

Table
Comparison of ligand exchange kinetics for FeHBED and Fe-Transferrin at pH 7.4^{a)}

	X = HBED	X = Transferrin	
	$k_{\text{HBED}}, \text{s}^{-1}$	$k_{\text{Tf}}, \text{s}^{-1}$	$k_{\text{Tf}}/k_{\text{HBED}}$
FeX + L \longrightarrow FeL + X			
L = 0.05 M EDTA	2.7×10^{-9}	$4.1 \times 10^{-4} \text{ b)}$	1.5×10^5
L = 0.1 M Thioglycolate	3.5×10^{-6}	$3.6 \times 10^{-4} \text{ c)}$	1.0×10^2
L = 0.06 M Pyrophosphate	1.3×10^{-7}	$1.9 \times 10^{-3} \text{ c)}$	1.5×10^4
$\text{Fe}^{\text{III}}\text{X} + \text{BPS} \xrightarrow{\text{R}} \text{Fe}^{\text{II}}(\text{BPS})_3 + \text{X}$			
R = 0.03 M Dithionite	5.7×10^{-3}	$4.3 \times 10^{-5} \text{ c)}$	7.5×10^{-3}
R = 0.1 M Thioglycolate	4.2×10^{-5}	$3.6 \times 10^{-4} \text{ c)}$	8.6

a) All data 25°C, I = 0.1 M KNO₃. b) [3]. c) [4].

The implications of this observation in terms of the role of the protein and/or HCO₃⁻/CO₃⁼ in influencing the lability of the iron in transferrin will be discussed.

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PS5.20 — TU

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NET ELECTRON ACCEPTOR/DONOR CHARACTER OF ISOCYANIDES AND DINITROGEN AT THE IRON(II) CENTRE {FeH(Ph₂PCH₂CH₂PPh₂)₂}⁺: AN ELECTROCHEMICAL STUDY

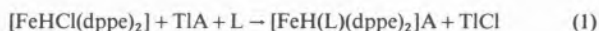
1 — INTRODUCTION AND RESULTS

Isocyanides (C≡NR) have been used as probes for the study of the electronic and chemical properties of dinitrogen activated by a transition metal centre [1].

Hence, *e.g.*, an analogy of chemical behaviour between N₂ and CNR was detected when they bind a d⁶ Mo or W phosphinic centre, both substrates being activated towards ready electrophilic attack. The net electron donor/acceptor character

of N_2 and CNR and their chemical reactivities were also compared [2,5] when they ligate $\{ReCl(dppe)_2\}$ and in the present work we extend to a group VIII centre, $\{FeH(dppe)_2\}^+$, the comparison between these two substrates.

Complexes $trans-[FeH(L)(dppe)_2]A$ ($L = N_2$ or CNR with $R = C_6H_4NO_2-4$, C_6H_4Me-4 , C_6H_5 , C_6H_4OMe-4 , Me, Et or Bu^1 ; $A^- = BF_4^-$ or PF_6^-), which were prepared according to reaction (1) [3],



undergo a partial reversible or an irreversible electrochemical oxidation at a Pt electrode, in thf (or NCMe)/ $[Bu_4N][BF_4]$ or in thf/ $LiClO_4$, and the values of $E_{p/2}^{ox}$ were compared with those obtained by other authors [4] for the analogous carbonyl, nitrile and thiocyanate compounds $trans-[FeH(L')(dppe)_2]^n$ ($n = +1$; $L' = CO$, NCMe or NCPH. $n = 0$; $L' = SCN^-$ or Cl^-). The following order of $E_{p/2}^{ox}$ is then observed: $CO > aryl \text{ isocyanides} > alkyl \text{ isocyanides} > NCPH > NCMe \approx N_2 > SCN^- > Cl^-$ —which corresponds to the order of decreasing net electron π acceptor — σ donor character of these ligands.

2 — DISCUSSION

2.1 — Isocyanide and dinitrogen ligand P_L parameter at the $\{FeH(dppe)_2\}^+$ centre

A linear relationship between $E_{1/2}^{ox}$ of complexes $[FeH(L')(dppe)_2]^n$ (see above) and the P_L ligand parameter for L' —defined [4] as $P_L = E_{1/2}^{ox}[Cr(CO)_5L] - E_{1/2}^{ox}[Cr(CO)_6]$ —was previously reported by other authors [4]. In the present study, this relationship is expressed for $E_{p/2}^{ox}$ by equation (2) which allows to estimate the P_L values for the isocyanide and the dinitrogen ligands

$$E_{p/2}^{ox} \approx 1 + P_L \text{ (volt)} \quad (2)$$

at the $\{FeH(dppe)_2\}^+$ centre (from the knowledge of the corresponding $E_{p/2}^{ox}$ which were obtained experimentally in this work): $P_L(CNR)$ falls in the range -0.1 to -0.2 V (depending on R) and $P_L(N_2) \approx -0.5$ V.

2.2 — Dependence of the net electron acceptor/donor character of isocyanides and dinitrogen on the electron-richness of the binding metal centre

The electron-richness, E_s , of a metal centre $\{M_s\}$, defined [4] as $E_s = E_{1/2}^{ox}[M_s(CO)]$ (a higher electron-richness corresponds to a lower E_s value), constitutes a relevant electrochemical parameter for the study of the electronic releasing ability of the metal centre. Isocyanide and dinitrogen ligand P_L values at the $\{FeH\}^+$ centre ($Fe = Fe(dppe)_2$) were compared with those estimated for metal centres with clearly distinct electron-rich characters, such as $\{Mo(N_2)\}$ and $\{Cr(CO)_5\}$ (Table) and a few observations may be presented:

— For both N_2 and CNR, the net electron acceptor/donor character (P_L) appears to be dependent on the electron-richness (E_s) of the metal centre: a decrease in the former may result from lowering the latter.

— A higher P_L dependence on E_s is observed for N_2 rather than for CNR: for the very high electron-rich $\{Mo(N_2)\}$ centre, N_2 is a strong net acceptor ligand (even better than isocyanide), whereas at $\{FeH\}^+$ the former presents a much lower electron acceptor character (weaker than isocyanide) and binds only weakly to the metal site;

Table
 P_L ligand parameter for CNR and N_2 at metal centres with different electron-richness (E_s)

Metal centre ^{a)}	E_s/V	$P_L(CNR)/V$	$P_L(N_2)/V$
$\{Mo(N_2)\}$	-0.13^b	$-0.23(CNBu^1)^c$	-0.07^b
$\{FeH\}^+$	$+1.04^b$	ca. -0.1 to -0.2 (e.g., -0.2 for $CNBu^1$) ^{c)}	ca. -0.5^c
$\{Cr(CO)_5\}$	$+1.53^b$	ca. -0.33 to -0.44 (e.g., -0.44 for $CNBu^1$) ^{b,d)}	— ^{e)}

a) $M = M(dppe)_2$. b) Ref. [4]. c) Estimated in the present study. d) Ref. [5]. e) Does not bind N_2 .

the least electron-rich centre, $\{Cr(CO)_5\}$, is even unable to bind N_2 (the isocyanides present then a considerably lower net electron-acceptance than when ligating the other more electron-rich centres which can bind N_2).

— Isocyanides appear to present a nearly constant (at least compared to the carbonyl reference ligand) net electron acceptor character when bound

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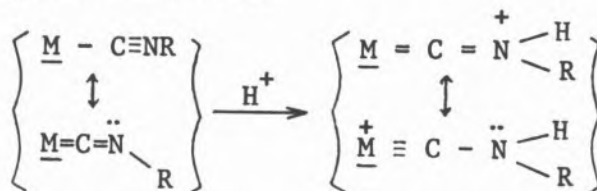
ELECTRON-RICH RHENIUM AND MOLYBDENUM METAL CENTRES AS POTENTIAL INORGANIC MODELS IN THE BIO-REDUCTION OF ISOCYANIDES?

Isocyanides ($C\equiv NR$) are organic species which are isoelectronic with dinitrogen (N_2) and can also be reduced by the enzyme nitrogenase with com-

plete 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).



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.