.0×10^{-2} M. [Fe]:[PYR]: (a) 1:2; (b) 1:15; (c) 1:1; (d) 1:0.5. Reaction times are all 2 h at 30 °C, except 3 h for d.

and 0.56 g of $FeSO_4 \cdot 7H_2O$ (2 mmol), a deaerated solution of pyridine-2-carboxaldehyde in acetone (0.4 ml/8 ml) was added at 40 °C. After 2 h at 40 °C, the solution was evaporated to dryness in vacuo. The neutral complex was purified by dissolving in water and passing through an alumina column (Merck acid type). The complex (0.45 g, 40% yield) after evaporation to dryness in vacuo was dried and kept over P_2O_5. The solid compound decomposes in the solid state, probably due to hydrolysis of the C=N bond. Anal. Calcd for $FeC_{18}N_4H_{18}O_4$: C, 52.70; N, 13.66; H, 4.42. Found: C, 50.0; N, 13.3; H, 4.25.

α-Alanine Exchange for 2-Aminomethylpyridine from Bis(pyridine-2-carboxaldehyde α-alanilimine)iron(II). To a deaerated solution of $Fe(PC)_2$ containing 0.17 g (0.28 mmol) in 5 ml of water, 0.09 ml (0.84 mmol) of 2-aminomethylpyridine was added at 30 °C. After 2 h at 30 °C under N_2, 2 ml of acetic acid was added. Then, 3 ml of 0.4 M $NaClO_4$ was added slowly. After 2 h at 0 °C, 0.14 g of $Fe(PP)_2(ClO_4)_2$ was isolated (~80% yield). Using a 10 times higher concentration of 2-aminomethylpyridine, the reaction was completed after 5 min. Addition of 5 ml of acetic acid and the same amount of $NaClO_4$ yielded approximately the same amount of a less pure $Fe(PP)_2(ClO_4)_2$. This material is triboexplosive.

Results and Discussion

The reaction between iron(II), sodium pyruvate (PYR), and 2-aminomethylpyridine (AMP) was supposed to yield an iron(II) complex of the iminocarboxylic ligand, $[C_5H_4NCH_2N{=}C(CH_3)COO^-]$, with a stoichiometry [Fe(II)]:[PYR]:[AMP] = 1:2:2, in analogy to reactions between iron(II), oxo acids, and aliphatic amines.[17] However, solutions of this composition showed a dark yellow color that changed slowly into a dark red solution after 24 h. This dark red color was produced much faster if the proportion of AMP was increased. Figure 1 shows the visible absorption spectra of the final product, for several compositions of Fe(II), PYR, and AMP.

The stoichiometry of the reaction was determined by measuring the maximum absorbance reached by the system for various compositions. A final stoichiometry [Fe(II)]:[PYR]:[AMP] = 1:2:4 was determined by the typical plots shown in Figures 2 and 3.

The visible absorption spectrum of the reaction product (see Figure 1) shows two absorption bands with pronounced shoulders, maxima of 568 and 483 nm, respectively. A clue to the nature of this reaction product was the shape of the visible absorption bands. In analogy to the diimine chromophore[21] for bidentate diimine complexes of iron(II), Krumholz[19] showed that iron complexes of terimine ligands also yield a characteristic visible absorption spectrum. A comparison between the visible absorption spectrum of bis[2-(2'-pyridylmethyleneaminomethyl)pyridine]iron(II), Fe-

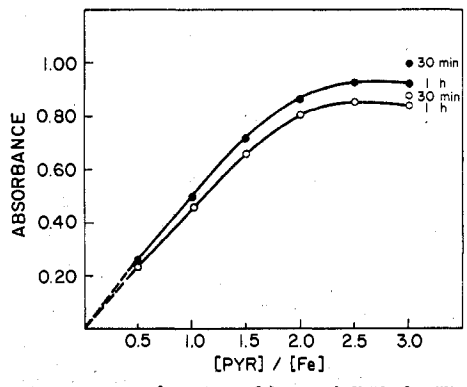


Figure 2. Absorbance as function of [Fe(II)]:[PYR]. The concentrations of iron(II) and AMP and the dilution are identical with those in Figure 1. Reaction times are 2 h; otherwise is stated in the figure; λ 568 nm: ○, absorbance readings 30 min after dilution; •, absorbance readings extrapolated to zero time.

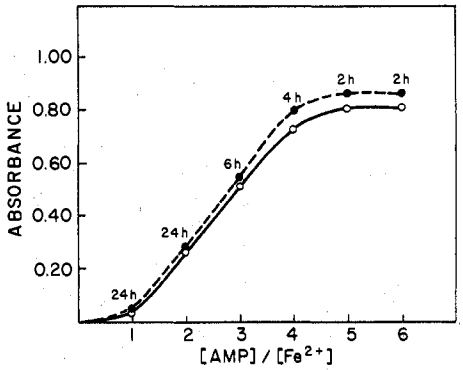


Figure 3. Absorbance as a function of [Fe(II)]:[AMP]. [Fe(II)] = 1.0×10^{-2} M; [PYR] = 2.0×10^{-2} M. Conditions are the same as in Figure 2.

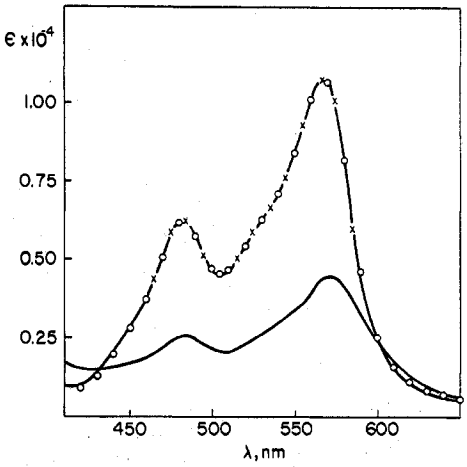


Figure 4. Upper curve: visible absorption spectrum of bis[2-(2'-pyridylmethyleneaminomethyl)pyridine]iron(II) prepared from pyridine-2-carboxaldehyde, 2-aminomethylpyridine, and iron(II); ○ points obtained from the reaction between iron(II), 2-aminomethylpyridine, and sodium pyruvate; × points obtained from the reaction between bis(pyridine-2-carboxaldehyde α-alanilimine)iron(II) and 2-aminomethylpyridine. Lower curve: visible absorption spectrum of bis(pyridine-2-carboxaldehyde α-alanilimine)iron(II). All spectra in water.

$(PP)_2^{2+}$, prepared from AMP, pyridine-2-carboxaldehyde (PCA), and iron(II),[19,20] and that of the main product of the reaction between Fe(II), PYR, and AMP is shown in Figure 4. Identical ^1H NMR spectra in CD_3CN were also obtained for the two products that show two singlets at 2.20 and 6.65 ppm, a complex aromatic pattern from 7.0 to 8.3 ppm, and another complex structure at 10.2 ppm, probably due to

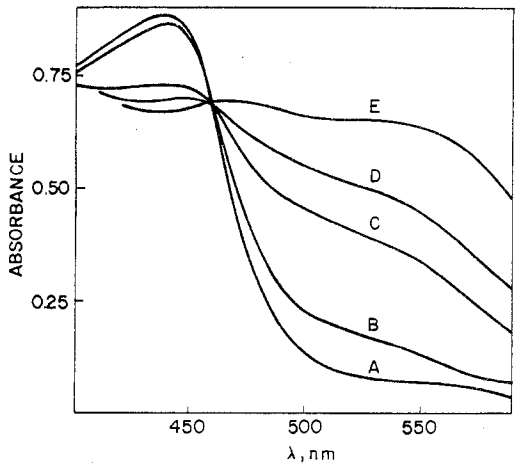


Figure 5. Visible absorption spectra of a solution containing iron(II), sodium pyruvate, and 2-aminomethylpyridine (1:2:2) as a function of reaction time; [Fe(II)] = 3.0×10^{-2} M: A, 1 min; B, 5 min; C, 15 min; D, 30 min; E, 50 min.

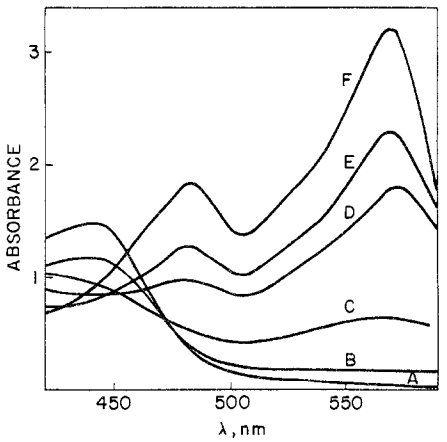


Figure 6. Visible absorption spectra of a solution containing iron(II), sodium pyruvate, and 2-aminomethylpyridine (1:2:4) as a function of reaction time; [Fe(II)] = 1.5×10^{-2} M: A, 1 min; B, 5 min; C, 10 min; D, 20 min; E, 30 min; F, 60 min.

protons in the ortho position in the pyridine rings. The ratio of protons found is 2:1:8, respectively, for the three regions mentioned. Spectroscopic and analytical evidence thus shows that the main product of the reaction between Fe(II), AMP, and PYR (85% yield) is the complex $Fe(PP)_2^{2+}$. This product and α-alanine, isolated in 75% yield, can only be explained if a transamination reaction between AMP and PYR occurs.

A transamination reaction between AMP and PYR was briefly reported by Asano et al.[22] These authors were able to obtain, in the pure organic system, 35% α-alanine after boiling (95 °C) the mixture for 3 h. These drastic conditions are not comparable to the rather mild ones used in the present paper (2 h at 30 °C).

It is thus necessary to invoke the participation of the metal ion in the transamination reaction, just in the same way that Mix and co-workers[3,4] had proposed for analogous systems.

In order to obtain more information on the reaction mechanism, visible absorption spectra of mixtures of Fe(II), PYR, and AMP in ratios 1:2:2 (Figure 5) and 1:2:4 (Figure 6) were obtained after several reaction times.

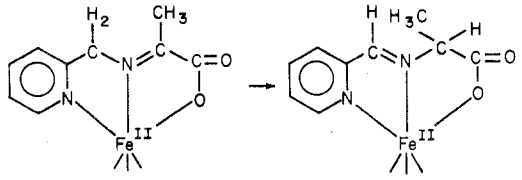
At the lowest AMP concentration, the first absorption spectrum obtained (see Figure 5) is practically identical with that of $Fe(AMP)_3^{2+}$, with a λ_{max} around 440 nm. This absorbance decreases continuously with a simultaneous increase of absorbance toward larger wavelengths. After 1 h two ill-defined peaks around 465 and 530 nm appear. These spectra clearly indicate the formation of other complexes, unstable at pH 3. These spectra resemble those of the iminocarboxylic complexes of iron(II).[17] The isosbestic point at 460 nm might not be real because in this mixture only a fraction of the total iron is present as $Fe(AMP)_3^{2+}$ in equilibrium with $Fe(AMP)_2^{2+}$.[23]

In the mixture with a higher concentration of AMP (Figure 6) there is no indication of an isosbestic point. After 30 min an absorption maximum is present at 568 nm. At lower reaction times this maximum is shifted to 572 nm. For longer reaction times, the absorption spectra get closer to that of $Fe(PP)_2^{2+}$.

It is interesting to notice that the formation of species absorbing at 568 nm, the absorption maximum of $Fe(PP)_2^{2+}$, is an autocatalytical process. The quantities formed after 5, 10, and 20 minutes keep an approximate ratio of 1:4:12 (see Figure 6).

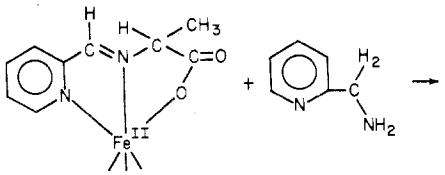
When taken together, these plots (Figures 5 and 6) clearly indicate the presence of complex intermediates. As the concentration of one of these intermediates increases, it reacts with AMP to form $Fe(PP)_2^{2+}$.

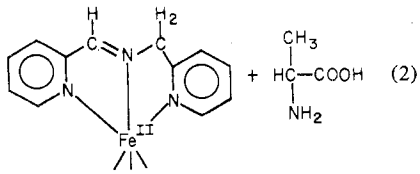
We thus believe that the reaction between Fe(II), AMP, and PYR involves a transamination reaction between AMP and PYR complexed to iron, as suggested previously by Mix et al..[3,4] The first stage of the reaction is the formation of Fe–AMP complexes. The reaction of these complexes with PYR leads to the formation of the α-imino acid complex derived from AMP and PYR, A. Through an intramolecular transamination reaction (eq 1), a complex derived from



(1)

pyridine-2-carboxaldehyde and α-alanine, B, is obtained. The next stage is the exchange of the amino acid residue for 2-aminomethylpyridine, yielding $Fe(PP)_2^{2+}$, C, and setting free α-alanine (eq 2).





(2)

In fact, in order to confirm the reaction mechanism, intermediate B, bis(pyridine-2-carboxaldehyde α-alanilimine)iron(II), was prepared from the condensation of pyridine-2-carboxaldehyde and α-alanine in the presence of iron(II). Figure 4 also shows the visible absorption spectrum of this compound, compared to that of $Fe(PP)_2^{2+}$. It is easily seen that this spectrum is very similar to that of the final product $Fe(PP)_2^{2+}$, with a 2.4 times smaller molar absorptivity of the maxima, probably as a result of a much weaker O donor ligand in B. It is interesting to notice that the λ_{max} occurs at 572 nm.

In conditions comparable to those employed in the study of the reaction between Fe(II), PYR, and AMP, $Fe(PC)_2$ was

allowed to react with AMP, yielding 80% $Fe(PP)_2^{2+}$. The visible absorption spectrum of this product is also shown in Figure 3, in comparison with the spectra of those obtained from the transamination reaction and the spectrum of original product.

Reaction 2 goes faster as the concentration of AMP increases. The driving force of this reaction where the incoming amine (AMP, $pK_1 = 8.57$, $pK_2 = 2.14$[24]) is less basic than the amine to be replaced (α-alanine, $pK_1 = 9.74$, $pK_2 = 2.33$[25]) is the formation of the iron complex of the terimine 3-N ligand, a thermodynamically more stable iron(II) complex than that obtained with PC, a 2-N,O ligand. This can be readily seen by comparison of the ligand field strengths of those ligands. Instead of comparing $10Dq$ values, we will compare energies of the inverse charge-transfer bands, since it is known that as $10Dq$ values increase, higher back-donation is observed,[26,27] meaning an increase of the energy of the inverse charge transfer $d \rightarrow \pi^*$. For the complex $Fe(PC)_2$ an inverse charge-transfer band of the main charge-transfer band occurs at 17.48 kK, with a molar absorptivity of 0.45×10^4 M^{-1} cm^{-1} (see Figure 4), whereas for $Fe(PP)_2^{2+}$, this transition occurs at 17.60 kK, with a molar absorptivity of 1.1×10^4 M^{-1} cm^{-1}, thus indicating a higher ligand field for the second complex. These data also suggest that the "intrachromophoric" conjugation in $Fe(PC)_2$ is less pronounced than in $Fe(PP)_2^{2+}$, thus explaining the direction of reaction 2.

The liberation of the more basic amine can also explain the autocatalytical pattern observed in Figure 6, by facilitating the transamination reaction.[2]

Partial hydrolysis of the imine bond in $Fe(PC)_2$ before or concerted with the exchange cannot be ruled out. In fact, this imine bond adds extremely rapidly alcohols or water (in alkaline media), as was found to occur in other iron–diimine complexes.[28] The labile green alcohol addition product also reacts with AMP yielding $Fe(PP)_2^{2+}$.

The kinetics of these reactions are presently under investigation. The analogous system with sodium glyoxylate shows the same behavior plus an aldol-type condensation[29] of glyoxylate to the methylene protons of $Fe(PP)_2^{2+}$, yielding a very unstable complex with glycollic acid residues.[30]

Conclusion

We have shown that in the reaction of iron(II), sodium pyruvate, and 2-aminomethylpyridine, a transamination reaction between pyruvate condensed to 2-aminomethylpyridine coordinated to iron(II) occurs, yielding a complex of the isomeric Schiff base. This intermediate reacts with excess 2-aminomethylpyridine by exchanging the α-alanine residue for that amine, yielding bis[2-(2'-pyridylmethyleneaminomethyl)pyridine]iron(II) and α-alanine. The exchange reaction was proved by preparing the intermediate derived from pyridine-2-carboxaldehyde and α-alanine, that is shown to exchange the amino acid residue for 2-aminomethylpyridine. It is to be emphasized that this is a novel amine-exchange reaction, where the incoming amine is less basic. The driving force for the reaction is the formation of a thermodynamically more stable iron(II) complex, with a 3-N ligand over the 2-N,O ligand.

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Registry No. $Fe(PP)_2(ClO_4)_2$, 14873-26-8; $Fe(PC)_2$, 58281-48-4; 2-aminomethylpyridine, 3731-51-9; sodium pyruvate, 113-24-6; pyridine-2-carboxaldehyde, 1121-60-4; DL-α-alanine, 302-72-7; Fe, 7439-89-6.

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