

## Metal Promoted Cleavage of Diethylenetriamine to give $\beta$ -Alanine

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An unusual, facile cleavage of C–N bonds of diethylenetriamine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2 = \text{dien}$ ) promoted by the reaction with the rhenium(v) nitrido complex  $[\text{ReNCl}_2(\text{PPh}_3)_2]$  to yield  $\beta$ -alanine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{CO}_2\text{H} = \beta\text{-ala}$ ) is reported.

Recently, we described the reactions of the nitrido metal(v)ate complexes  $[\text{MnCl}_2(\text{PPh}_3)_2]$  ( $\text{M} = \text{Tc}, \text{Re}$ ) with bidentate and tetradentate chelating amines and cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane).<sup>1,2</sup> The products of these reactions were different for the two metals, yielding the cationic nitrido  $\text{Tc}^{\text{V}}$  complexes  $[\text{TcN}(\text{L})_n\text{Cl}]^+$  ( $n = 1, 2$ ;  $\text{L} = \text{polyamine ligand}$ ) when  $\text{M} = \text{Tc}$ , and the cationic *trans*-dioxo  $\text{Re}^{\text{V}}$  complexes  $[\text{ReO}_2(\text{L})_n]^+$  when  $\text{M} = \text{Re}$ . The impossibility of isolating the corresponding nitrido  $\text{Re}^{\text{V}}$  complexes  $[\text{ReN}(\text{L})_n\text{Cl}]^+$  indicates that the  $[\text{Re}\equiv\text{N}]^{2+}$  group is unstable in these complexes and easily converted to the *trans*- $[\text{O}=\text{Re}=\text{O}]^+$  group by reaction with  $\text{H}_2\text{O}$ .<sup>2</sup> Extension of these studies to include the reactions of the technetium complex  $[\text{TcNCl}_2(\text{PPh}_3)_2]$  with the ligand diethylenetriamine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2 = \text{dien}$ ) resulted in the unexpected isolation of the dicationic complex  $[\text{TcN}(\text{en})_2(-\text{O}_2\text{CNHCH}_2\text{CH}_2\text{NH}_3^+)]^{2+}$  [ $\text{en} = \text{ethylenediamine}$ ;  $-\text{O}_2\text{CNHCH}_2\text{CH}_2\text{NH}_3^+ = \text{zwitterionic form of } N\text{-(2-aminoethyl)carbamic acid}$ ].<sup>3</sup> The formation of this species revealed that under certain experimental conditions cleavage of the C–N bonds of the polyamine ligand can occur to produce either *en* or *N*-(2-aminoethyl)carbamic acid, presumably in different reactions. We investigated the analogous reaction of dien with the rhenium complex  $[\text{ReNCl}_2(\text{PPh}_3)_2]$  and observed a more extensive cleavage of the C–N bonds of the polyamine ligand with quantitative formation of  $\beta$ -alanine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{CO}_2\text{H} = \beta\text{-ala}$ ). To our knowledge, this process constitutes the first reported example of a facile conversion of a linear polyamine ligand to give  $\beta$ -amino acids through the efficient cleavage of ligand C–N bonds. Although degradation of amines by cleaving C–N linkages is known, these reactions generally take place under drastic conditions, and lead to the elimination of a single amino group.<sup>4</sup> In addition, synthetic methods involving the conversion of polyamines to  $\beta$ -amino acids have not yet been reported. The reaction described here

therefore may constitute a new, efficient route to the preparation of  $\beta$ -amino acids from linear polyamines.

Reaction of excess of dien with  $[\text{ReNCl}_2(\text{PPh}_3)_2]$  (30:1) in  $\text{CHCl}_3$ , at room temperature and under aerobic conditions, led to the formation of an oily residue and of a pale yellow solution. After separation of the two phases, the solution was evaporated to dryness to give a pale cream solid, which was dissolved in  $\text{H}_2\text{O}$  and treated with  $\text{HCl}$  which caused the quantitative precipitation of thin, white crystals of  $\beta$ -alanine hydrochloride (yield 90%, based on the conversion  $\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2 \rightarrow 2\text{H}_2\text{NC}_2\text{H}_4\text{CO}_2\text{H}$ ). The identity of this compound was established by elemental analysis, and IR and  $^1\text{H}$  NMR spectroscopy. The oily residue was found to be a side product of the reaction. Treatment of this species with  $\text{MeOH}$  and  $\text{Et}_2\text{O}$  gave a yellow-brown solid, which showed a strong IR band at  $802\text{ cm}^{-1}$  characteristic of the stretching vibration of the *trans*- $\text{ReO}_2$  group, and absorptions in the interval  $3200\text{--}3300\text{ cm}^{-1}$  attributable to the stretching vibrations of N–H bonds. The solid was soluble in  $\text{H}_2\text{O}$ , but decomposed in solution to yield free dien and  $[\text{ReO}_4]^-$ . We observed that the yield of this product increased after addition of few drops of  $\text{H}_2\text{O}$  to the reaction solution, and that under these conditions the conversion of dien to  $\beta$ -ala was drastically reduced. These facts suggest that the starting complex  $[\text{ReNCl}_2(\text{PPh}_3)_2]$  could be transformed by reaction with dien and  $\text{H}_2\text{O}$  in a compound containing the dien ligand coordinated to a *trans*- $\text{ReO}_2$  group, and that this species is inactive in promoting the degradation of dien to  $\beta$ -ala. The presence of  $\text{H}_2\text{O}$  appears therefore to interfere with the conversion of dien to  $\beta$ -ala through the replacement of the active  $[\text{ReNCl}_2(\text{PPh}_3)_2]$  complex by the inactive *trans*- $\text{ReO}_2$  complex. In order to give support to this hypothesis, we carried out the reactions of dien with the dioxo complexes  $[\text{ReO}_2(\text{L})_2]^+$  ( $\text{L} = \text{en}$  or  $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , *pn*) and the monooxo complex  $[\text{ReOCl}_3(\text{PPh}_3)_2]$ , and we failed to observe the

formation of any detectable quantity of  $\beta$ -ala. It seems therefore that only the five-coordinate 16-electron complex  $[\text{ReNCl}_2(\text{PPh}_3)_2]$  is effective in promoting the cleavage of C–N bonds of dien, the six-coordinate 18-electron oxo complexes being inert.

The conversion of dien to  $\beta$ -ala promoted by the complex  $[\text{ReNCl}_2(\text{PPh}_3)_2]$  requires the presence of atmospheric  $\text{O}_2$  and  $\text{CO}_2$ . When this reaction was carried out in anhydrous, deoxygenated chloroform, and under an argon stream the starting reagents were recovered unaltered. No conversion was also observed when either  $\text{O}_2$  or  $\text{CO}_2$  was excluded from the same reaction carried out under anhydrous conditions. However, introduction of a weak flow of both  $\text{O}_2$  and  $\text{CO}_2$  into the reaction solution led readily to the formation of  $\beta$ -ala.

The most unusual feature of the reaction described here lies in the very facile conversion of dien to  $\beta$ -ala. The starting dien ligand was purified by standard techniques prior to use, and its purity checked by HPLC and gas chromatography to eliminate the possibility that  $\beta$ -ala was present in the starting sample. The overall process may be schematically viewed as resulting from the metal-promoted cleavage of the two C–N bonds between the secondary amine nitrogen and the two  $\text{H}_2\text{NCH}_2\text{CH}_2$ - groups of dien, followed by the reaction with atmospheric  $\text{CO}_2$  to form  $\beta$ -ala. This would require the production of  $\text{NH}_3$  or of other nitrogen-containing molecules (e.g.  $\text{NH}_2\text{OH}$ ,  $\text{N}_2\text{H}_4$ ), but we failed to detect these products by gas chromatography. However, the exact path of this conversion remains obscure. In particular, the exact role played by the complex  $[\text{ReNCl}_2(\text{PPh}_3)_2]$ , and by atmospheric  $\text{O}_2$  and  $\text{CO}_2$ , has not yet been established in the overall reaction which could be depicted as a four electron process. A further comparison of the results of this reaction with those found using the analogous complex  $[\text{TcNCl}_2(\text{PPh}_3)_2]$  indicates that some differences exist, the most obvious being the failure

to isolate the analogous rhenium nitrido intermediate complex  $[\text{ReN}(\text{en})_2(-\text{O}_2\text{CNHCH}_2\text{CH}_2\text{NH}_3^+)]^{2+}$ . The X-ray crystal structure of the technetium complex  $[\text{TcN}(\text{en})_2(-\text{O}_2\text{CNHCH}_2\text{CH}_2\text{NH}_3^+)]^{2+}$  revealed that the carbamate ligand lies in an uncommon 'transient state' where the C–N bond between the  $-\text{CH}_2\text{CH}_2\text{NH}_3^+$  and  $-\text{NHCO}_2^-$  groups is abnormally long.<sup>3</sup> We suggest that the lower stability of the rhenium nitrido intermediate allows the reaction to proceed further to cleave this stretched C–N bond and, after rearrangement, to form  $\beta$ -ala. In contrast, the higher stability of the technetium intermediate enables the 'transient form' of the carbamate ligand to be trapped in the crystal structure of this compound. It follows therefore that, in view of the application of the present reaction to the preparation of a wider class of  $\beta$ -amino acids, the use of the complex  $[\text{ReNCl}_2(\text{PPh}_3)_2]$  appears more promising. Studies devoted to the elucidation of the true mechanism of this new degradation process of polyamines are currently underway.

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