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Syntheses and properties of hydride–cyanamide and derived hydrogen-cyanamide complexes of molybdenum(IV). Crystal structure of $[MoH_2(NCNH_2)_2(Ph_2PCH_2CH_2PPh_2)_2][BF_4]_2$

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Received 11th August 2003, Accepted 13th August 2003
First published as an Advance Article on the web 26th August 2003

The first hydride–cyanamide (or –cyanoguanidine) complexes of molybdenum, $[MoH_2(NCR)_2(dppe)_2][BF_4]_2$ (R = NH_2 **1a**, NMe_2 **1b**, NEt_2 **1c** or $NC(NH_2)_2$ **1d**; dppe = $Ph_2PCH_2CH_2PPh_2$), have been prepared by treatment of $[MoH_4(dppe)_2]$ in THF with the appropriate cyanamide (or cyanoguanidine) in the presence of HBF_4. Reaction of **1a** with a base leads to the bis(hydrogen-cyanamide) [or bis(hydrogen-cyananoimide)] complex *trans*-$[Mo(NCNH)_2(dppe)_2][BF_4]_2$ **2** or to the bis(cyanoimide) complex *trans*-$[Mo(NCN)_2(dppe)_2]$ **3**, *via* base-catalysed or base-promoted dehydrogenation, whereas cathodically-induced dehydrogenation appears to form $[MoH_2(NCNH)(NCNH_2)(dppe)_2]^+$ **4**. The spectroscopic properties of the complexes are also reported along with their electrochemical behaviours and the molecular structure of **1a** as established by X-ray crystallography which indicates the presence of the $NCNH_2$ ligands involved in two hydrogen bonds connecting the ions in dimeric units.

Introduction

The coordination chemistry of cyanamide (N≡C–NH_2) is still an underdeveloped field of research[1–10] in spite of the recognized interest of this species namely as a substrate of Mo- and V-nitrogenases[11] and of cyanamide hydratase,[12] a reagent in chemical synthesis,[13] a fertiliser,[14] a drug for treatment of alcoholism,[15] an amino acid precursor, a prebiotic[16] and an interstellar space[17] compound. Organocyanamides, *e.g.* phenylcyanamides,[18] have also been little explored in coordination chemistry.

Within our interest on the activation of small molecules with biological significance,[19] we have already reported the syntheses of a number of cyanamide, diorgano derivatives (N≡CNR_2) or cyanoguanidine *i.e.* its dimeric form, $NCNC(NH_2)_2$, complexes of Mo,[2,3] Re,[20–22] Fe[23] or Pt.[24–26]

Further reactions of the organocyanamide ligands have been achieved only scantly and they include insertion into a metal–carbon multiple bond,[27] C–C coupling with a μ-C_4Me_4 ligand derived from MeC≡CMe,[28] metathesis with a metal–metal triple bond,[29] nucleophilic addition of an alcohol (to cyanoguanidine)[26] or of an oxime,[25] nucleophilic attack by an adjacent hydroxide ligand[30] or, very recently, protonation at the unsaturated C atom to form amidoazavinylidene species.[3] Even less studied are the reactions of the ligated cyanamide itself, although we have reported[21] its deprotonation by base to form the hydrogen-cyanamide ($NCNH^-$) ligand at a rhenium centre, whereas the formation of the cyanoimide (NCN^{2-}) ligands in *trans*-$[Mo(NCN)_2(dppe)_2]$ (**3**, dppe = $Ph_2PCH_2CH_2PPh_2$) occurs[2] in the reaction of $NCNH_2$ with the bis(dinitrogen) complex *trans*-$[Mo(N_2)_2(dppe)_2]$ in which the electron-rich molybdenum(0) centre {$Mo(dppe)_2$} behaves as a dehydrogenating and reducing agent of the cyanamide. The cyanoimide ligand in **3** is susceptible to attack by various electrophiles (E^+ = H^+, Et^+, $EtCO^+$ or Me_3Si^+) to give the corresponding *trans*-$[Mo(NCN)(NCNE)(dppe)_2]^+$ derivatives which, in some cases, can be further protonated to the cyanamide *trans*-$[Mo(NCN)(NCNHE)(dppe)_2]^{2+}$ products.[2]

Of particular biological significance, *e.g.* towards the understanding of the enzymatic reactions of cyanamide, are those involving proton- or hydrogen-transfer and, in view of the expected[31] relevance of molybdenum-hydride centres in the activity of nitrogenase, we have now extended the investigation of the coordination chemistry of cyanamide (and related cyanoguanidine or diorganocyanamides) to a Mo-hydride centre by selecting, as its source, the tetra-hydride *trans*-$[MoH_4(dppe)_2]$ complex which is derived[32] from reaction of H_2 with *trans*-$[Mo(N_2)_2(dppe)_2]$. We have thus observed the formation of $[MoH_2(NCNH_2)_2(dppe)_2][BF_4]_2$ (**1a**) (to our knowledge the first cyanamide–hydride molybdenum complex), produced upon protic partial dehydrogenation of the tetra-hydride compound in the presence of $NCNH_2$ (the corresponding organocyanamide compounds have been obtained similarly from the reactions with the organocyanamides). We also now report further deprotonation or dehydrogenation reactions of **1a**, induced by base or by electron-transfer, allowing the preparation of complexes with the $NCNH_x$ (x = 2, 1 or 0) ligands with overall preservation of the 18-electron count and of the molybdenum oxidation state (+4).

Results and discussion

Biscyanamide–dihydride complexes $[MoH_2(NCR)_2(dppe)_2][BF_4]_2$

Treatment of a THF solution of $[MoH_4(dppe)_2]$ with $HBF_4\cdot Et_2O$ followed by addition of the appropriate cyanamide (or cyanoguanidine) (in a tenfold molar ratio), under an inert atmosphere and at room temperature, leads to the formation of $[MoH_2(NCR)_2(dppe)_2][BF_4]_2$ (**1**; R = NH_2 **1a**, NMe_2 **1b**, NEt_2 **1c** or $NC(NH_2)_2$ **1d**; dppe = $Ph_2PCH_2CH_2PPh_2$) (eqn. (1)).

$$[MoH_4(dppe)_2] + 2\,NCR + 2\,HBF_4 \xrightarrow{THF} [MoH_2(NCR)_2(dppe)_2][BF_4]_2 + 2\,H_2 \quad (1)$$

DOI: 10.1039/b306368b

This preparative method involves hydride abstraction (by acid) from the tetrahydride metal centre and is analogous to that reported[33] for the synthesis of dihydride-Mo(IV) complexes with other small molecules. It shows that, under the conditions used, $[MoH_4(dppe)_2]$ is a convenient starting material for the preparation of such a type of complex bearing two cyanamide (its organo-derivatives or its dimeric form *i.e.* cyanoguanidine) ligands. The observed behaviour of cyanamide itself at this Mo(IV) centre contrasts with that known[2,34] in the case of its reaction with *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W), which involves dehydrogenation by the electron-rich reducing metal(0) centre to give the bis(cyanoimido) complexes *trans*-$[M(NCN)_2(dppe)_2]$ **3**. Such a reaction does not occur in the current study which involves a non-reducing and much higher oxidation state metal centre.

Complexes **1** were obtained in good yields (80–88%) as yellow solids, and their solid-state IR spectra (KBr pellets) exhibit strong bands in the 2260–2220 cm^{-1} range which are assigned to the N≡C stretching mode of the cyanamide ligands, as observed in other Mo(IV),[2] Fe(II),[23] Re(II)[20] or Pt(II)[24,25] compounds. The increase of $\nu(N{\equiv}C)$ (by *ca* 30 cm^{-1}) on coordination of NCR is indicative of the η^1-coordination mode *via* the cyano group[35] which acts as an effective electron-donor. Complexes **1a** and **1d** display broad and strong bands in the range 3250–3140 cm^{-1} or 3440–3350 cm^{-1} which are assigned to $\nu(NH)$ of $NCNH_2$ or $NCNC(NH_2)_2$, respectively, whereas other strong bands at 1630–1590 cm^{-1} (**1a**) or 1650–1550 cm^{-1} (**1d**) are due to $\delta(NH)$ of these ligands and/or $\nu(N{=}C)$ of the cyanoguanidine. The IR $\nu(MoH)$ vibrations are detected as weak and broad bands at 1910–1890 cm^{-1}.

A *cis* stereochemical arrangement is assigned to the dppe ligands for all complexes **1** on the basis of a pair of triplets ($^2J_{PP}$ *ca* 8 Hz) at δ −67.17 to −72.70 and δ −82.30 to −88.01 relative to $P(OMe)_3$, in the $^{31}P\text{–}\{^1H\}$ NMR spectra, typical of an A_2B_2 spin system. Consistent with the *cis* configuration, the hydride resonance in the ^1H NMR spectra appears as a complex multiplet at δ *ca* −3. The resonances of the dppe methylene protons occur as two (or four, for **1b**) broad multiplets at δ *ca* 2–3, suggesting the non-equivalency of the CH_2 groups. For complex **1a** the signal from the amino protons of the binding cyanamide is observed at δ 6.67 (and, as expected, disappears upon addition of D_2O), a value comparable with those quoted for the cyanamide complexes of iron(II)[23] *trans*-$[FeH(NCNH_2)(dppe)_2][BF_4]$, *trans*-$[FeBr(NCNH_2)(depe)_2][BF_4]$ or *trans*-$[Fe(NCNH_2)_2(depe)_2][BF_4]_2$, but somewhat higher than those reported for *trans*-$[Mo(NCN)(NCNH_2)(dppe)_2][BF_4]_2$[2] and *trans*-$[Re(CNR)(NCNH_2)(dppe)][BF_4]$[21] where the cyanamide ligand is expected [on the basis of the lower IR $\nu(N{\equiv}C)$ values] to behave as a weaker electron donor to the metal centre. In the ^{13}C NMR spectra (both ^1H-decoupled and coupled) of complexes **1** the cyano N*C*R resonance is observed as a singlet at δ *ca* 124 which corresponds to a slight downfield shift (by *ca* 6 ppm) upon coordination. For the cyanoguanidine complex **1d**, the imine carbon $NCNC(NH_2)_2$ resonance is observed at δ 161.45.

In the FAB^+ mass spectra of the complexes, the corresponding molecular clusters are clearly detected and their isotopic patterns match with the theoretical ones obtained by simulation,[36] being consistent with the known seven molybdenum stable isotopes. The peak detected at the highest *m*/*z* is due to the monocationic aggregate $[MoH_2(NCR)_2(dppe)_2.BF_4]^+$ as expected on the basis of the behaviour observed for $[ML_n^{2+}][Y^-]_2$ type salts[37] and for the related complexes $[Mo(NCN)(NCNH_2)(dppe)_2][BF_4]_2$[2] and $[FeL_2(depe)_2][BF_4]_2$ (L = cyanamide[23] or organonitrile[38]). The fragmentation pathways occur either by cleavage of the metal–ligand bonds or by rupture of the bonds within the various ligands. They can be initiated by loss of the monodentate ligands which appears to be favoured relative to elimination of the chelating diphosphine. Moreover, metal fluorination under FAB^+-MS conditions was detected for fragments with *m*/*z* > 900. Oxygenation of the metal fragment $[Mo(dppe)_2]^+$ also occurs, although the site (metal or phosphorus atom) could not be ascertained. Decomposition of the coordinated dppe follows a pathway that is different from that of the free diphosphine,[39] but similar to that of the related bis(cyanoimido) molybdenum(IV) complex *trans*-$[Mo(NCN)_2(dppe)_2]$,[2] revealing the influence of coordination in the process.

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses for $[MoH_2(NCNH_2)_2(dppe)_2][BF_4]_2\cdot THF$ (**1a**·THF)

(a) About the Mo atom

Mo–P(1)	2.483(6)	Mo–N(5)	2.20(2)
Mo–P(2)	2.506(6)	Mo–N(6)	2.19(3)
Mo–P(3)	2.476(6)	Mo–H(7)	1.61(12)
Mo–P(4)	2.503(6)	Mo–H(8)	1.84(13)
P(1)–Mo–P(2)	81.7(2)	N(5)–Mo–N(6)	79.0(8)
P(1)–Mo–P(3)	123.6(2)	P(1)–Mo–H(7)	55(4)
P(1)–Mo–P(4)	105.1(2)	P(1)–Mo–H(8)	35(5)
P(2)–Mo–P(3)	106.2(2)	P(2)–Mo–H(7)	137(4)
P(2)–Mo–P(4)	165.4(2)	P(2)–Mo–H(8)	47(5)
P(3)–Mo–P(4)	81.0(2)	P(3)–Mo–H(7)	97(4)
P(1)–Mo–N(5)	79.0(6)	P(3)–Mo–H(8)	128(4)
P(2)–Mo–N(5)	78.8(6)	P(4)–Mo–H(7)	52(4)
P(3)–Mo–N(5)	157.1(6)	P(4)–Mo–H(8)	137(5)
P(4)–Mo–N(5)	89.7(6)	N(5)–Mo–H(7)	94(4)
P(1)–Mo–N(6)	157.4(6)	N(5)–Mo–H(8)	72(4)
P(2)–Mo–N(6)	89.2(7)	N(6)–Mo–H(7)	132(4)
P(3)–Mo–N(6)	78.8(6)	N(6)–Mo–H(8)	131(5)
P(4)–Mo–N(6)	79.6(7)	H(7)–Mo–H(8)	90(6)

(b) In the cyanamide ligands

N(5)–C(51)	1.17(4)	N(6)–C(61)	1.09(4)
C(51)–N(52)	1.33(4)	C(61)–N(62)	1.42(4)
Mo–N(5)–C(51)	174(2)	Mo–N(6)–C(61)	163(3)
N(5)–C(51)–N(52)	174(3)	N(6)–C(61)–N(62)	173(3)

(c) Proposed hydrogen-bonding contacts[a]

N(52) ··· F(102′)	2.79(3)	C(51)–N(52) ··· F(102′)	107(2)
N(52) ··· F(104″)	2.76(3)	C(51)–N(52) ··· F(104″)	126(2)
N(62) ··· F(93)	2.77(3)	C(61)–N(62) ··· F(93)	109(2)
N(62) ··· O(113)	2.79(4)	C(61)–N(62) ··· O(113)	109(2)

[a] Symmetry relations: ′ ½ + *x*, ½ − *y*, *z*. ″ ½ − *x*, *y* − ½, 1 − *z*.

The molecular structure of $[MoH_2(NCNH_2)_2(dppe)_2][BF_4]_2$ **1a**, as established by X-ray diffraction analysis, is depicted in Fig. 1 and selected bond lengths and angles are listed in Table 1. The crystal comprises the Mo-complex cation, two independent BF_4^- anions, one THF solvent molecule and a further unresolved solvent molecule. In the cation, the Mo atom has

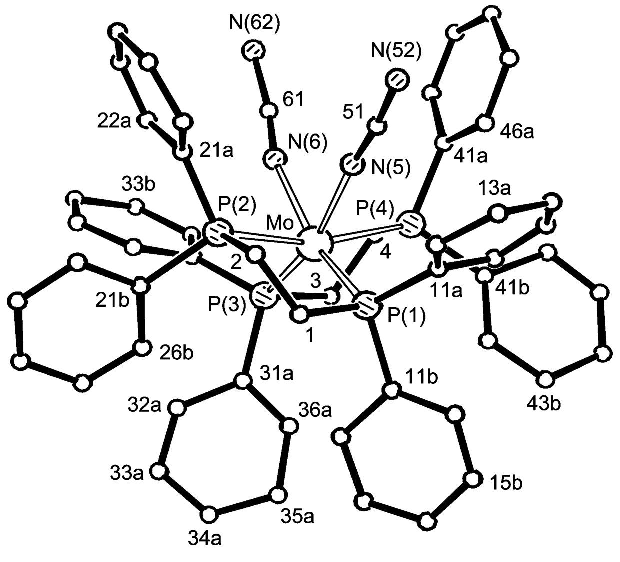


Fig. 1 Molecular structure of the complex cation of $[MoH_2(NCNH_2)_2(dppe)_2][BF_4]_2\cdot THF$ (**1a**·THF), indicating the atom numbering scheme; atoms labelled "*n*" represent the carbon atoms "C(*n*)".

dodecahedral coordination geometry, with the two diphosphine ligands chelating in the "equatorial" B-sites of the dodecahedron, in agreement with the NMR results discussed above; the two $NCNH_2$ ligands occupy adjacent A-sites and the two hydrides are assumed to be in the opposite A-sites; the two hydride atoms were located in difference Fourier maps but their refinement should not be considered reliable. There is a pseudo-2-fold symmetry axis passing between the $NCNH_2$ ligands and through the Mo atom: the two dppe ligands are related closely by this pseudo-symmetry. The diphosphines show P(1)–C(1)–C(2)–P(2) and P(3)–C(3)–C(4)–P(4) with normal *gauche* torsion angles, 55.5(16) and 55.0(16)° respectively. The cyanamide ligands have an essentially linear coordination and the Mo–N distances, 2.20(2) and 2.19(3) Å, are identical to those of $[MoH_2(NCMe)_2(PMe_2Ph)_4][BF_4]_2$[40] (also with a dodecahedral coordination) and comparable to the average value (2.282 Å) quoted[41] for nitrile complexes of Mo, being longer than those reported for the Mo–N (cyanoimido) bond lengths in *trans*-$[Mo(NCN)_2(dppe)_2]$ [1.860(11) Å][34] or *trans*-$[Mo(NCN)(NCNE)(dppe)_2][BF_4]$ [1.906(9) (E = H) or 1.801(13) (E = Et) Å].[2]

The average metal–phosphorus bond length, 2.492(7) Å, is comparable to that quoted for $[MoH_2(NCMe)_2(PMe_2Ph)_4][BF_4]_2$, [2.514(4) Å],[40] and only slightly longer than the short distance, 2.420(3) Å,[42] observed for $[MoH_4(dppe)_2]$. The Mo–P [2.506(6) and 2.503(6) Å] distances for the approximately *trans* phosphorus atoms, P(2) and P(4), are longer than those [2.483(6) and 2.476(6) Å] for P(1) and P(3), which are roughly opposed to the cyanamide ligands rather than to each other, suggesting a stronger *trans* effect from the phosphine ligands in comparison with the cyanamide ligands. This effect could be due to a decrease in the π back-donation ability from the metal to an empty 3d orbital of the phosphorus, hence a longer Mo–P distance. A similar arrangement is found[43] in $[MoH_3(C{\equiv}CBu^t)(dppe)_2]$ where the approximately *trans* Mo–P distances have a mean value of 2.442(6) Å and the Mo–P distance opposite the mid-point between the fourth phosphine and the alkynyl ligand is 2.403(3) Å; we note also that the fourth Mo–P distance, opposite the mid-point of the third phosphine and a hydrido ligand, is longest at 2.465(3) Å.

The hydrogen atoms on the $NCNH_2$ ligands were not located in the analysis but inspection of intermolecular contacts suggests that one of the $NCNH_2$ groups is involved in two hydrogen bonds with BF_4^- anions, the other with one BF_4^- anion and the oxygen atom of the THF solvent molecule, Table 1(c). Hydrogen bonding thus connects the ions in dimeric units (Fig. 2) about centres of symmetry; two cations are bridged by two B(10) anions, with terminal bonds to two B(9) anions and two THF molecules.

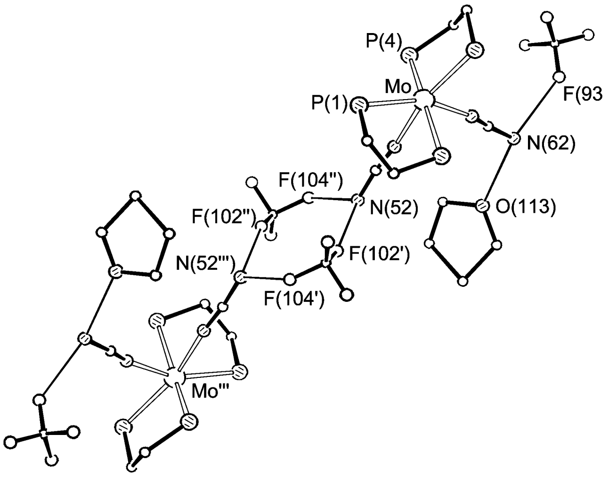
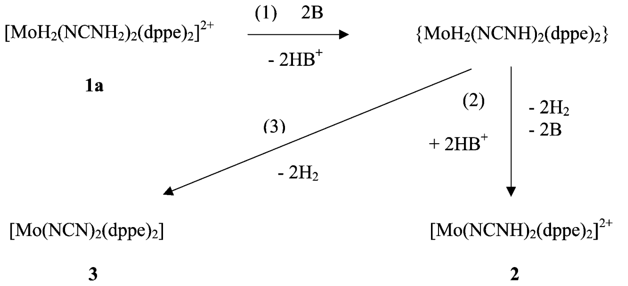


Fig. 2 View of the hydrogen-bonded dimeric unit in crystals of $[MoH_2(NCNH_2)_2(dppe)_2][BF_4]_2{\cdot}THF$ (**1a**·THF). The phenyl rings of the cation have been omitted for clarity.

Bis(hydrogen-cyanamide) complex $[Mo(NCNH)_2(dppe)_2][BF_4]_2$ 2

In contrast with the organocyanamide complexes **1b** and **1c**, for which no reaction was observed with a base, like KOH, $[{}^nBu_4N]OH$, H_2O, $K[B\{CH(CH_3)(C_2H_5)\}_3H]$ (K-selectride) or ^nBuLi, treatment of a THF solution of the cyanamide compound $[MoH_2(NCNH_2)_2(dppe)_2][BF_4]_2$ **1a** with any of those bases, at room temperature, affords a product formulated (see below) as the bis(hydrogen-cyanamide) [or bis(hydrogen-cyanoimide)] complex *trans*-$[Mo(NCNH)_2(dppe)_2][BF_4]_2$ **2**.

The formation of this product, which does not result from a simple deprotonation, involves an overall base promoted dehydrogenation of the parent dihydride–cyanamide complex **1a**. Although the mechanism of the reaction is unknown, electrochemical evidence (see below) suggests that a cyanamide ligand deprotonation step precedes the metal dehydrogenation and therefore, by assuming also a further acid promoted metal dehydrogenation similar to that followed by $[MoH_4(dppe)_2]$ (see eqn. (1)), one can postulate the pathway show in Scheme 1 (B = base) or related ones involving stepwise $+B/-HB^+$ sequences. Hence, base (B) deprotonation of a cyanamide ligand ("step" 1) would be followed by hydride abstraction from the metal by acid (HB^+) ("step" 2), in an overall base catalysed process.



Scheme 1 Proposed base-catalysed pathway for the formation of complex **2**.

However, the second "step" of this mechanism (protonation by the conjugate acid of base B) cannot hold for K-selectride or ^nBuLi in view of the non-acidic character of their protonated derivatives. The product **2** is then formed only in low yield, and traces of moisture conceivably can account for the occurrence of the protonation "step" 2 (in fact, complex **2** is also obtained on reaction of **1a** with H_2O). Moreover, the known[2] bis(cyanoimide) complex *trans*-$[Mo(NCN)_2(dppe)_2]$ **3** is also an obtained product from the K-selectride and ^nBuLi reactions (it even becomes the main one when using any of those reagents in a greater amount, *i.e.* in a twofold molar ratio relative to **1a**, when no complex **2** is then detected). The formation of product **3** involves an overall combined deprotonation/dehydrogenation ("steps" 1 and 3 in Scheme 1) and the latter "step" can be accounted for by considering that the hydrogen-cyanamide ligands in the postulated $\{MoH_2(NCNH)_2(dppe)_2\}$ intermediate exhibit a sufficient acidic character to lead to a further acid promoted metal dehydrogenation. The NCNH ligand (conjugate acid of the ligated cyanoimide NCN) or the conjugate acid of the solvent, $THF{\cdot}H^+$, formed by partial acid dissociation of that ligand, would behave in "step" 3 as HB^+ in "step" 2.

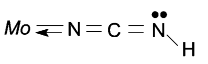
The propensity of $\{MoH_2(NCNH)_2(dppe)_2\}$ to undergo protic metal dehydrogenation is expected in view of the observation of such a behaviour (see above) for the related $[MoH_4(dppe)_2]$ complex. The former species can also be postulated as an intermediate in the conversion of *trans*-$[Mo(N_2)_2(dppe)_2]$ into *trans*-$[Mo(NCN)_2(dppe)_2]$ **3** upon reaction with cyanamide, being formed by N_2 loss and oxidative addition of two $NCNH_2$ ligands to the electron-rich metal centre.

Mixtures of other unidentified products are also obtained, besides **2** or **3**, in the cases of the K-selectride, $[{}^nBu_4N]OH$ or H_2O reactions.

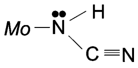
The formation of the hydrogen-cyanamide ($NCNH^-$) and of the cyanoimide (NCN^{2-}) ligands by deprotonation of cyanamide[21,44] and hydrogen-cyanamide[45] is known to occur in other systems. Protonation of the NCN^{2-} ligand to give the ligated $NCNH^-$ has also been reported,[2,46] although rather scantly.

Interestingly, complex **2** is not obtained by a stepwise protonation of *trans*-$[Mo(NCN)_2(dppe)_2]$ **3** which, in CH_2Cl_2, on treatment with HBF_4 affords, as we have shown previously,[2] the mono(hydrogen-cyanamide) complex *trans*-$[Mo(NCN)(NCNH)(dppe)_2][BF_4]$ that, upon further protonation, leads to the cyanamide product *trans*-$[Mo(NCN)(NCNH_2)(dppe)_2][BF_4]_2$, *i.e.* the second proton adds to the $NCNH^-$ ligand rather than to the ligated NCN^{2-} group. Hence, if **2** represents the thermodynamically favoured species, the conversion of that $NCN/NCNH_2$ complex requires a considerable activation energy at least in a non-basic solvent where proton dissociation from the N–H groups does not occur spontaneously.

Complex **2** was isolated (in moderate yields, *ca* 30%) as an orange solid which was characterized by IR and multinuclear NMR spectroscopies, FAB^+-MS, elemental and electrochemical analyses. The IR $\nu(NH)$ vibrations are detected (KBr pellet) as broad bands at 3055 cm^{-1}, whereas the strong band at 2056 cm^{-1} is assigned to the $\nu_{as}(N{=}C{=}N)$ of the ligated hydrogen-cyanamide, a value that is much lower than that observed, 2260 cm^{-1}, for the cyanamide ligand $N{\equiv}C{-}NH_2$ in the parent complex **1a** but is comparable (although slightly lower) to those of the $[NCNH][{}^nBu_4N]$ salt (2080 cm^{-1})[21] and of the ligated $NCNH^-$ (2082 cm^{-1})[2] in *trans*-$[Mo(NCN)(NCNH)(dppe)_2][BF_4]$, where this ligand was obtained by protonation of one cyanoimide of *trans*-$[Mo(NCN)_2(dppe)_2]$. This is indicative of the $NCNH^-$ linear coordination mode (a), by the cyano-N atom, rather than the bent one, by the amido- (or imino-) –N atom (b), since the latter would be expected[10,21,46,47] to correspond to a significant high coordination frequency shift. Hence, the hydrogen-cyanamide ligand in **2** can be considered as a formal 3-electron donor hydrogen-cyanoimide ligand, thus conferring the 18-electron count to the electronic configuration of the complex. In the complexes *trans*-$[Re(NCNH)(CNR)(dppe)_2]$ (R = Me or Bu*t*), obtained by single deprotonation of the parent cyanamide–isocyanide complexes,[21] the hydrogen-cyanamide ligand exhibits an IR band (2135 or 2160 cm^{-1}, respectively) at a higher wavenumber than that of **2** and is believed to present the bent coordination mode (b), thus behaving as a formal single-electron donor and providing also the closed shell configuration.



a



b

The strong and sharp IR band at 1290 cm^{-1} in **2** is assigned[2] to the $\nu_s(N{=}C{=}N)$ or to the metalimide $\nu(MoN)$ vibrations. In the ^{13}C NMR spectrum, the N*C*NH $^-$ resonance is observed as a singlet at δ 125.02, a value very close to that (124.96)[2] of this ligand (which is also linearly coordinated) in *trans*-$[Mo(NCN)(NCNH)(dppe)_2][BF_4]$. The *trans* geometry of **2** is indicated by the singlet resonance observed in its $^{31}P-\{^1H\}$ spectrum, whereas the FAB^+-MS spectrum clearly shows the molecular ion, with the expected[36] isotopic pattern, as well as expected fragments from fragmentation pathways.

Electrochemical studies

All the complexes **1** and **2** exhibit by cyclic voltammetry, at a Pt electrode and in non-aqueous aprotic medium (0.2 M $[{}^nBu_4N][BF_4]$ in THF or CH_2Cl_2), at least a first single-electron reversible oxidation wave, assigned to the oxidation of the formal Mo^{IV} to Mo^V, and one reduction wave (Table 2). Controlled-potential electrolyses at the first oxidation wave confirmed the involvement of a single-electron transfer. The measured values of the first half-wave oxidation potentials (${}^IE_{1/2}{}^{ox}$) lie in the 0.89–1.04 V *vs* SCE range, being significantly higher than that (0.79 V)[34] of *trans*-$[Mo(NCN)_2(dppe)_2]$ **3** (neutral complex of Mo^{IV}) and much higher than those for *trans*-$[MoL_2(dppe)_2]$ [−0.16 (L = N_2),[48] −0.11 (L = CO)[48] or −0.55 (L = CNMe)[49,50]], neutral complexes and with the Mo in the zero oxidation state.

Table 2 Cyclic voltammetric data[a] for $[MoH_2(NCR)_2(dppe)_2][BF_4]_2$ **1** and $[Mo(NCNH)_2(dppe)_2][BF_4]_2$ **2**

R	${}^IE_{1/2}{}^{ox}$	${}^{II}E_p{}^{ox}$	${}^IE_p{}^{red}$ (${}^IE_{1/2}{}^{red}$)
1a NH_2[b]	1.04		−0.68[c]
1b NMe_2	0.90		−1.54
1c NEt_2	0.91		−1.61
1d $NC(NH_2)_2$	0.89	1.51	(−0.63)[d]
2 —	1.03	1.51	(−0.83)

[a] Values in V ± 0.02 relative to SCE (see Experimental); scan rate of 200 mV s^{-1}. [b] An irreversible anodic wave at $E_p{}^{ox}$ = 0.67 V (see text) is observed upon scan reversal following the cathodic scan up to the first reduction wave. [c] Two other irreversible cathodic waves appear at ${}^{II}E_p{}^{red}$ = −0.85 and ${}^{III}E_p{}^{red}$ = −1.53 V. [d] Another irreversible cathodic wave appears at ${}^{II}E_p{}^{red}$ = −1.61 V.

The cyanamide complex **1a** (Fig. 3) shows a first irreversible reduction wave at a potential (${}^IE_p{}^{red}$ = −0.68 V) that is much less cathodic than those of the related organocyanamide complexes [${}^IE_p{}^{red}$ = −1.54 (**1b**) or −1.61 (**1c**) V]. This suggests the involvement of the $NCNH_2$ ligand in the chemical reaction of the irreversible cathodic process, rather than a purely metal centred

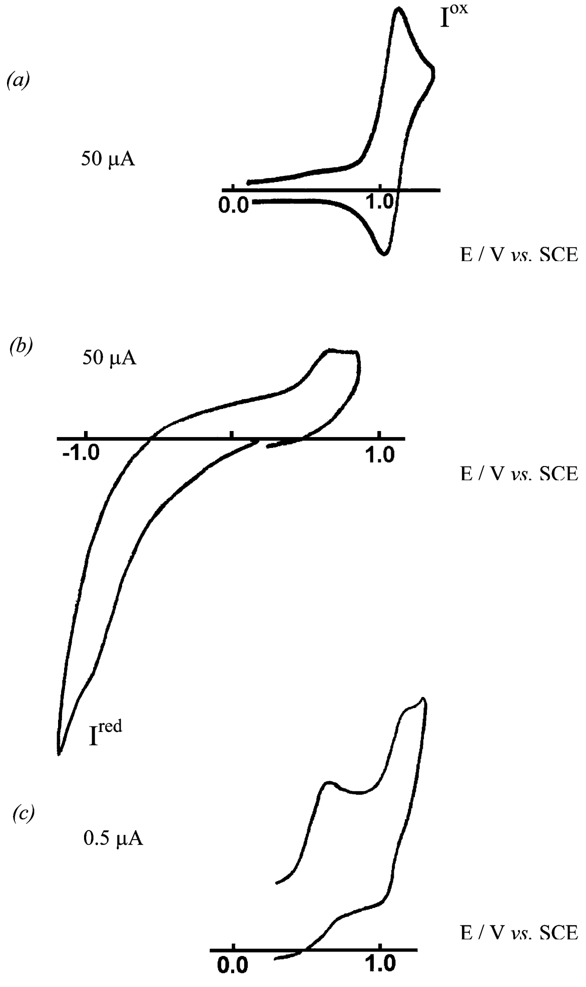
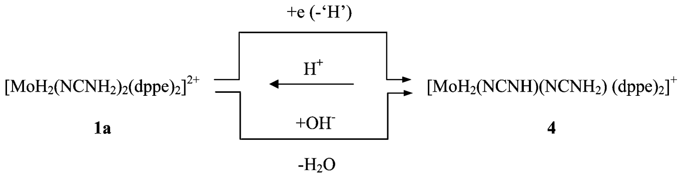


Fig. 3 Cyclic voltammograms of $[MoH_2(NCNH_2)_2(dppe)_2][BF_4]_2$ **1a**, at a Pt electrode, in THF/0.2 M $[{}^nBu_4N][BF_4]$ solution (ν = 200 mV s^{-1}): (a) initiated by the anodic sweep; (b) initiated by the cathodic sweep; (c) initiated by the anodic sweep upon addition of $[{}^nBu_4N]OH$ (twofold molar ratio). Complex concentration: 50 mM (a,b), 1 mM (c).



Scheme 2 Electron-transfer induced first dehydrogenation and first deprotonation of complex **1a**.

one when similar reduction potential values would be expected for the three complexes. In the free state, cyanamide is reduced irreversibly at a much lower potential, $E_p^{red} = -1.67$ V (in NCMe), whereas no reduction wave has been detected for the free dialkylcyanamides.[51] Moreover, a new irreversible oxidation wave appears at $E_p^{ox} = 0.67$ V upon scan reversal following the cathodic scan up to that reduction wave, indicating that such an oxidation wave corresponds to the oxidation of a species (**4**) formed in this cathodic process. This species is also obtained upon addition of a base (1M $[^nBu_4N]OH$/methanol solution) to the solution of complex **1a** in the voltammetric cell, as detected *in situ* by the appearance of the oxidation wave at 0.67 V when the potential scan is initiated by anodic sweep, with a concomitant decrease of the peak current intensity of the original oxidation wave at $E_{1/2}^{ox} = 1.04$ V. Conversely, subsequent neutralization by acid (HBF_4) leads to the disappearance of the new oxidation wave at 0.67 V with full regeneration of the initial one at 1.04 V, showing the reversibility of the deprotonation reaction of **1a**.

These results suggest the occurrence, at the first reduction process of **1a**, of a cathodically-induced dehydrogenation at a cyanamide ligand to give a deprotonated species (**4**) that is also formed upon reaction with base and which we formulate as $[MoH_2(NCNH)(NCNH_2)(dppe)_2]^+$ (Scheme 2).

Complex **4** is oxidized at a significantly lower oxidation potential than that of the parent **1a** and the corresponding oxidation potential shift (ΔE^{ox} *ca* -0.4 V), which results from the single deprotonation of a cyanamide ligand in the latter complex, is comparable with those observed for the hydrogen-cyanamide/cyanamide complexes *trans*-$[Re(NCNH)(CNR)(dppe)_2]$ / *trans*-$[Re(NCNH_2)(CNR)(dppe)_2]^+$ [ΔE^{ox} *ca* -0.4 (R = Me) or -0.5 (R = Bu^t) V][21]. These rhenium base/acid couples exhibit electrochemical behaviours[21] similar to those mentioned above for the molybdenum **4**/**1a** couple, in particular the cathodically-induced dehydrogenation of the acidic cyanamide form to give the corresponding hydrogen-cyanamide species, and all these observations corroborate the above proposed formulation of **4**, although attempts to isolate and characterize fully this product have not been successful. Nevertheless, the electrochemical detection *in situ* of **4**, upon reaction of **1a** with a base, suggests that a first deprotonation step of ligated cyanamide precedes the base promoted dehydrogenation that leads to the non-hydride bis(hydrogen-cyanamide) product **2** as described above in the chemical studies.

Other examples of cathodically-promoted ligand dehydrogenation are known, namely for the cyanoguanidine or the aminocarbyne complexes *trans*-$[Re\{NCNC(NH_2)_2\}(CNMe)(dppe)_2][BF_4]$[22] or *trans*-$[ReCl(CNH_2)(dppe)_2][BF_4]$,[52] leading to the corresponding basic forms with ligating CNH or NCNC(NH)NH_2, respectively. Cathodic dehydrogenation of a ligand C–H bond can also occur, in particular for the carbyne *trans*-$[ReCl(\equiv CCH_2R)(dppe)_2]^+$ (R = alkyl or aryl) or the η^2-vinyl *trans*-$[ReCl\{=C(CH_2Ph)CH_2\}(dppe)_2]^+$ complexes which thus generate the corresponding vinylidene *trans*-$[ReCl(=C=CHR)(dppe)_2]$[53] or η^2-allene *trans*-$[ReCl(\eta^2\text{-}CH_2\text{-}C=CHPh)(dppe)_2]$[54] species.

Conclusion

This work has extended to molybdenum(IV) hydride centres the still underdeveloped coordination chemistry of cyanamides, in particular the unsubstituted cyanamide itself, $NCNH_2$. In contrast with the activation of this substrate by the electron-rich molybdenum(0) centre $\{Mo(dppe)_2\}$ in *trans*-$[Mo(N_2)_2(dppe)_2]$ which leads to $NCNH_2$ reductive dehydrogenation to cyanoimide (NCN^{2-}), the reaction (in acidic medium) of cyanamide with the tetrahydride molybdenum(IV) complex $[MoH_4(dppe)_2]$ does not result in dehydrogenation of $NCNH_2$ which binds as such to form a stable biscyanamide–dihydride complex $[MoH_2(NCNH_2)_2(dppe)_2]^{2+}$ **1a**. The formation of this product also involves dehydrogenation, but this occurs at the metal (*via* protic abstraction of two hydride ligands) rather than at the cyanamide which cannot be reduced by the molybdenum (IV) centre.

Further dehydrogenation or deprotonation occurs in **1a**, at the metal or at the ligated cyanamide, in processes assisted by base or by electron-transfer. The cyanamide ligand appears to be more prone to a first deprotonation than the binding $\{MoH_2(dppe)_2\}^{2+}$ centre, but this site adapts to a change in the electronic requirements of the ligands by undergoing further dehydrogenation allowing the formation of multiple Mo–N bonds (in hydrogen-cyanamide and cyanoimide derived products) with preservation of the 18-electron count and of the metal oxidation state. Hence, the metal–hydrogen bonds appear to be able to act as an "electron-buffer" towards the preservation of the metal d^n configuration, allowing the formation of multiple metal–nitrogen bonds without a change in the overall electron count, an observation that deserves to be further explored and of possible biological significance *e.g.* for the understanding of the nitrogenase action in the enzymatic reduction of substrates like dinitrogen, cyanamide and organonitriles.

Experimental

All manipulations and reactions were performed under an atmosphere of dinitrogen using standard vacuum and inert-gas flow techniques. Solvents were purified by standard procedures and freshly distilled immediately prior to use. The complex $[MoH_4(dppe)_2]$ was prepared by literature methods.[32,55] The cyanamides were used as purchased from Aldrich.

Infrared spectra (4000–400 cm^{-1}) were recorded on a Perkin-Elmer 683 spectrophotometer or on a Bio-Rad FTS 3000MX instrument in KBr pellets; wavenumbers are in cm^{-1}; abbreviations: vs = very strong, s = strong, m = medium, w = weak, br = broad. ^1H, ^{31}P and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer at ambient temperature; δ values are in ppm relative to $SiMe_4$ (^1H or ^{13}C) or $P(OMe)_3$ (^{31}P). In the ^{13}C NMR data, assignments and coupling constants common to the ^{13}C–$\{^1H\}$ NMR spectra are not repeated. Coupling constants are in Hz; abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = complex multiplet; br = broad, dd = doublet of doublets, dt = doublet of triplets, tm = triplet of complex multiplets. Positive-ion FAB mass spectra were obtained on a Trio 2000 spectrometer by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (*ca* 1.28×10^{15} J) Xe atoms. Nominal molecular masses were calculated using the most abundant isotopes, *i.e.* ^{98}Mo (24.13%), and the expected natural abundance isotope cluster patterns were observed for the various ion clusters. However, further complexity due to addition (from the matrix) or loss of hydrogen was usually not taken into account. Mass calibration for data system acquisition was achieved using CsI. The calculation of the theoretical isotopic patterns was performed by using a computer program[36] taking into account the natural abundance of the various isotopes. The C, H, N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico.

The electrochemical experiments were performed either on an EG&G PAR 273A potentiostat/galvanostat connected to personal computer through a GPIB interface, on a EG&G PAR 173 potentiostat/galvanostat or on a VoltaMaster 2 program of VoltaLab 31 potentiostat.

Cyclic voltammograms were obtained in 0.2 M $[^n\mathrm{Bu_4N}][\mathrm{BF_4}]$ in $\mathrm{CH_2Cl_2}$ or THF, at a platinum disc working electrode (d = 1 mm) whose potential was controlled *vs.* a Luggin capillary connected to a silver wire pseudo-reference electrode; a Pt auxiliary electrode was employed.

Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the above-mentioned composition, in a three-electrode H-type cell. The compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. A Luggin capillary connected to a silver wire pseudo-reference electrode was used to control the working electrode potential. The CPE experiments were monitored regularly by cyclic voltammetry (CV), thus assuring no significant potential drift occurred along the electrolyses. The oxidation potentials of the complexes were measured by CV (see above) in the presence of ferrocene as the internal standard, and the redox potential values are quoted relative to the SCE by using the $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})_2]^{0/+}$ ($E_{1/2}^{\mathrm{ox}}$ = 0.55 V *vz.* SCE) redox couple in 0.2 M $[^n\mathrm{Bu_4N}][\mathrm{BF_4}]$ in $\mathrm{CH_2Cl_2}$. The use, as reference, of an electrode in aqueous medium was avoided due to the sensitivity of the complexes to water.

$[\mathrm{MoH_2(NCR)_2(dppe)_2}][\mathrm{BF_4}]_2$ (1; R = $\mathrm{NH_2}$ 1a, $\mathrm{NMe_2}$ 1b, $\mathrm{NEt_2}$ 1c or $\mathrm{NC(NH_2)_2}$ 1d)

Complexes **1** were prepared by a common method, and a typical procedure is given as follows for the compound **1a** (R = $\mathrm{NH_2}$). To a solution of $[\mathrm{MoH_4(dppe)_2}]$ (0.21 g, 0.23 mmol) in THF (60 $\mathrm{cm^3}$) was added a freshly prepared $\mathrm{HBF_4.Et_2O}$ (in a fivefold molar ratio) solution (2.3 $\mathrm{cm^3}$, 1.21 mmol, obtained by dilution from a commercial 85% solution, 5.77 M, in $\mathrm{Et_2O}$). The solution colour turned immediately to brown. Subsequent slow addition of a crushed cyanamide powder (98.6 mg, 2.35 mmol *i.e.* in a tenfold molar ratio relative to the starting complex) resulted in the change of the solution colour to yellow. Addition of $\mathrm{Et_2O}$ (10 $\mathrm{cm^3}$) and cooling to *ca* −18 °C led to the precipitation of **1a** as yellow crystals which were separated by filtration, washed with THF/$\mathrm{Et_2O}$ 1:10 and dried *in vacuo* (*ca* 0.21g, 80% yield).

$[\mathrm{MoH_2(NCNH_2)_2(dppe)_2}][\mathrm{BF_4}]_2$ 1a

IR: 3250–3140 [w, br; ν(N–H)], 2260 [s; ν(N≡C)], 1910 [w, br; ν(Mo–H)], 1630–1590 [δ(NH) or ν(N=C=N)], 1120–1000 [vs, br; ν(BF)]. NMR: ^{1}H $[(\mathrm{CD_3})_2\mathrm{CO}]$, δ 7.90–7.40 [m, 40H, $\mathrm{C_6}H_5$ (dppe)], 6.67 [s (lower intensity than expected due to proton exchange with traces of water present in the solvent), 2H, $\mathrm{NCN}H_2$], 3.53–3.28 (m, 4H, ½$\mathrm{Ph_2PC}H_2\mathrm{C}H_2\mathrm{PPh_2}$), 2.68–2.45 (m, 4H, ½$\mathrm{Ph_2PC}H_2\mathrm{C}H_2\mathrm{PPh_2}$), −3.25 (m, 2H, hydride); ^{31}P–{^{1}H}$[(\mathrm{CD_3})_2\mathrm{CO}]$, δ −68.32 (t, $^2J_{\mathrm{pp}}$ 7.9), −82.82 (t, $^2J_{\mathrm{pp}}$ 9.1); ^{13}C–{^{1}H}($\mathrm{CD_2Cl_2}$), δ 139.20–133.20 [m, $C_6\mathrm{H_5}$ (dppe)], 121.65 (s, $\mathrm{N}C\mathrm{NH_2}$), 31.46 (m, $\mathrm{Ph_2P}C\mathrm{H_2}C\mathrm{H_2PPh_2}$); ^{13}C ($\mathrm{CD_2Cl_2}$), δ 139.20–133.20, 121.65, 31.46 [tm, $^1J_{\mathrm{CH}}$ 136.4, $\mathrm{Ph_2P}C\mathrm{H_2}C\mathrm{H_2PPh_2}$]. FAB$^+$-MS: *m/z* 978 ([M]$^+$), 936 ([M–$\mathrm{NCNH_2}$]$^+$), 956 ([M–$\mathrm{NCNH_2}$+F]), 926 ([$\mathrm{MoO_2(dppe)_2}$]), 894 ([M-2$\mathrm{NCNH_2}$]$^+$), 497([M-dppe-2$\mathrm{NCNH_2}$]$^+$). Found: C, 56.4; H, 4.9; N, 4.8. **1a** requires C, 56.3; H, 4.7; N, 4.9.

$[\mathrm{MoH_2(NCNMe_2)_2(dppe)_2}][\mathrm{BF_4}]_2$ 1b

IR: 2240 [s; ν(N≡C)], 1890 [w, br; ν(Mo–H)], 1120–1000 [vs, br; ν(BF)]. NMR: ^{1}H ($\mathrm{CD_2Cl_2}$), δ 7.69–7.32 [m, 32H, $\mathrm{C_6}H_5$ (dppe)], 7.19 [qt, 8H, $\mathrm{C_6}H_5$ (H_{o} dppe), J 7.2 (quintet resultant from the partial overlap of two triplets resulting from two partially overlaped doublets with $^3J_{\mathrm{HH}}{\approx}^3J_{\mathrm{HP}}$)], 3.14–2.88 (m, br, 2H, ¼$\mathrm{Ph_2PC}H_2\mathrm{C}H_2\mathrm{PPh_2}$), 2.76–2.60 (m, br, 2H, ¼$\mathrm{Ph_2PC}H_2\mathrm{C}H_2\mathrm{PPh_2}$), 2.60–2.38 (m, br, 2H, ¼$\mathrm{Ph_2PC}H_2\mathrm{C}H_2\mathrm{PPh_2}$), 2.04 [s, 12H, $\mathrm{NCN(C}H_3)_2$], 1.98–1.78 (m, br, 2H, ¼$\mathrm{Ph_2PC}H_2\mathrm{C}H_2\mathrm{PPh_2}$), −3.31 (m, 2H, hydride); ^{31}P–{^{1}H}$[(\mathrm{CD_3})_2\mathrm{CO}]$, δ −72.20 (t, $^2J_{\mathrm{pp}}$ 7.8), −78.01 (t, $^2J_{\mathrm{pp}}$ 7.3); ^{13}C–{^{1}H}($\mathrm{CD_2Cl_2}$), δ 134.81–127.83 [m, $C_6\mathrm{H_5}$ (dppe)], 123.25 [s, $\mathrm{N}C\mathrm{N(CH_3)_2}$], 39.48 [s, $\mathrm{NCN(}C\mathrm{H_3)_2}$], 28.16 (m, $\mathrm{Ph_2P}C\mathrm{H_2}C\mathrm{H_2PPh_2}$); ^{13}C ($\mathrm{CD_2Cl_2}$), δ 134.81–127.83, 123.25, 39.48 [q, $^1J_{\mathrm{CH}}$ 141.4, $\mathrm{NCN(}C\mathrm{H_3)_2}$], 28.16 (tm, $^1J_{\mathrm{CH}}$ 137.9, $\mathrm{Ph_2P}C\mathrm{H_2}C\mathrm{H_2PPh_2}$). FAB$^+$-MS: *m/z* 965 ([M–$\mathrm{NCNMe_2}$]$^+$), 984 ([M–$\mathrm{NCNMe_2}$+F], 895 ([M-2$\mathrm{NCNMe_2}$]$^+$), 926 ([$\mathrm{MoO_2(dppe)_2}$]), 914 ([$\mathrm{MoHF(dppe)_2}$]). Found: C, 57.2; H, 6.2; N, 4.4. **1b** requires C, 57.6; H, 6.0; N, 4.6.

$[\mathrm{MoH_2(NCNEt_2)_2(dppe)_2}][\mathrm{BF_4}]_2$ 1c

IR: 2240 [m; ν(N≡C)], 1900 [w, br; ν(Mo–H)], 1120–1000 [vs, br; ν(BF)]. NMR: ^{1}H ($\mathrm{CD_2Cl_2}$), δ 7.65–7.14 [m, 32H, $\mathrm{C_6}H_5$ (dppe)], 7.09 [qt, 8H, $\mathrm{C_6}H_5$ (H_{o} dppe), J 7.3 (quintet resultant from the partial overlap of two triplets resulting from two partially overlaped doublets with $^3J_{\mathrm{HH}}{\approx}^3J_{\mathrm{HP}}$)], 2.99–2.77 (m, br, 4H, ½$\mathrm{Ph_2PC}H_2\mathrm{C}H_2\mathrm{PPh_2}$), 2.58–2.41 (m, br, 4H, ½$\mathrm{Ph_2PC}H_2\mathrm{C}H_2\mathrm{PPh_2}$), 2.30 [q, 8H, $^3J_{\mathrm{HH}}$ 7.2, $\mathrm{NCN(C}H_2\mathrm{CH_3)_2}$], 0.64 [t, 6H, $^3J_{\mathrm{HH}}$ 7.3, ½$\mathrm{NCN(CH_2C}H_3)_2$], 0.57 [t, 6H, $^3J_{\mathrm{HH}}$ 7.2, ½$\mathrm{NCN(CH_2C}H_3)_2$], −3.36 (m, 2H, hydride); ^{31}P–{^{1}H}($\mathrm{CDCl_3}$), δ −69.72 (t, $^2J_{\mathrm{pp}}$ 8.6), −82.30 (t, $^2J_{\mathrm{pp}}$ 9.1); ^{13}C–{^{1}H}($\mathrm{CD_2Cl_2}$), δ 135.81–128.09 [m, $C_6\mathrm{H_5}$ (dppe)], 124.52 [s, $\mathrm{N}C\mathrm{N(CH_2CH_3)_2}$], 45.19 [s, $\mathrm{NCN(}C\mathrm{H_2CH_3)_2}$], 30.72 (m, $\mathrm{Ph_2P}C\mathrm{H_2}C\mathrm{H_2PPh_2}$); 13.77 [s, $\mathrm{NCN(CH_2}C\mathrm{H_3)_2}$], ^{13}C ($\mathrm{CD_2Cl_2}$), δ 135.81–128.09, 124.52, 45.19 [t, $^1J_{\mathrm{CH}}$ 140.1, $\mathrm{NCN(}C\mathrm{H_2CH_3)_2}$], 30.72 [tm, $^1J_{\mathrm{CH}}$ 135.7, $\mathrm{Ph_2P}C\mathrm{H_2}C\mathrm{H_2PPh_2}$], 13.77 [q, $^1J_{\mathrm{CH}}$ 133.2, $\mathrm{NCN(CH_2}C\mathrm{H_3)_2}$]. FAB$^+$-MS: *m/z* 993 ([M-$\mathrm{NCNEt_2}$]$^+$), 1012 ([M-$\mathrm{NCNEt_2}$+F]), 895 ([M-2$\mathrm{NCNEt_2}$]$^+$), 497 ([M-dppe-2$\mathrm{NCNEt_2}$]$^+$), 926 ([$\mathrm{MoO_2(dppe)_2}$]), 914 ([$\mathrm{MoHF(dppe)_2}$]). Found: C, 58.6; H, 5.5; N, 4.1. **1c** requires C, 58.9; H, 5.6; N, 4.4.

$[\mathrm{MoH_2(NCNC(NH_2)_2)(dppe)_2}][\mathrm{BF_4}]_2$ 1d

IR: 3440–3350 [w, br; ν(N–H)], 2220 [s; ν(N≡C)], 1900 [w, br; ν(Mo–H)], 1650–1550 [δ(NH) or ν(N=C=N)], 1120–1000 [vs, br; ν(BF)]. NMR: ^{1}H $[(\mathrm{CD_3})_2\mathrm{CO}]$, δ 7.90–7.42 [m, 40H, $\mathrm{C_6}H_5$ (dppe)], 6.22 [m, br, 8H, $\mathrm{NCNC(N}H_2)_2$], 3.26–2.94 [m, br, 4H, ½$\mathrm{Ph_2PC}H_2\mathrm{C}H_2\mathrm{PPh_2}$], 2.44–2.41 [m, br, 4H, ½$\mathrm{Ph_2PC}H_2\mathrm{C}H_2\mathrm{PPh_2}$), −3.20 (m, 2H, hydride); ^{31}P–{^{1}H}$[(\mathrm{CD_3})_2\mathrm{CO}]$, −67.17 (t, $^2J_{\mathrm{pp}}$ 9.0), −83.95 (t, $^2J_{\mathrm{pp}}$ 9.1); ^{13}C–{^{1}H}($\mathrm{CD_2Cl_2}$), δ 161.45 [s, $(\mathrm{NCN}C\mathrm{NH_2)_2}$], 134.37–127.08 [m, $C_6\mathrm{H_5}$ (dppe)], δ 122.03 [s, $(\mathrm{N}C\mathrm{NC(NH_2)_2}$], 28.83 [m, $\mathrm{Ph_2P}C\mathrm{H_2}C\mathrm{H_2PPh_2}$]; ^{13}C ($\mathrm{CD_2Cl_2}$), δ 161.45, 134.37–127.08, 122.03, 28.83 [tm, $^1J_{\mathrm{CH}}$ 136.7, $\mathrm{Ph_2P}C\mathrm{H_2}C\mathrm{H_2PPh_2}$]. FAB$^+$-MS: *m/z* 1063 ([M]$^+$), 979 ([M-NCNC($\mathrm{NH_2}$)]$^+$), 895 ([M-2NCNC($\mathrm{NH_2}$)]$^+$), 926 ([$\mathrm{MoO_2(dppe)_2}$]), 914 ([$\mathrm{MoHF(dppe)_2}$]). Found: C, 54.1; H, 4.9; N, 8.9. **1d** requires C, 54.4; H, 4.7; N, 9.1.

$[\mathrm{Mo(NCNH)_2(dppe)_2}][\mathrm{BF_4}]_2$ 2

A solution of the complex **1a** (0.043 g, 3.77×10^{-5} mol) in THF (30 $\mathrm{cm^3}$), with vigorous stirring, was treated with a MeOH diluted solution of KOH (6.0 $\mathrm{cm^3}$, 6.0×10^{-3} M, 3.6×10^{-5} mol) added dropwise. The colour of the reaction solution turned immediately to yellowish orange. Concentration *in vacuo* followed by slow addition of $\mathrm{Et_2O}$ resulted in the precipitation of **2** which was separated by filtration, washed with $\mathrm{Et_2O}$ and dried *in vacuo* (0.013 g, 30 % yield). Complex **2** could also be obtained (although in lower yields and in less pure forms) by treatment (i) of a THF solution (40 $\mathrm{cm^3}$) of the complex **1a** (0.067 g, 5.85×10^{-5} mol) with a K-selectride (K[B{CH-($\mathrm{CH_3}$)($\mathrm{C_2H_5}$)}$_3$H]) 1 M THF solution (0.060 $\mathrm{cm^3}$, 6.0×10^{-5}

mol) added dropwise, or (ii) of a THF solution (40 cm^3) of **1a** (0.082 g, 7.12×10^{-5} mol) with a ^{n}BuLi 1.6 M solution in hexane (0.045 cm^3, 7.2×10^{-5} mol), or (iii) of a THF solution (30 cm^3) of the complex **1a** (0.035 g, 3.05×10^{-5} mol) with a [^{n}Bu$_4$N]OH 0.02 M MeOH/THF solution (1.55 cm^3, 3.05×10^{-5} mol), added dropwise, or (iv) of a THF solution of **1a** with H_2O (one drop, *ca.* 0.025 cm^3, 1.39×10^{-3} mol). Concentration *in vacuo*, after *ca.* 3–4 h, followed by slow addition of n-pentane, led, in the case of K-selectride and ^{n}BuLi, to the precipitation of a whitish solid (inorganic BF_4^- salt) that is removed by filtration. Further concentration of the filtered solution and slow addition of n-pentane resulted in the precipitation of **2** as an orange solid which was separated by filtration, washed with a 1:5 THF/n-pentane mixture and dried *in vacuo.* Similar procedures were used for the cases of [^{n}Bu$_4$N]OH and of H_2O, but the whitish precipitate of the inorganic BF_4^- salt naturally did not form. IR (KBr ν/cm^{-1}): 3055 [w, br; ν(NH)], 2056 [vs, ν_{as}(N=C=N)], 1617 [m; δ(NH)], 1290 [vs; ν_s(N=C=N) and/or ν_s(MoN)], 1120–1000 [vs, br, ν(BF)]. NMR (298 K): ^{1}H [$(CD_3)_2CO$], δ 7.59 [t, 8H, $^3J_{HH}$ 7.4, H_p (dppe)], 7.41 [t, 16H, $^3J_{HH}$ 7.8,H_m (dppe)], 7.30 [(m, 16H, H_o (dppe)]; ^{31}P–{^{1}H}[$(CD_3)_2CO$], −95.83 (s); ^{13}C–{^{1}H}(CD_2Cl_2), δ 133.36–128.82 [m, C_6H_5 (dppe)], 125.02 (s, N*C*NH), 38.09 (m, $Ph_2PCH_2CH_2PPh_2$); ^{13}C (CD_2Cl_2), δ 133.36–128.82, 125.02, 30.09 [tm, $^1J_{CH}$ 136.1, $Ph_2PCH_2CH_2PPh_2$]. FAB$^+$-MS: *m*/*z* 977 ([M]$^+$), 935 ([M − NCNH]$^+$), 578 ([M − dppe]$^+$), 537 ([M − dppe − NCNH]$^+$), 926 ([MoO_2(dppe)$_2$]), 995 ([M + F]$^{2+}$), 954 ([M + F-NCNH]$^{2+}$. Found: C, 55.9; H, 4.2; N, 4.5. **2** requires C, 56.5; H, 4.4; N, 4.8.

Crystallography

Crystal data: $C_{54}H_{54}MoN_4P_4$, 2(BF_4), C_4H_8O, (solvent?), M = 1224.6. Monoclinic, space group $P2_1/a$ (equiv. to no. 14), a = 32.620(5), b = 14.848(2), c = 12.440(3) Å, β = 96.06(2) °, U = 5991.5(19) Å^3. Z = 4, D_c = 1.358 g cm^{-3}, F(000) = 2520, T = 293(2) K, μ(Mo Kα) = 3.9 cm^{-1}, λ(Mo Kα) = 0.71069 Å.

Diffraction data were measured on an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation). Intensities were measured to θ_{max} 18°, the limit of observable data, and corrected for Lorentz-polarization effects, crystal deterioration (*ca* 22 % overall), absorption (by semi-empirical Ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). Of the 4060 unique reflections entered into the SHELX system,[56] 2118 were “unobserved”, having $I < 2\sigma_I$. The structure was determined by the heavy atom method and refined by full-matrix least-squares methods, initially on *F*s in SHELX and SHELXN,[57] finally on F^2s SHELXL.[58] Hydrogen atoms in the diphosphine ligands were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms; the two hydride ligands were located in Fourier difference maps and were refined freely. The non-hydrogen atoms in the cation and the anionic fluorine atoms were refined anisotropically. The boron atoms, the THF solvent (disordered) atoms and two further, discrete “solvent” atoms were refined isotropically. The bond lengths of one BF_4^- ion were constrained to *ca* 1.33 Å; the other refined satisfactorily without constraints. Refinement was concluded with wR_2 and R_1 = 0.29 and 0.156[58] for all 4060 reflections weighted $w = [\sigma^2(F_o^2) + (0.153P)^2]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the “observed” data only, R_1 = 0.094. In the final difference map, the highest peak (*ca* 0.44 e Å^{-3}) was separated from all other moieties and is perhaps of another solvent molecule. Scattering factors for neutral atoms were taken from *International Tables*.[59] Computer programs used in this analysis[60] were run on a DEC-AlphaStation 200 4/100 in the Nitrogen Fixation Laboratory, John Innes Centre.

CCDC reference number 212459.

See http://www.rsc.org/suppdata/dt/b3/b306368b/ for crystallographic data in CIF or other electronic format.

Acknowledgements

This work was partially supported by the Fundação para a Ciência e a Tecnologia (FCT), the PRAXIS XXI and POCTI (FEDER funded) Programmes (Portugal) and the JNICT-ICCTI (Portugal)/The British Council protocol. We also thank Dr Maria Cândida Vaz for the elemental analysis service and Mr Indalécio Marques for running the FAB-MS spectra.

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