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Note

Coordination and reactivity of benzyloxycarbonyl-Ala(CN)-OR (R = H, CH_3) in complexes of platinum(II)

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Abstract

The conversion of a nitrile to an oxazoline group in an amino acid side chain promoted by platinum(II) was investigated. While benzyloxycarbonyl-β-cyano-alanine (Z-Ala(CN)-OH) did not give any evidence of coordination of the nitrile group to Pt(II) in different complexes, the corresponding methyl ester Z-Ala(CN)-OCH_3 readily afforded the Pt(II)–nitrile complex *trans*-$[Pt(CF_3)\{Z\text{-}Ala(CN)\text{-}OCH_3\}(PPh_3)_2][BF_4]$ in good yield by reaction with the cationic derivative *trans*-$[Pt(CF_3)(PPh_3)_2(solv)][BF_4]$ (solv = CH_2Cl_2). The reactivity of the CN group in the complex *trans*-$[Pt(CF_3)\{Z\text{-}Ala(CN)OCH_3\}(PPh_3)_2][BF_4]$ with $ClCH_2CH_2O^-$ to form the oxazoline ligand **2** was examined. The presence of the oxazoline ring in the final products was evidenced by IR, ^1H and ^{13}C NMR data and confirmed by FAB and MALDI mass spectra, but its isolation was hampered by the cleavage of the oxazoline ring under the chromatographic conditions applied.

Keywords: Platinum complexes; Amino acid complexes; Oxazoline complexes; Nitrile complexes

1. Introduction

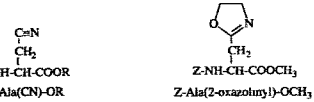
Many biologically active peptides (neurotransmitters, neuromodulators and hormones), which influence various physiological processes concerning signal transduction mediated through receptors, have been discovered in the last thirty years [1,2]. An important step in the synthesis and development of peptide ligands is the identification of the amino acid side chains necessary for receptor recognition.

In the group of structural changes involving amino acid side chains, an interesting modification could be achieved upon substitution of the imidazole side chain of histidine by an oxazoline ring to give H-Ala(2-oxazolinyl)-OH.

H-His-OH H-Ala(2-oxazolinyl)-OH

This modification could be particularly important since histidine plays a significant role in enzyme activity due to its proton donating and accepting ability [3]. Substitution of imidazole by oxazoline will cause a change in the above-mentioned characteristics since the oxazoline ring still contains a basic nitrogen, but is now lacking in the proton-donating center. A further interest arises from the fact that it has been found that some 2-alkyloxazolines are effective antimicrobials and antibacterials [4]. Nitrile ligands coordinated to electron-withdrawing transition metal ions such as Pt(II) are susceptible to nucleophilic attack by various nucleophiles [5]. In particular, we have recently shown the conversion of Pt(II)-coordinated RCN ligands to the corresponding 2-oxazolines $\overline{N{=}C(R)OCH_2CH_2}$, by reaction with $^-OCH_2CH_2Cl$, under mild conditions [6].

Here we report the coordination ability to Pt(II) of Z-Ala(CN)-OR (R = H (**1a**), CH_3 (**1b**)).



Z-Ala(CN)-OR (**1a**, R = H, **1b**, R = CH_3) Z-Ala(2-oxazolinyl)-OCH_3 (**2**)

and the conversion of **1b** to the corresponding oxazoline derivative **2** promoted by Pt(II).

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2. Experimental

2.1 General procedures and materials

The coordination and cyclization reactions were carried out under nitrogen, but work up of the reaction products was performed in air. Dichloromethane was distilled from calcium hydride, tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl and n-hexane was distilled from sodium hydride. Diethyl ether was kept on sodium wires under nitrogen.

K_2PtCl_4 [7], *trans*-$[Pt(CF_3)Br(PPh_3)_2]$ [8], Z-Ala(CN)-OH [9] and Z-Ala(CN)-OCH_3 [10] were prepared according to already described procedures. Z-Ala(CN)-OH (**1a**) and Z-Ala(CN)-OCH_3 (**1b**) were also characterized by IR and ^1H NMR. **1a**: IR (KBr, cm^{-1}) ν(NH) 3323, ν(OH) 3212, ν(CN) 2273, $\nu(C{=}O)_{acid}$ 1743, $\nu(C{=}O)_{urethane}$ 1697, ^1H NMR (200 MHz, DMSO) δ 7.99 [d, ^3J(HH) 16.39, NH], 7.35 (m, Ph), 5.06 (s, CH_2Ph), 4.36 (m, CH_α), 2.93 (m, βCH_2). **1b** IR (KBr, cm^{-1}) ν(NH) 3322, ν(CN) 2253, $\nu(C{=}O)_{ester}$ 1739, $\nu(C{=}O)_{urethane}$ 1689, ^1H NMR (200 MHz, $CDCl_3$) δ 7.30 (m, Ph), 5.75 [d, ^3J(HH) 6.98, NH], 5.08 (s, CH_2Ph), 4.53 (m, $CH\alpha$), 3.78 (s, OCH_3), 2.92 (m, βCH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.57 (*C*ONH), 155.75 (*C*OOCH$_3$), 128.84–128.33 (Ph), 136.43 (*C*$_i$Ph), 116.51 (*C*N), 67.63 (*C*H$_2$Ph), 53.64 (O*C*H$_3$), 50.94 (*C*H$_\alpha$), 22.00 (β*C*H$_2$).

$AgBF_4$ was used as a 0.92 M solution in acetone. n-BuLi (1.6 M solution in n-hexane), ethyl acetate, methanol and petroleum ether were commercially available products and they were used as received. Commercial $ClCH_2CH_2OH$ was stored on molecular sieves before use.

IR spectra were recorded on a Perkin-Elmer 580-B spectrophotometer connected with a Perkin-Elmer IR data station and on a Perkin-Elmer 983 spectrophotometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were run on a Bruker AC-200 or AC-400 spectrometer in DMSO, CD_2Cl_2 or $CDCl_3$ solutions; proton chemical shifts are reported from Me_4Si by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm, dimethyl sulfoxide-d_6 as +2.50 ppm and chloroform-d as +7.21 ppm. $^{31}P\{^1H\}$ NMR spectra were run on a Varian FT 80-A spectrometer operating at 32.203 MHz and ^{19}F NMR spectra were run on a Varian FT 80-A spectrometer operating at 72.588 MHz (abbreviations s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, *J* are given in Hz). The fast atom bombardment (FAB) [11] mass spectra were obtained using *m*-nitrobenzyl alcohol or glycerol/CH_3COOH as a matrix on a VG ZAB 2F [12] instrument operating with an Xe atom beam energy of 8 keV. The matrix assisted low degree ionization (MALDI) [13] mass spectra were obtained using 2,5-dihydroxybenzoic acid in $CHCl_3$ as a matrix on a Reflex Bruker instrument working in a linear way with positive ions. These positive ions were generated by an N_2 pulsed laser (337 nm) and were accelerated at 15 keV. Spectra were obtained summing 10 shots and the sample was mixed with the matrix in the ratio sample/matrix 1/7000.

The medium pressure liquid chromatography (MPLC) separations were performed on a Buchi 688 chromatographic pump with Buchi 687 gradient former (Silica Gel F 60 column 2.6 × 23 cm, flow rate 20 ml min^{-1}), connected with an LKB UV CORD S2138 (254 nm) detector and with a 2210 LKB recorder. A solution of petroleum ether and ethyl acetate (7:3 vol/vol) was used as eluant for the purification of Z-Ala(CN)-OCH_3 (**1b**) and a solution of dichloromethane and methanol (93:7 vol/vol) was used for the MPLC of the solid residue obtained in the cyclization reaction of compound **3** and also of 2-methyl-Δ^2-oxazoline. The high performance liquid chromatography (HPLC) analyses (Aquapore RP-300 column 220 × 4.6 mm, 7 μm, Brownlee Labs, flow rate 1.5 ml min^{-1}) were performed on a Perkin-Elmer series 410 liquid chromatograph with a pressure box of solvents (SEC-4), an LC-90UV spectrophotometer detector and an LC-100 integrator. Eluants A (H_2O) and B (aqueous 90% acetonitrile) were used for preparing binary gradients. The following conditions of elution were used: isocratic 10% B for 2 min, linear gradient 10–90% B for 20 min, isocratic 100% B for 5 min.

The elemental analyses were performed by the Department of Analytical Chemistry of the University of Padua. The melting points were obtained by a Buchi model 150 apparatus and are uncorrected.

2.2 Synthesis of *trans*-$[Pt(CF_3)\{Z\text{-}Ala(CN)\text{-}OMe\}(PPh_3)_2][BF_4]$

A 0.92 M acetone solution of $AgBF_4$ (7.5 ml) was added to a suspension of *trans*-$[Pt(CF_3)Br(PPh_3)_2]$ (5.83 g, 6.7 mmol) in 100 ml of CH_2Cl_2. The reaction mixture was stirred for 40 min at room temperature, the precipitate of AgBr was filtered off and the yellow solution was concentrated to ~30 ml. Diethyl ether (150 ml) was added and the resulting white precipitate of the cationic complex *trans*-$[Pt(CF_3)(PPh_3)_2(CH_2Cl_2)][BF_4]$ was collected by filtration and dried under vacuum (5.9 g, 6.1 mmol). The solvato–cationic complex was dissolved in 80 ml of CH_2Cl_2, and then solid Z-Ala(CN)-OCH_3 (1.44 g, 5.49 mmol) was added. The yellow solution became immediately colorless. The reaction mixture was stirred for 30 additional min and taken to dryness. The white solid residue was then stirred with n-hexane (100 ml) for 20 min and then collected by filtration. Yield 5.64 g, 90%. M.p. 115–120 °C. $[\alpha]_D^{25} = -2.35°$ (c = 1.0, CH_2Cl_2). *Anal.* Calc. for $C_{50}H_{44}N_2O_4F_7P_2BPt \cdot 1/2CH_2Cl_2$: C, 51.39; H, 3.84; N, 2.37. Found: C, 50.98; H, 3.76; N, 2.24%. IR (KBr, cm^{-1}) ν(NH) 3370, ν(CN) 2310, $\nu(C{=}O)$ 1721, $\nu(C{=}C)$ 1587, 1482, 694, δ(NH) 1520, ν(C–C–O) 1187, ν(O–C–C) 1106, 1045. ^1H NMR (200 MHz, $CDCl_3$) δ 7.40 (m, Ph), 5.99 [d, ^3J(HH) 7.79], 4.87 (s, CH_2Ph), 3.45 (s, OCH_3), 3.39 (m, CH_α), 2.17–1.99 (m, CH_2CN). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.0 [q, ^1J(PPt) 2882.6, ^3J(PF) 20.5]. ^{19}F NMR ($CDCl_3$) δ −51.37 [t,

^2J(PtF) 725, ^3J(PF) 20 5]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 168 78 (CONH), 155 76 ($COOCH_3$), 134 45–127 32 (Ph), 111 25 (CN), 66 74 (CH_2Ph), 53 85 (OCH_3), 49 30 (CH_α), 19 88 (CH_2CN) FAB mass spectrum (*m*-nitrobenzylalcohol as matrix) *m/e* 1051 (10%, *trans*-[$Pt(CF_3)$\{Z-Ala(CN)-OMe\}$(PPh_3)_2]^+$), 719 (30%, $[Pt(PPh_3)_2]^+$)

2 3. Reaction of *trans*-[$Pt(CF_3)$\{Z-Ala(CN)-OCH_3\}$(PPh_3)_2$][BF_4] with $ClCH_2CH_2O^-$

$ClCH_2CH_2OH$ (3 0 ml, 45 mmol) and a 1 6 M n-hexane solution of n-BuLi (3.1 ml, 4 96 mmol) were dissolved in 200 ml of THF *Trans*-[$Pt(CF_3)$\{Z-Ala(CN)-OCH_3\}-$(PPh_3)_2$][BF_4] (5.64 g. 4 96 mmol) was then added and the uncolored solution turned yellow. The reaction proceeded for 23 h at room temperature and a white precipitate formed. An IR spectrum of the reaction mixture showed the disappearance of the CN absorption at 2310 cm^{-1} of the coordinated nitrile group, while a C=N absorption at 1638 cm^{-1} appeared The white precipitate was collected by filtration and identified as *trans*-[$Pt(CF_3)Cl(PPh_3)_2$] [6c] (2 86 g, 3.47 mmol; yield 70%). Addition of 50 ml of diethyl ether to the filtrate solution gave a white precipitate (0 740 g) IR (KBr, cm^{-1}): ν(NH) 3414, ν(C=O) 1708, ν(C=N) 1656, δ(NH) 1525, ν(C–C–O) 1192, ν(O–C–C) 1066, ν(*cis*-PPh_3PtPPh_3) 547 ^1H NMR (CD_2Cl_2, 400 MHz). δ 6 6 (br, NH), 6 0 (br, NH), 5.09 (s, CH_2Ph), 4 47 (m, CH_α), 3.72 (s, OCH_3), 3 60 (s, OCH_3), 3.58 (s, OCH_3), 2.92 (m, βCH_2), 2 77 and 2 73 (m, NCH_2), $\delta(OCH_2)$ masked $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 172.94 (br, *C*=O), 172.31 (br, *C*=O), 156 77 (br, *C*=O), 68 06, 67 54, 67 38, 67 20 (br, CH_2Ph and OCH_2), 51.52, 50 51, 50.27 (br. *C*H and N*C*H_2), $\delta(OCH_3)$ masked by CD_2Cl_2, 19.90 (br, CH_2CN) FAB mass spectrum (glycerol/CH_3COOH as matrix) *m/e* 457 (5%, $[Pt(PPh_3)]^+$), 306 (8%, Z-Ala(2-oxazolinyl)-OCH_3), 262 (15%, Z-Ala(CN)-OCH_3). MALDI mass spectrum (2,5-dihydroxybenzoic acid as matrix) *m/e* 719 ($[Pt(PPh_3)_2]^+$), 758 ($[Pt(PPh_3)_2]^+ + K^+$), 873 ($[Pt(PPh_3)_2]^+$ by addition of the matrix), 1095 (*trans*-[$Pt(CF_3)$\{Z-Ala(2-oxazolinyl)-OCH_3\}$(PPh_3)_2]^+$), 1249 (*trans*-[$Pt(CF_3)$\{Z-Ala(2-oxazolinyl)-OCH_3\}$(PPh_3)_2]^+$ by addition of the matrix)

3. Results and discussion

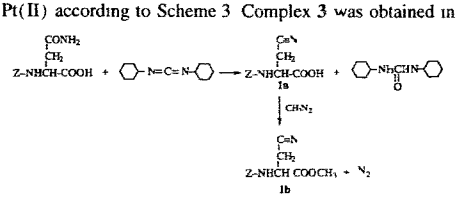
3 1 Synthesis and coordination reactions of the nitrile ligands Z-Ala(CN)-OH and Z-Ala(CN)-OCH_3

Z-Asn-OH was dehydrated using *N,N*-dicyclohexylcarbodiimide (Scheme 1) as already described [9] Esterification of Z-Ala(CN)-OH (**1a**) was achieved by using diazomethane [10] and the resulting Z-Ala(CN)-OCH_3 (**1b**) was purified by MPLC

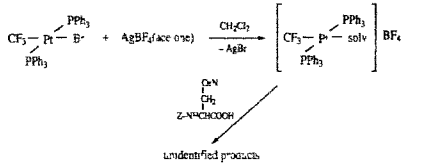
1a and **1b** were also characterized by IR and ^1H NMR (see Section 2) A small amount of the starting reagent (Z-Asn-OH) was still present in the final product of dehydration **1a** The contaminant could not be separated either by changing reaction conditions or by recrystallization [14].

The reaction of **1a** with *trans*-[$Pt(CF_3)Br(PPh_3)_2$] was carried out according to Scheme 2. The products of this reaction did not show the presence of any Pt(II)-coordinated nitrile as evidenced by the lack in the IR spectrum of the CN absorption at higher wavenumbers compared to the free ligand [6] Furthermore, the $^{31}P\{^1H\}$NMR spectrum did not show the quartet due to the coupling of the phosphorus atoms with the three equivalent fluorine atoms of the $-CF_3$ group The absence of the trifluoromethyl group in the final products can be tentatively explained by a possible reaction of the C–F bonds with the –COOH group of Z-Ala(CN)-OH, as previously observed for other reactions in which the Pt(II)–CF_3 group readily undergoes electrophilic attack by protic or Lewis acids [15] This possible reaction between the trifluoromethyl group of the complex and the carboxylic group of the amino acid led us to examine the reaction of Z-Ala(CN)-OH with K_2PtCl_4, but also in this case there was no evidence of nitrile coordination, while reduction of Pt(II) to Pt(0) was observed, possibly due to the interaction of the carboxylic group with the metallic center, as reported for similar reactions with weak acids like alcohols [16].

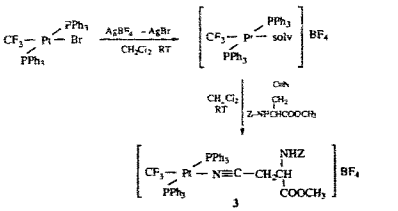
In order to avoid these side reactions, the carboxylic group was protected by esterification with diazomethane [10]. Z-Ala(CN)-OCH_3 (**1b**) was observed to readily coordinate to Pt(II) according to Scheme 3 Complex **3** was obtained in



Scheme 1



Scheme 2



Scheme 3

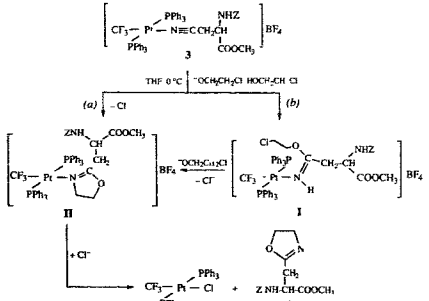
90% yield, together with a small amount of free nitrile, as confirmed by the presence of $\nu(CN) = 2255\ cm^{-1}$. The IR spectrum showed the presence of $\nu(CN)$ of the coordinated nitrile at 2310 cm^{-1}. The value $\Delta\nu = \nu(CN)_{coord} - \nu(CN)_{free} = 55\ cm^{-1}$ indicates that it would be susceptible to nucleophilic attack [17]. The *trans* geometry of **3** was confirmed by the presence of a quartet in the $^{31}P\{^1H\}$ NMR spectrum [δ 20.0, ^1J(PPt) 2882.6, ^3J(PF) 20.5]. The ^{19}F NMR spectrum showed a triplet due to the coupling of the fluorine atoms with the two equivalent phosphorus atoms at δ −51.37 [^3J(PF) 20.5] with two satellites [^2J(PtF) 725]. The ^1H NMR spectrum (see Section 2) of the coordinated nitrile showed that the proton signals were shifted to higher field with respect to the free ligand, except for the NH resonance.

As observed for **1a**, also the reaction of **1b** with K_2PtCl_4 gave the reduction of Pt(II) to Pt(0) with no evidence of nitrile coordination. A plausible explanation stems from the initial hydrolysis of the $-COOCH_3$ group of **1b** by H_2O to give **1a**, which then makes the reaction proceed as described earlier.

3.2 Reaction of *trans*-[Pt(CF$_3$){Z-Ala(CN)-OCH$_3$}(PPh$_3$)$_2$][BF$_4$] with ClCH$_2$CH$_2$O$^-$

The conversion of a coordinated nitrile to 2-oxazoline was previously investigated with cationic Pt(II) complexes of the type *trans*-[Pt(R′)(NCR)(PPh$_3$)$_2$][BF$_4$] (R′ = CF_3, CH_3, H, R = various alkyls and aryls). These complexes react under very mild conditions with 1 equiv. of $^-OCH_2CH_2Cl$, obtained from $HOCH_2CH_2Cl$ and n-BuLi, which initially attacks the nitrile carbon. Subsequent intramolecular cyclization through nucleophilic attack of the imino nitrogen to the $-CH_2Cl$ group affords the oxazoline ring. The Cl^- ion then attacks the metal affording free oxazoline and *trans*-[Pt(R′)(Cl)(PPh$_3$)$_2$]. This procedure appears to offer several advantages in comparison with other methods, often requiring more drastic conditions [4], and was thus applied to complex **3** as illustrated in Scheme 4.

The reaction could proceed via route (a) involving a direct cyclization process of the nitrile ligand by 2-chloroethoxide



Scheme 4

or via route (b) through the initial formation of the open ligand **I**, which then affords the oxazoline ring in the presence of a base. Both routes have been independently evidenced in previous experiments [6]. Whatever was the reaction pathway, the formation of a white precipitate of *trans*-[Pt(CF$_3$)Cl(PPh$_3$)$_2$] in 70% yield confirmed the occurrence of the cyclization process of the nitrile ligand [6c]. An IR spectrum of the solution showed the disappearance of the absorption of the coordinated nitrile at 2310 cm^{-1} and the appearance of a new absorption at 1638 cm^{-1}, which could be assigned to a C=N stretching, likely due to the oxazoline ligand as observed earlier [6c]. The solution, taken to dryness, gave a solid residue, whose ^1H NMR spectrum was very complicated, owing to the complexity of the oxazoline ligand itself as well as to the possible presence of some intermediates like **I** and **II**, which are known to be formed in these types of reactions and have been previously isolated and characterized [6]. However, in the range δ 2.5–3.5 two broad triplets were observed, partially overlapping with the β-CH_2– protons, which could be assigned to the $-NCH_2$ protons [δ 2.73 and 2.77, ^3J(HH) 9.4] of the oxazoline. The resonance of the $-OCH_2$ group of the ring was masked by those of the $-OCH_3$ moieties, centered at δ 3.5, of products contained in the mixture and the $-CH_2Ph$ protons appeared as a single resonance at δ 5.1.

According to previous results [6c], the signals at δ 68.06 and 51.52 in the ^{13}C NMR spectrum of the reaction products were assigned to the $-OCH_2$– and $-NCH_2$– groups, respectively, of the oxazoline ring.

The crude residue was also analyzed by mass spectrometry. The FAB mass spectrum showed the presence of ions with $m/e = 306$ that could be attributed to the free oxazoline. The MALDI mass spectrum showed strong signals at $m/e = 1095$ and $m/e = 1249$, the former was assigned to the cation of complex **II** while the latter was due to the cation of complex **II** by addition of the matrix 2,5-dihydroxybenzoic acid [13].

Attempts to separate the components of the residue by fractional crystallization or by liquid chromatography (MPLC, HPLC) failed. In particular, the various fractions obtained using different chromatographic techniques always showed the presence of a mixture of products, as evidenced by the complexity of the ^1H NMR spectra in which the appearance of new multiplets indicated that the oxazoline ring was not stable in the chromatographic conditions applied. In particular, after MPLC chromatography, we observed a triplet at δ 3.60 [^3J(HH) 5.5] that could be assigned to an $-NCH_2$– group and a triplet at δ 4.33 (^3J(HH) 5.5) that could be due to an $-OCH_2$– group [^3J(HH) 5.5]. The observed value of ^3J(HH) is typical of opened forms, while higher values ($\sim$9–10 Hz) are reported for cyclic structures [6].

The low stability of the oxazoline ring is supported also by the fact that 2-methyl-Δ^2-oxazoline (a commercially available product), chromatographed (MPLC, HPLC) in the same conditions used for **2**, undergoes ring cleavage as evidenced by the ^1H NMR data of the eluate, which indicate the

presence of four compounds containing the C=O group. Two of these were identified as $CH_3(CO)NHCH_2CH_2OH$ and $CH_3(CO)NHCH_2CH_2OCH_3$ [18], while no other resonance could be assigned to the oxazoline

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