Electroreduction of Co-ordinated Cyanide to the Aminocarbyne Ligand (CNH_2) and a Pathway for Isomerisation of Ligating Methyleneamide (NCH_2): Reactions at Molybdenum of Relevance to Cyanide Reduction by Nitrogenase

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Electroreduction of *trans*-[Mo(CN)Cl($Ph_2PCH_2CH_2PPh_2$)$_2$] in the presence of phenol gives *trans*-[Mo(CNH_2)Cl($Ph_2PCH_2CH_2PPh_2$)$_2$], this is the first example of the conversion of co-ordinated cyanide to the aminocarbyne ligand, a reaction of relevance to reduction of cyanide by nitrogenase; the methyleneamide, *trans*-[Mo(NCH_2)Cl($Ph_2PCH_2CH_2PPh_2$)$_2$], is oxidised to the cyanide and therefore the redox reactions provide a pathway for the isomerisation of the group (MoNCH_2) to (MoCNH_2).

We report the first examples of the oxidation of a methyleneamido-ligand to co-ordinated cyanide, the reduction of a cyanide ligand to an aminocarbyne, reactions which occur at a single Mo-site and provide a pathway for isomerisation of (Mo–N=CH_2) to (Mo≡C–NH_2) see Scheme 1.

This chemistry may bear upon recent biochemical studies of cyanide reduction by the molybdenum enzyme nitrogenase[1] and also upon the diversification of the N-products which can be made from molecular nitrogen ligating mononuclear centres.[2]

Deprotonation of the methylimide *trans*-[Mo(NCH_3)Cl($Ph_2PCH_2CH_2PPh_2$)$_2$]$^+$ (**A**) by K[ButO] gives the neutral *trans*-[Mo(NCH_2)Cl($Ph_2PCH_2CH_2PPh_2$)$_2$] (**B**) which was isolated as an air-sensitive yellow solid, see Scheme 1, step i. $^{31}P\{^1H\}$ N.m.r. spectroscopy shows a singlet resonance which demonstrates that (**B**) retains the square-planar array of P-atoms about the molybdenum; the relative ^{31}P n.m.r. chemical shifts of the chloro- and bromo-analogues of (**A**) and of (**B**) are consistent with conservation of the axial halide ligands.[3] The deprotonation is reversible, treatment of (**B**) in tetrahydrofuran (THF) with aqueous HCl regenerates (**A**).[4]

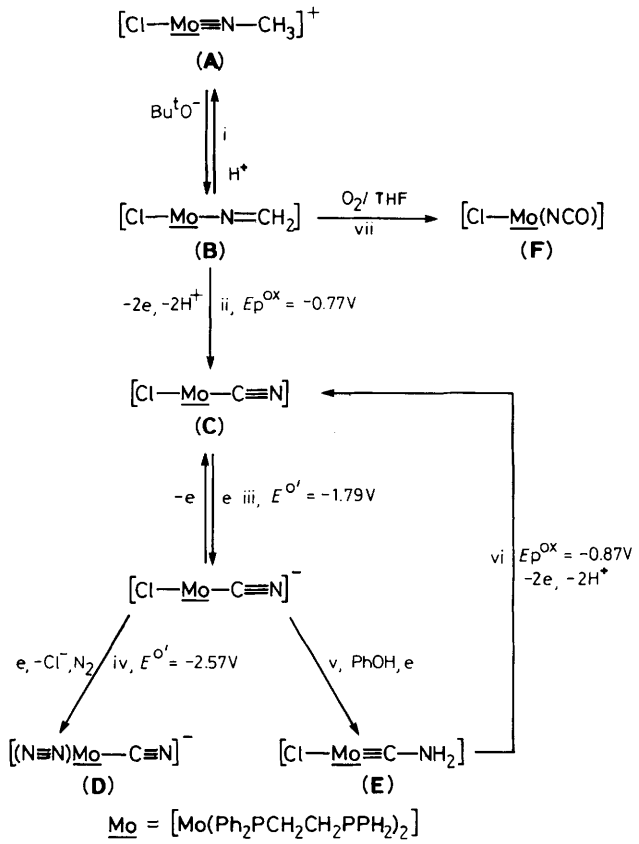
The configuration of the nitrogen ligand in (**B**) as an (NCH_2)-group was established by ^{13}C n.m.r. spectroscopy. The ^{13}C-methyl labelled (**A**) shows a quartet [δ 50.4, ($|^1J_{CH}|$ 150 Hz)] which is replaced on deprotonation by the triplet of the ^{13}C-methylene carbon of (**B**) [δ 111.4, ($|^1J_{CH}|$ 181 Hz)]. ^{31}P–^{13}C coupling was not observed in the n.m.r. spectra of either P or C nuclei and this rules against a side-ways bound NCH_2 ligand.

Oxidation of (**B**) in THF, by I_2 or anodically, gives the cyanide *trans*-[Mo(CN)Cl($Ph_2CH_2CH_2PPh_2$)$_2$], (**C**), Scheme 1, step ii. The structure of this complex was established by an *X*-ray crystallographic analysis of green prisms isolated from an anolyte. Compound (**C**) shows ν (C≡N) at 2046 cm^{-1} (^{13}C≡N at 2005 cm^{-1}): it is n.m.r.-silent.†

The rearrangement of the (MoNC)-framework to (MoCN) is probably an intramolecular process: iodine oxidation of ^{13}C-methylene (**B**) in the presence of an excess of [NBu_4][^{12}CN] and examination of the isolated product by Fourier transform i.r. spectroscopy showed no evidence for the incorporation of the ^{12}C-cyanide label.

Cyclic voltammetry {THF–[NBu_4][BF_4] (0.2 M); vitreous carbon} shows that (**C**) undergoes two successive one-electron reduction steps. The first of these is reversible, the second involves the irreversible loss of Cl^- and gives, under molecular nitrogen, the known anion *trans*-

† Full crystallographic details of the *X*-ray structural analysis of (**C**) will be given elsewhere.



Scheme 1. The redox potentials are relative to fc^+–fc and were measured in a THF electrolyte. Satisfactory microanalyses (CHN) were obtained for all the new compounds (**B**), (**C**), (**E**), and (**F**). i, solution n.m.r. spectroscopic data indicate that this step is essentially quantitative, (**B**) was isolated as an orange–yellow air-sensitive solid in 52% yield. ii, the electrochemical oxidation is inefficient because poorly soluble (**C**) fouls the working electrode and yields are low *ca.* 15%. The cyanide is best prepared by oxidation with iodine which gives (**C**) as a yellow–green solid in 65% yield based on (**A**). iii, the primary reduction is electrochemically reversible on the voltammetric timescale (s) and parallels that of *trans*-$[MoCl_2(Ph_2CH_2CH_2PPh_2)_2]$.† iv, cyclic voltammetry shows that the second reduction step of (**C**) is partially reversible; comparative voltammetric experiments under N_2 and argon, with independently synthesised (**D**) and with the bromo-analogue of (**C**) unequivocally established the formation of the dinitrogen complex. v, solution n.m.r. spectroscopic data and voltammetry show that preparative-scale reduction of (**C**) gives an essentially quantitative yield of the aminocarbyne. Work-up with MeCN gives (**C**) as an analytically pure yellow solid together with orange–brown crystals of a solvated species which we formulate as *trans*-$[Mo(CNH_2)(CH_3CN)(PPh_2PCH_2CH_2PPh_2)_2]Cl$. vi, the irreversible oxidation of (**E**) to (**C**) was established by cyclic voltammetry. vii, the oxygenation reaction [CARE : PEROXIDES] gives the isocyanate which was isolated as a bright yellow solid in about 60% yield, some cyanide (**C**) is also produced in this reaction but can be removed by recrystallisation. The formal oxidation states for (**A**)—(**F**) are as follows: (**A**), Mo^{IV}(18e); (**B**) Mo^{II}(18e); (**C**), Mo^{II}(16e); (**D**), Mo^{0}(18e); (**E**) Mo^{IV}(18e); (**F**), Mo^{II}(16e). Note: the $2e/2H^+$ reduction of the Mo^{II}-cyanide (**C**) leads to a formal oxidation of the metal centre to Mo^{IV}, (**E**) in a 16e → 18e conversion.

$[Mo(CN)(N_2)(Ph_2PCH_2CH_2PPh_2)_2]^-$, (**D**), Scheme 1, steps iii and iv.[5,6]

The primary reduction of the cyanide (**C**) becomes an irreversible two-electron process in the presence of phenol as a source of protons and the product is the aminocarbyne *trans*-$[Mo(CNH_2)Cl(Ph_2PCH_2CH_2PPh_2)_2]$, (**E**), Scheme 1, steps iii and v. Preparative controlled-potential reduction {THF–$[NBu_4][BF_4]$ (0.2 M) + PhOH (0.2 M); Hg-pool cathode; −1.9 V *v.* ferrocinium–ferrocene (fc^+–fc)} allows the quantitative electrosynthesis of (**E**) in an overall $2F\ mol^{-1}$ (**C**) process. The formulation of (**E**) as the aminocarbyne was established in the following way.

Compound (**E**) electrosynthesised from 50% ^{13}C-enriched cyanide (**C**) shows by ^{13}C n.m.r. the ligating carbyne resonance as a quintet, δ 225.9 ($|^2J_{PC}|$ 17.2 Hz), (coupling to four equivalent ^{31}P nuclei). The chemical shift and the coupling constant are closely similar to those of the hitherto unique aminocarbyne ligand in *trans*-$[Re(CNH_2)Cl(Ph_2PCH_2CH_2PPh_2)_2]^+$, [δ 222.4 ($|^2J_{PC}|$ 13 Hz)] the structure of which has been determined by *X*-ray analysis.[7] Appropriately the $^{31}P\{^1H\}$ n.m.r. spectrum of the ^{13}C-enriched (**E**) shows a doublet $|^2J_{PC}|$ 17.2 Hz (coupling to ^{13}C carbyne) and the central singlet resonance of the unlabelled material at 80.74 p.p.m. relative to trimethyl phosphite in THF. I.r. spectroscopy confirmed the presence of the amino-group and the lowering of the CN bond-order: ν(NH) 3380 w, 3287 m, 1568 m, bend; ν(CN) 1396 m, $\nu(^{13}CN)$ 1362 cm^{-1}. Electrochemical oxidation of (**E**) regenerates the parent cyanide (**C**), Scheme 1, step vi.

The reduction of the group (Mo–C≡N) to (Mo≡C–NH_2) provides a chemical precedent for a possible role for ligating aminocarbyne in the biological reduction of aqueous cyanide by molybdenum nitrogenase. The enzymic reduction gives the '4-electron' product methylamine and the '6-electron' products ammonia and methane.[1] We find that the ($MoNCH_2$)-group of the methyleneamide (**B**) lies on a 4-electron pathway to methylamine;[8] whether or not the isomeric aminocarbyne (**E**) lies on a parallel 6-electron pathway to ammonia and methane remains to be studied.

The N-atom in the methylimide (**A**) can be introduced from molecular nitrogen *via* reactions at the $\{Mo(Ph_2PCH_2CH_2PPh_2)_2\}$ assembly. The chemistry outlined in Scheme 1 should therefore provide a means of extending the range of N-products that can be made under mild conditions from N_2; oxygenation of the methyleneamide (**B**) to give the isocyanate (**F**) is of relevance in this latter context, Scheme 1, step vii.

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