Preliminary communication

Synthesis of the cyanamide-derived bis(cyanoimido) complexes *trans*-[M(NCN)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] (M = Mo or W) and crystal structure of the molybdenum compound

Armando J.L. Pombeiro * **and M. Fatima C.G. Silva**

Centro de Quimica Estrutural, Complexo 1, Instituto Superior Tecnico, Av. Rovisco Pais,
1096 Lisbon Codex (Portugal)

David L. Hughes and Raymond L. Richards

AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex,
Brighton, BN1 9RQ (U.K.)

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Abstract

Reaction of cyanamide (NCNH$_2$) with *trans*-[M(N$_2$)$_2$(dppe)$_2$] (M = Mo or W, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) leads to the formation of the bis(cyanoimido) complexes *trans*-[M(NCN)$_2$(dppe)$_2$]. The crystal structure of *trans*-[Mo(NCN)$_2$(dppe)$_2$] has been determined by an X-ray diffraction study.

Cyanamide (N≡CNH$_2$) has recently been recognized [1] as a substrate of both Mo- and V-nitrogenase, being reduced to methylamine and ammonia (6-electron pathway) or to methane and ammonia (8-electron pathway). This has prompted much interest in the study of its coordination chemistry, which is virtually unexplored in spite of the rich organic chemistry which has been developed for this species [2].

In pursuance of our interest in the activation by transition metal centres of alternative substrates of nitrogenase, such as isocyanides or alkynes [3], we thus decided to initiate a study of the activation of cyanamide by dinitrogen-binding sites, and now we report our preliminary observations on the reactions of NCNH$_2$ with the dinitrogen complexes *trans*-[M(N$_2$)$_2$(dppe)$_2$] (**1**, M = Mo or W; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$).

From THF (tetrahydrofuran) solutions of the complexes (**1**) and cyanamide in a twofold molar ratio under argon we isolated dark red crystalline solids (**2**), the IR spectra of which exhibit a strong band at 2040 or 2063 cm^{-1} (for M = Mo or W, respectively), assigned to ν(N≡C). Interestingly, no ν(NH) band was observed, in agreement with the ^{1}H NMR spectra, in which no N*H* resonance was detected. The
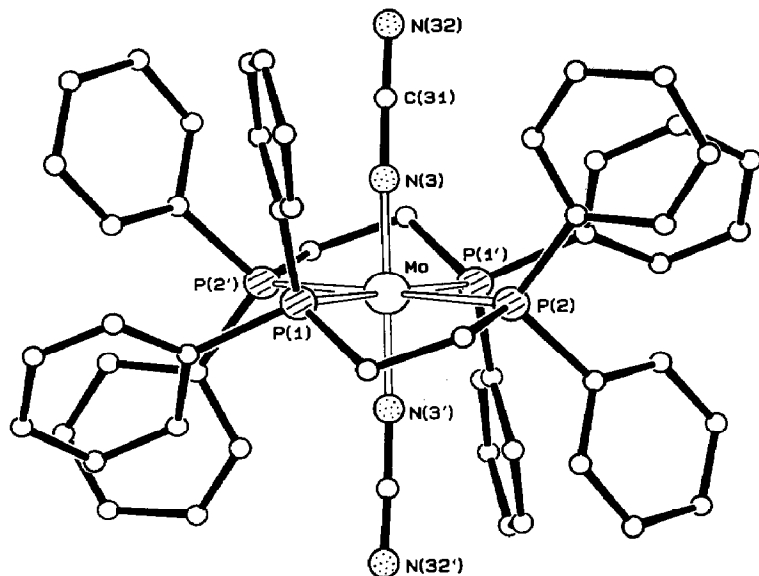
Fig. 1. Molecular structure of *trans*-[Mo(NCN)$_2$(dppe)$_2$]. Principal dimensions (with e.s.d.s in parentheses) include: Mo–N(3) 1.860(11), N(3)–C(31) 1.297(20), C(31)–N(32) 1.167(19), Mo–P(1) 2.509(3), Mo–P(2) 2.514(4)Å. Mo–N(3)–C(31) 173.8(10), N(3)–C(31)–N(32) 177.8(16), N(3)–Mo–P(1) 95.9(3), N(3)–Mo–P(2) 95.9(3), P(1)–Mo–P(2) 79.3(1)°.

singlet observed in the ^{31}P NMR spectrum (δ −102.2 ppm (M = Mo) or −119.6 ppm (M = W, with the two expected ^{183}W satellites, J(WP) 277.9 Hz), rel. P(OMe)$_3$ in CD$_2$Cl$_2$) is indicative of a *trans* arrangement of the two diphosphine ligands.

These data, together with those from elemental microanalyses, suggested the formulation of species (**2**) as the bis(cyanoimido) complexes of M^{IV}, *trans*-[M(NCN)$_2$(dppe)$_2$]. This was confirmed by a single-crystal X-ray diffraction study for **2** (M = Mo), which is, to our knowledge, the first example of a cyanoimide transition-metal complex to be structurally characterized by X-rays.

The molecular structure of **2** (M = Mo) is depicted in Fig. 1, which confirms the expected octahedral-type geometry with two cyanoimido(2 −) ligands in *trans* position in a centrosymmetrical arrangement *.

The apical MoNCN group is almost linear and presents a Mo–N bond length (1.860(11) Å) shorter than the 2.014(5) Å observed [4] for *trans*-[Mo(N$_2$)$_2$(dppe)$_2$], but longer than those quoted for related cationic hydrazido(2 −) complexes (nor-

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* X-ray analysis of *trans*-[Mo(NCN)$_2$(dppe)$_2$]. Crystal data: C$_{54}$H$_{48}$MoN$_4$P$_4$, M = 972.8. Triclinic, space group $P\bar{1}$ (no. 2), a 9.384(3), b 11.683(5), c 12.867(5) Å, α 109.65(3), β 100.44(3), γ 109.59(3)°, V 1180.8 Å^3. Z = 1, D_c 1.368 g cm^{-3}, $F(000)$ = 502, μ(Mo-K_α) 4.4 cm^{-1}. λ(Mo-K_α) 0.71069 Å.

Small prism, deep red crystal coated in silicone grease. Preliminary photographs, then CAD4 diffractometer for cell parameters and intensity data (θ_{max} 20°, 2195 unique reflections). Corrections were made for Lorentz-polarisation effects, slight deterioration, and negative intensities.

Structure determination by heavy-atom method; refinement by full-matrix least-squares methods to R = 0.076, R_w = 0.080 for 1546 reflections ($I > \frac{3}{2}\sigma(I)$), weighted $w = (\sigma^2(F) + 0.02 F^2)^{-1}$. All non-hydrogen atoms allowed anisotropic thermal parameters; hydrogen atoms in idealised positions, with parameters riding on bonded C atoms. No significant features in final difference map.

A table of atomic coordinates and a full list of structural parameters has been deposited with the Cambridge Crystallographic Data Centre.

mally 1.70–1.80 Å) [5] and also longer than most metal–imide distances (approx. 1.65–1.85 Å, depending upon complex) [6]. Moreover, the N_α–C bond length (1.297(20) Å) suggests a bond order greater than one. The cyanoimido(2 −) ligand is thus best represented by the linear forms $M \equiv N_\alpha\text{–}C\equiv N \leftrightarrow M \stackrel{+}{\rightleftharpoons} N_\alpha\text{=}C\text{=}\overline{N}$.

Complexes 2, in 0.2 M [Bu$_4$N][BF$_4$]/THF, undergo, in cyclic voltammetry at a Pt electrode, a single-electron reversible oxidation at values of half-wave oxidation potentials ($E_{1/2}^{ox}$ 0.79 or 0.65 V, vs. SCE, for M = Mo or W, respectively) which are much higher than those known for the related dinitrogen, dicarbonyl or diisocyanide complexes trans-[MoL$_2$(dppe)$_2$] (−0.16 [7], −0.11 [7] or −0.55 V [8], for L = N$_2$, CO or CNMe, respectively) in which the metal is in a much lower oxidation state (zero).

The formation of the cyanoimido(2 −) ligand is consistent with the known [9] tendency of Mo and W to form multiple bonds to nitrogen. Moreover, it involves metal-induced dehydrogenation of cyanamide, a reaction which relates to the direct synthesis of cyanamide salts, such as MgNCN [2,10] or Na$_2$NCN [2,10] formed by attack on NCNH$_2$ (or its polymers) by Mg or Na with liberation of H$_2$. In our system, the electron-rich and readily oxidizable d^6 metal centre {M(dppe)$_2$} (M = Mo or W) conceivably plays the role of the reducing magnesium or alkali metal.

The mechanism of the enzymatic reduction of cyanamide is still unknown and no intermediate has yet been detected, but the present study suggests the possible involvement of cyanoimido-species.

References

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