to the centres which can ligate N_2, $\{Mo(N_2)\}$ and $\{FeH\}^+$, in spite of their so different E_s values which may perhaps be accounted for by the electronic effects of the *trans* ligand.

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PS5.21 — TU

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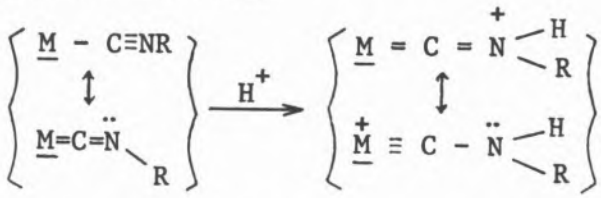
ELECTRON-RICH RHENIUM AND MOLYBDENUM METAL CENTRES AS POTENTIAL INORGANIC MODELS IN THE BIO-REDUCTION OF ISOCYANIDES?

Isocyanides ($C\equiv NR$) are organic species which are isoelectronic with dinitrogen (N_2) and can also be reduced by the enzyme nitrogenase with complete cleavage of the unsaturated bond to afford amines and methane, *e.g.*, according to reaction (1) (C_2 and C_3 hydrocarbons are also formed in lower yields).

$$C\equiv NMe + 6H^+ + 6e^- \rightarrow CH_4 + H_2NMe \qquad (1)$$

The mechanism of the $C\equiv N$ bond cleavage is yet unknown, but the study of the activation of isocyanides by transition-metal centres in well defined coordination compounds may provide some useful information for the understanding of the process. When bound to a transition metal centre with a low π-electron releasing ability, isocyanides can undergo attack by a nucleophile at the ligating carbon; however, the isocyanide ligand can be activated towards electrophilic attack (which occurs at the *N* atom) by a metal centre with a high electron-richness (high π-electron donor character). The latter type of reaction occurs typically for d^6 Mo(0) or Re(I) centres of the types $\{Mo(dppe)_2\}$ or $\{ReCl(dppe)_2\}$ (where $dppe = Ph_2PCH_2CH_2PPh_2$), *e.g.*, in complexes *trans*-$[Mo(CNMe)_2(dppe)_2]$ and *trans*-$[ReCl(CNMe)(dppe)_2]$, respectively, and carbyne-type ligands are formed by protonation of isocyanide ligand according to the following general VB scheme [1]:



where the weakening of the unsaturated CN bond is evident, although without occurrence of the complete rupture of this bond. However, protonation of the isocyanide may proceed until CN bond cleavage, at a related electron-rich metal centre with labile co-ligands such as monophosphines or phosphites. Hence, in complexes $[M(CNMe)_nL_{6-n}]$ ($M = Mo$ or W; $n = 2$ or 3; $L = PMe_2Ph$) [2] and $[ReCl(N_2)(CNR)\{P(OMe)_3\}_3]$ ($R = Me$, Et, *t*-Bu, C_6H_4Me-*4* or C_6H_4Cl-*4*) [3], the isocyanide ligand undergoes protic attack (by HA acid) to afford the corresponding primary ammonium salt. The presence of labile ligands plays a fundamental role due to their facile replacement by a stronger electron donor anion, A^-, which promotes further protonation at CNR to give complete reduction to amine.

Hydrocarbons are also detected in some of these systems, although in minor yields; hence, it is yet unknown the fate of most of the terminal CNR carbon atom, although species with carbon hydrides or ≡CA ligating the metal atom seem likely intermediates.

The protonation of the isocyanide ligand occurs with concomitant oxidation of the metal (which behaves as the reducing agent), and the systems are not catalytic (the maximum yield for the reductive cleavage of the isocyanide corresponds to the consumption of nearly all the available metal six d electrons).

Hence, *electron-richness* of the metal centre and the presence of a *labile co-ligand* appear to play a fundamental role in the activation of isocyanides towards reductive cleavage to primary amines upon protonation which occurs in a stepwise way. However, these systems fail to mimic the formation (in a considerable amount) of the other products (hydrocarbons) of the enzymatic reduction. The poisoning of the ligating carbon atom (which possibly exhibits an electrophilic character) by the anion of the acid may conceivably occur, and the use of an *auxiliary reducing agent* (or the imposition, by electrochemical techniques, of a suitable cathodic potential) would be required to reduce the oxidized central metal and, hence, activate the ligating carbon atom towards protonation and also regenerate an active electron-rich metal centre, although in a discontinuous process — Fig. 1 where L is a labile ligand (may be more than one) such as phosphine or phosphite and A^- is a stronger net electron donor species such as OR^- or an halide.

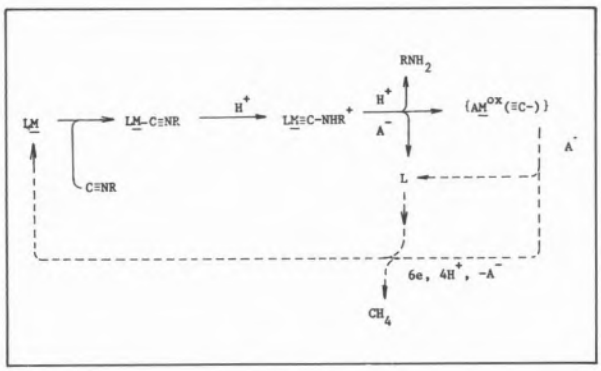


Fig. 1
Hypothetical catalytic cycle for the protic reduction of isocyanide to amine and methane at an electron-rich metal centre

The metal centre *M* may be a poly-hydridic moiety which would account for H_2 evolution by protic reduction. It may also bind other substrates such as dinitrogen which may be activated to reduction affording ammonia by protonation (as it is observed [4] for the Mo or W monophosphine centres). In the natural systems, water may behave as the protic source.

We are pursuing this work namely by attempting to isolate metallic intermediates, to increase the yield of hydrocarbon formation and by extending this type of study to other activating centres (*e.g.*, with a group VIII transition metal site) and to other substrates (such as nitriles).

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PS5.22 — TH

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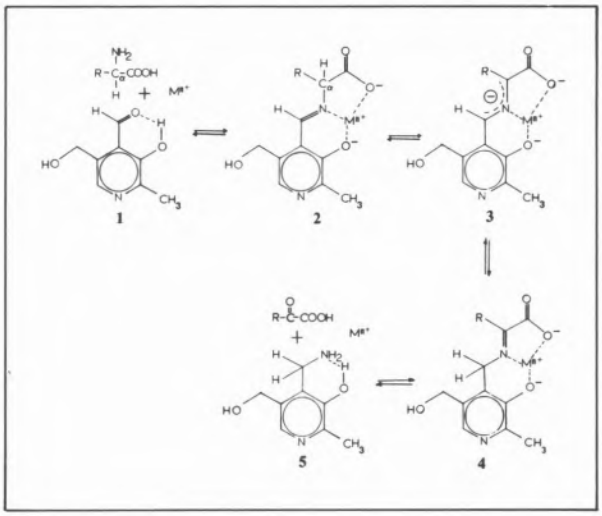
A PROTON-NMR STUDY OF THE KINETICS OF FORMATION OF THE GENERAL INTERMEDIATE IN VITAMIN B-6-CATALYZED TRANSAMINATION

The rates of the transamination reactions of α-amino acids and α-keto acids have been determined by measurement of the 200 MHz proton NMR spectra of the functional groups of the Al(III) complexes of the Schiff bases **2, 4** formed with pyridoxal **1** and pyridoxamine **5** respectively. Reaction systems measured in D_2O at 10°C consisted of 1:1:1 molar ratios of pyridoxal:α-amino acid:Al(III) or pyridoxamine:α-keto acid:Al(III). Amino and keto acids employed are alanine, α-aminoisobutyric acid, valine, phenylglycine, pyruvic acid, and α-ketobutyric acid. A negative deprotonated intermediate **3** was detected in all systems that undergo transamination (*i.e.*, except α-aminoisobutyric acid). The intermediate resembles the aldimine with NMR resonances shifted upfield in accordance with its greater negative charge. With Al(III) and pyridoxal as catalysts the equilibrium concentrations of the intermediate formed from α-amino acids are reached in the time required to reach transamination equilibrium and is maintained in solution at a fraction (±10-20%) of the aldimine Schiff base concentration. In the reverse reaction with Al(III) and pyridoxamine as catalysts, α-keto acids produce the intermediate initially at higher concentrations than those of the aldimine reaction product. The ratios of these species change as equilibrium is reached, to give the same fraction of Al(III)-stabilized intermediate as that obtained in the forward reaction. The relative changes in concentration of the α-deprotonated carbanion **3** and reaction products (the Schiff base chelates **2** and **4**) with time clearly demonstrate it to be the common mandatory intermediate in both the forward and reverse metal ion-catalyzed transamination reactions.



For the metal-free enzyme systems it is suggested that the active intermediate is an analogous deprotonated intermediate with a proton coordinated to the azomethine nitrogen in place of the metal ion in **3**. This type of intermediate, first suggested by ABBOTT and MARTELL [1], is suggested as the transamination intermediate in place of the quinonoid-type Schiff base tautomer previously suggested [2,3].

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