

Electroreduction of Co-ordinated Cyanide to the Aminocarbyne Ligand (CNH₂) and a Pathway for Isomerisation of Ligating Methyleneamide (NCH₂): Reactions at Molybdenum of Relevance to Cyanide Reduction by Nitrogenase

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Electroreduction of *trans*-[Mo(CN)Cl(Ph₂PCH₂CH₂PPh₂)₂] in the presence of phenol gives *trans*-[Mo(CNH₂)Cl(Ph₂PCH₂CH₂PPh₂)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(NCH₂)Cl(Ph₂PCH₂CH₂PPh₂)₂], is oxidised to the cyanide and therefore the redox reactions provide a pathway for the isomerisation of the group (MoNCH₂) to (MoCNH₂).

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=CH₂) to (Mo≡C-NH₂) see Scheme 1.

This chemistry may bear upon recent biochemical studies of cyanide reduction by the molybdenum enzyme nitrogenase¹ 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(NCH₃)Cl(Ph₂PCH₂CH₂PPh₂)₂]⁺ (**A**) by K[ButO] gives the neutral *trans*-[Mo(NCH₂)Cl(Ph₂PCH₂CH₂PPh₂)₂] (**B**) which was isolated as an air-sensitive yellow solid, see Scheme 1, step i. ³¹P{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 ³¹P 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 (NCH₂)-group was established by ¹³C n.m.r. spectroscopy. The ¹³C-methyl labelled (**A**) shows a quartet [δ 50.4, (|¹J_{CH}| 150 Hz)] which is replaced on deprotonation by the triplet of

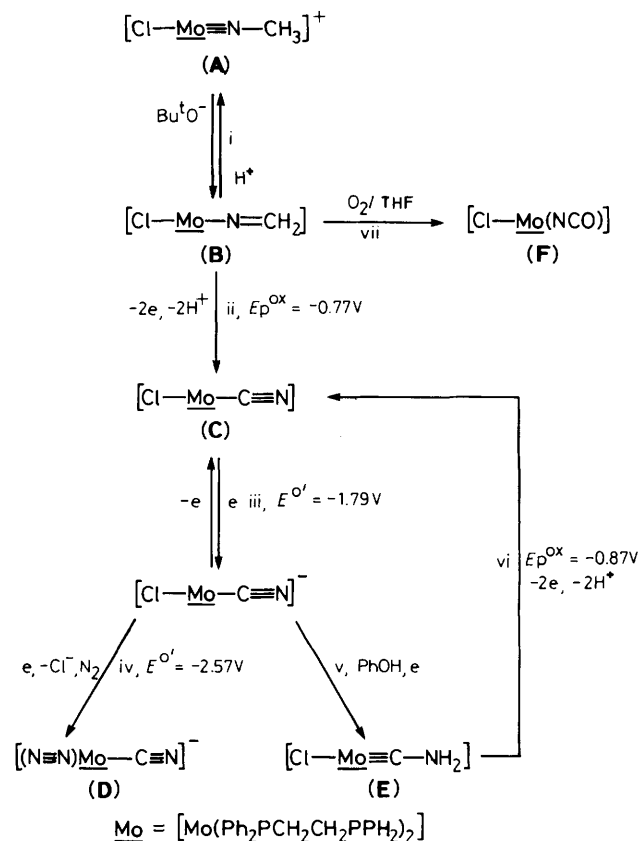
the ¹³C-methylene carbon of (**B**) [δ 111.4, (|¹J_{CH}| 181 Hz)]. ³¹P-¹³C coupling was not observed in the n.m.r. spectra of either P or C nuclei and this rules against a side-ways bound NCH₂ ligand.

Oxidation of (**B**) in THF, by I₂ or anodically, gives the cyanide *trans*-[Mo(CN)Cl(Ph₂CH₂CH₂PPh₂)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 (¹³C≡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 ¹³C-methylene (**B**) in the presence of an excess of [NBu₄][¹²CN] and examination of the isolated product by Fourier transform i.r. spectroscopy showed no evidence for the incorporation of the ¹²C-cyanide label.

Cyclic voltammetry {THF-[NBu₄][BF₄] (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*-[MoCl₂(Ph₂CH₂CH₂PPh₂)₂].† iv, cyclic voltammetry shows that the second reduction step of (C) is partially reversible; comparative voltammetric experiments under N₂ 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 aminocarbene. 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(CNH₂)(CH₃CN)(PPh₂PCH₂CH₂PPh₂)₂]Cl. vi, the irreversible oxidation of (E) to (C) was established by cyclic voltammetry. vii, the oxygenation reaction [CARE:PER-OXIDES] 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), Mo⁰(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)(N₂)(Ph₂PCH₂CH₂PPh₂)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 aminocarbene *trans*-[Mo(CNH₂)Cl(Ph₂PCH₂CH₂PPh₂)₂], (E), Scheme 1, steps iii and v. Preparative controlled-potential reduction

{THF-[NBu₄][BF₄] (0.2 M) + PhOH (0.2 M); Hg-pool cathode; -1.9 V v. ferrocinium-ferrocene (fc⁺-fc)} allows the quantitative electro-synthesis of (E) in an overall 2F mol⁻¹ (C) process. The formulation of (E) as the aminocarbene was established in the following way.

Compound (E) electro-synthesised from 50% ¹³C-enriched cyanide (C) shows by ¹³C n.m.r. the ligating carbene resonance as a quintet, δ 225.9 (|²J_{PC}| 17.2 Hz), (coupling to four equivalent ³¹P nuclei). The chemical shift and the coupling constant are closely similar to those of the hitherto unique aminocarbene ligand in *trans*-[Re(CNH₂)Cl(Ph₂PCH₂CH₂PPh₂)₂]⁺, [δ 222.4 (|²J_{PC}| 13 Hz)] the structure of which has been determined by X-ray analysis.⁷ Appropriately the ³¹P{¹H} n.m.r. spectrum of the ¹³C-enriched (E) shows a doublet |²J_{PC}| 17.2 Hz (coupling to ¹³C carbene) 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, ν(¹³CN) 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-NH₂) provides a chemical precedent for a possible role for ligating aminocarbene 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 (MoNCH₂) group of the methyleneamide (B) lies on a 4-electron pathway to methylamine;⁸ whether or not the isomeric aminocarbene (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(Ph₂PCH₂CH₂PPh₂)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 N₂; 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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