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Activation of cyanamide by a molybdenum(0) diphosphinic centre. Formation of cyanoimide and its reactivity with electrophiles

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Cyanamide $N{\equiv}C{-}NH_2$, on reaction with *trans*-$[Mo(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) in thf, undergoes reductive dehydrogenation to cyanoimide NCN^{2-} with formation of *trans*-$[Mo(NCN)_2(dppe)_2]$ **1** which is susceptible to protonation, alkylation, acylation, aroylation and silylation, on treatment with electrophiles (E^+) such as HBF_4, $[Et_3O][BF_4]$, RC(O)Cl (R = Et, Ph) or Me_3SiI, affording the corresponding addition products *trans*-$[Mo(NCN)(NCNH)(dppe)_2][BF_4]$ **2**, *trans*-$[Mo(NCN)(NCNH_2)(dppe)_2][BF_4]_2$ **3**, *trans*-$[Mo(NCN)(NCNEt)(dppe)_2][BF_4]$ **4**, *trans*-$[Mo(NCN)(NCNHEt)(dppe)_2][BF_4]_2$ **7**, *trans*-$[Mo(NCN)\{NCNC(O)R\}(dppe)_2]Cl$ (R = Et **5a**, Ph **5b**) and *trans*-$[Mo(NCN)(NCNSiMe_3)(dppe)_2]I$ **6**. The electrophilic addition to the *exo*-N atom is confirmed by the X-ray crystal structures of **2** and **4** which also show a linear multiple-bond coordination of the cyanoimide and the derived NCNE (E = H or Et) ligands, the latter behaving as weaker π-electron donors than the former.

Introduction

In spite of the widespread interest of cyanamide ($N{\equiv}C{-}NH_2$), namely as an amino acid precursor and a prebiotic molecule[1] which has been identified in interstellar space,[2] a (recently) recognised substrate of both Mo- and V-nitrogenases[3] and of cyanamide hydratase,[4] with applications in agriculture as a fertiliser,[5] in chemical synthesis[6] and in the treatment of alcoholism,[7] its coordination chemistry still remains relatively unexplored,[8–21] mainly that of its basic forms ($NCNH^-$ and NCN^{2-}),[13,15,16,20,21] although organic forms,[9,19,22–33] in particular diorganocyanamides $N{\equiv}C{-}NR_2$, have been more investigated.

In pursuit of our interest in the activation of small molecules with biological, environmental or synthetic significance,[8,34,35] we have previously obtained some cyanamide, diorganocyanamide or cyanoguanidine [dimeric form of cyanamide, $NCNC(NH_2)_2$] complexes of (i) rhenium, such as *trans*-$[Re(L)(CNR)(dppe)_2][BF_4]_n$ [L = $NCNH_2$, $n = 1$;[16] L = $NCNH^-$, $n = 0$;[16] L = $NCNC(NH_2)_2$, $n = 1$;[36] R = Me or ^tBu; dppe = $Ph_2PCH_2CH_2PPh_2$], *mer*-$[ReCl(N_2)(L)(PMePh_2)_3]$ (L = $NCNH_2$, $NCNMe_2$, $NCNEt_2$),[10] *mer*-$[Re(N_2)\{NCNC(NH_2)_2\}_2(PMePh_2)_3]^+$ [10] or *mer*-$[ReCl_2(NCNEt_2)(PMePh_2)_3]$,[10] (ii) iron *i.e.* *trans*-$[FeH(L)(dppe)_2][BF_4]$ [L = $NCNH_2$, $NCNMe_2$, $NCNEt_2$, $NCNC(NH_2)_2$],[9] *trans*-$[FeBr(L)(depe)_2]^+$ [9] [depe = $(Et_2PCH_2CH_2PEt_2)$] or *trans*-$[Fe(L)_2(depe)_2]^{2+}$,[9] and (iii) platinum *i.e.* *trans*-$[PtX(L)(PPh_3)_2]^+$ [X = CF_3 or Cl; L = $NCNH_2$, $NCNMe_2$, $NCNEt_2$ or $NCNC(NH_2)_2$],[12] *cis*-$[PtCl(L)(PPh_3)_2]^+$ [L = $NCNH_2$,[12] $NCNMe_2$, $NCNEt_2$,[37] $NCNC(NH_2)_2$ [12]] and *cis*-$[Pt(L)_2(PPh_3)_2]^{2+}$ [L = $NCNMe_2$, $NCNEt_2$,[37] $NCNC(NH_2)_2$ [38]].

In these complexes, no further reactions of the $NCNH_2$ ligand were obtained (apart from the single deprotonation by base of the above mentioned cyanamide/isocyanide complexes of rhenium[16]) although, at some of the above platinum centres, cyanoguanidine[38] or diorganocyanamides $NCNR_2$ (R = Me or Et)[37] are activated towards nucleophilic attack by alcohols or by oximes (the latter in a process promoted by Ag^+ or Cu^{2+}) to afford 6-membered or 5-membered azametallacycles, respectively. However, at the electron-rich Mo(0) or W(0) metal sites *trans*-$\{M(dppe)_2\}$ (M = Mo or W) we have observed that $NCNH_2$ undergoes dehydrogenation to give the bis(cyanoimide) complexes *trans*-$[M(NCN)_2(dppe)_2]$, as reported[17] previously in a preliminary and undetailed way. We have now investigated the reactivity of these cyanoimide complexes and found that the NCN^{2-} ligand undergoes a variety of electrophilic addition reactions (protonation, alkylation, acylation, aroylation and silylation) on treatment with suitable electrophiles, thus being susceptible to further functionalization to give derived organo-nitrogen species whose direct organic synthesis could not be easily achieved. We now report these reactions and the full characterisation of the complexes.

Results and discussion

Bis(cyanoimide) complex *trans*-$[Mo(NCN)_2(dppe)_2]$ 1

Treatment of a thf solution of the bis(dinitrogen) complex *trans*-$[Mo(N_2)_2(dppe)_2]$ with cyanamide (1 : 2), at room temperature, results (the W analogue undergoes a similar reaction) in the formation of the bis(cyanoimide) complex *trans*-$[Mo(NCN)_2(dppe)_2]$ **1** [reaction (1), Scheme 1] whose formulation was unambiguously authenticated by an X-ray structural analysis.[17]

The reaction involves reductive dehydrogenation of $NCNH_2$ (with liberation of H_2) by the electron-rich (as shown by the electrochemical electron-richness E_s parameter[39]) d^6 metal centre in the readily oxidisable Mo(0) dinitrogen complex (with the rather low oxidation potential value of −0.16 V *vs.* SCE, as measured by cyclic voltammetry in 0.2 M $[NBu_4][BF_4]$/thf). It relates to the direct synthesis[6b,40] of the cyanamide salts MgNCN and Na_2NCN by reaction of Mg or Na with cyanamide, with concomitant liberation of H_2, the electron-rich Mo(0) centre playing the role of the metal reducing agent, being oxidised to the +4 oxidation state (a two-electron oxidation for each cyanamide). Cyanamide is not reduced by the other types of metal sites mentioned above, with a lower electron-richness than that of the Mo(0) site, in particular the related Re(I) centres *trans*-$\{Re(CNR)(dppe)_2\}^+$ which bind $NCNH_2$ as such.[16]

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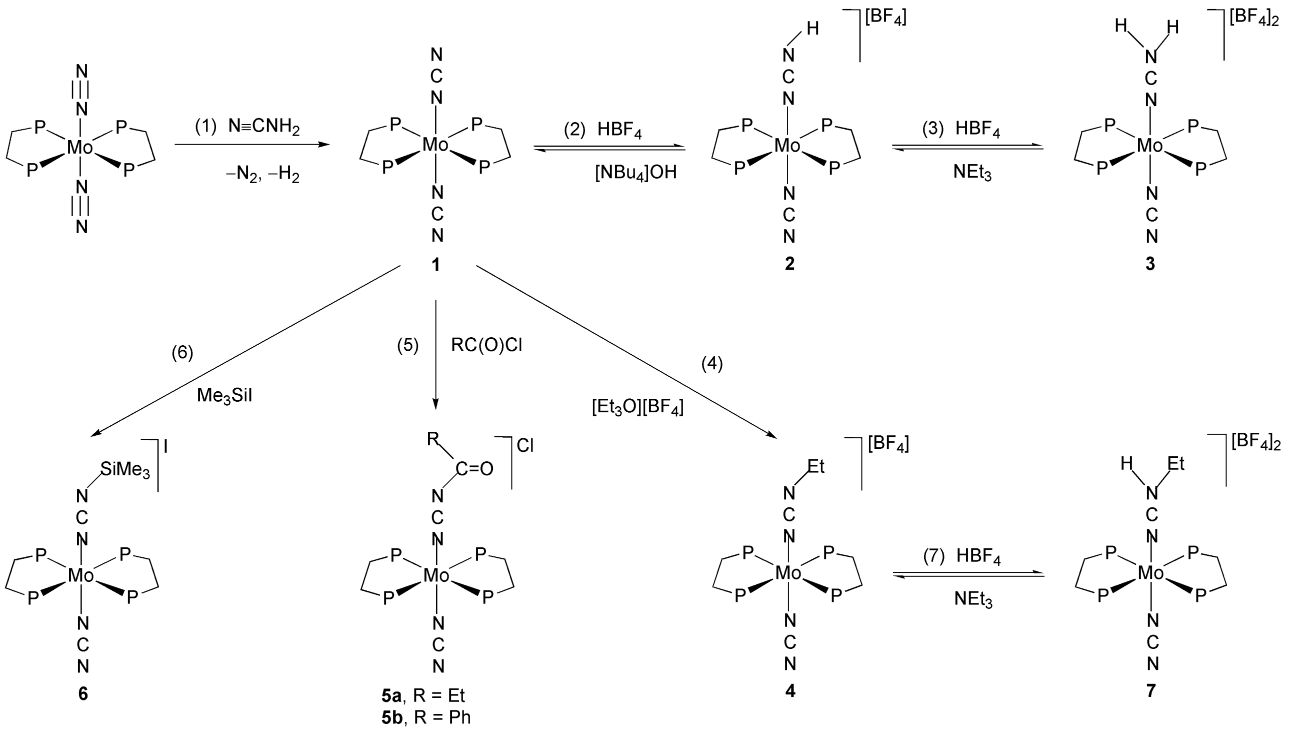
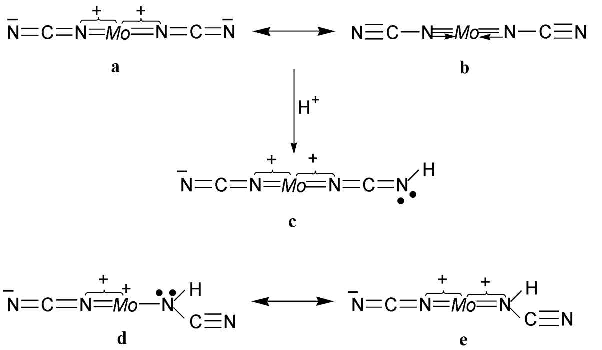


Scheme 1

The strong and sharp bands at 2043 and 1279 cm^{-1} exhibited by the IR spectrum of **1** are assigned to ν_{as}(N=C=N) and ν_{s}(N=C=N), respectively, the former wavenumber approaching the values (2150–2100 cm^{-1})[41] shown by organic carbodiimides RN=C=NR, and the latter being analogous to the estimated value, 1275 cm^{-1},[42] for the unsubstituted carbodiimide. However, the band at lower wavenumber can also comprise the ν(MoN) vibration since it falls within the reported[43] range, 1300–1100 cm^{-1}, for metal–imide vibrations.

The IR features point to a significant contribution of the canonical form **a** (Scheme 2) in the VB representation of the cyanoimide ligand which thus can be considered formally as either an anionic 3-electron donor ($^{+}Mo\overset{\cdots}{=}N{=}C{=}^{-}N$) or as a neutral 2-electron donor ($Mo{=}^{+}N{=}C{=}^{-}N$) ligand, conferring an 18-electron configuration to the complex. Form **b** (with two Mo–N π-bonds for each imide ligand) would result in a 22-electron count and, as known[43,44] for other complexes with a maximum electron count greater than 18 electrons, the number of π-metal–ligand bonds is reduced with a resulting decrease of the number of electrons donated by the ligands, the excess electrons being located therein.



Scheme 2

The significance of form **a** is confirmed by the X-ray analysis[17] of **1** which shows that the cyanoimide groups are in *trans* positions, almost collinear with the metal atom, and present (i) a short N$_{\alpha}$–C distance, 1.297(20) Å, indicating a bond order greater than one, and (ii) a Mo–N bond length, 1.860(11) Å, that, although shorter than that reported,[45] 2.014(5) Å, for the parent bis(dinitrogen) complex and similar to those of the alkylideneamide complexes *trans*-[MoCl(N=CHCO$_2$Me)(dppe)$_2$] and [Mo(N=C^{t}Bu$_2$)(η^5-C$_5$H$_5$)(CO)$_2$], 1.892(5)[46] and 1.853(8) Å,[47] respectively (thus being consistent with a multiple bond), is longer than the estimated molybdenum–imido-nitrogen triple bond length, 1.71 Å,[43a] and than most metal–imide distances (1.65–1.85 Å).[43]

In the ^{13}C NMR spectrum of complex **1**, the N*C*N resonance occurs as a singlet at δ 125.78, a value that is intermediate between those of the corresponding C-atoms in the dialkylcarbodiimides RN=*C*=NR (R = C$_6$H$_{11}$ or ^{i}Pr), *ca.* 140,[48] and in the dialkylcyanamides N≡*C*–NR$_2$ (R = Me or Et), *ca.* 119. In the FAB^{+}-MS spectrum of the complex, its molecular ion is clearly detected as a cluster at *m*/*z* = 974, with the expected isotopic pattern.

Protonation

In accord with the significance of form **a** (Scheme 2), the ligated cyanoimide in *trans*-[Mo(NCN)$_2$(dppe)$_2$] **1** is susceptible to electrophilic attack at the *exo*-N atom. Hence, treatment of a CH$_2$Cl$_2$ solution of **1** with a stoichiometric amount of HBF$_4$ affords the hydrogen cyanamide (or hydrogen cyanoimide) complex *trans*-[Mo(NCN)(NCNH)(dppe)$_2$][BF$_4$] **2** in good yield [reaction (2), Scheme 1] which, upon further treatment with acid, undergoes a second protonation to form (also in good yield) the cyanamide product *trans*-[Mo(NCN)(NCNH$_2$)(dppe)$_2$][BF$_4$]$_2$ **3** [reaction (3), Scheme 1] that can also be obtained directly from **1** upon treatment with HBF$_4$ in a two-fold molar amount. Interestingly, the second protonation occurs at the hydrogen cyanamide ligand (NCNH^{-}) in **2** rather than at the ligated cyanoimide (NCN^{2-}), the former thus behaving as a stronger base than the latter.

Both protonation reactions (2) and (3) are reversible and the cyanamide ligand in complex **3** undergoes a single deprotonation, by NEt$_3$, to give the NCNH^{-} complex **2** which, on reaction with a stronger base, [NBu$_4$]OH, regenerates the parent cyanoimide (NCN^{2-}) compound **1** that can also be formed on treatment of **3** with the latter base. The interconversion of these complexes can be easily monitored by ^{31}P-{^{1}H} NMR and IR spectroscopies.

Complexes **2** and **3** have been characterised by IR and multinuclear NMR spectroscopies, FAB-MS and elemental analyses, as well as, in the case of the former compound, by X-ray diffraction analysis although of a low quality crystal. The *trans* geometries are suggested by the singlet resonances observed in their ^{31}P-{^{1}H} NMR spectra.

The IR ν(NH) vibrations are detected (KBr pellets) as broad bands at 3270 (**2**) or 3255 and 3199 (**3**) cm^{-1}, whereas the strong bands at 2082 (**2**) and 2086 (**3**) cm^{-1} are assigned to ν_{as}(N=C=N). The latter complex exhibits ν(N≡C) of the cyanamide ligand at 2250 cm^{-1}, a frequency close to that (2260 cm^{-1}) of free N≡C–NH$_2$ and comparable to that quoted (2240 cm^{-1})[9] for *trans*-[Fe(NCNH$_2$)$_2$(depe)$_2$]$^{2+}$. The presence of the NCNH$_2$ ligand is also corroborated by the observed broad resonance, at δ 5.42, in the ^{1}H NMR spectrum of **3**, which integrates for 2 H$^+$ and disappears on addition of D$_2$O. The strong band at 1280 (**2**) or 1290 (**3**) cm^{-1} is assigned to ν_s(N=C=N) and/or ν(MoN) (see above).

In **2**, the NCNH$^-$ ligand could bind the metal, in principle, either by the cyano-N (as in the linear form **c**, Scheme 2) or the amido (or imino)-N atom (as in forms **d** or **e**, Scheme 2, bent at N$_\alpha$). However, the observed IR band at a wavenumber (2082 cm^{-1}) that is very close to that of the [NCNH][NBu$_4$] salt (2080 cm^{-1})[16] suggests the former binding mode (**c**), since the latter would be expected[16,21,32] to lead to a significant shift to a higher frequency towards that of cyanamide itself. Such a linear coordination mode, which maximises the ligand–metal π-interactions and minimises the steric hindrance by the bulky dppe-phenyl rings, has been authenticated by the X-ray analysis of **2**. The crystal structure consists of two independent complex cations, A and A′ (the molecular structure of the former is depicted in Fig. 1, and selected bond lengths and angles are given in Table 1), with octahedral coordination, the four P-atoms in the equatorial positions and the ligated N-atoms of the nitrogen ligands in the axial ones. In spite of the low quality of the crystal and although the molybdenum ion lies on a crystallographic inversion centre in both cations, and the NCN*H* hydrogen atom has not been located, the linear coordination mode of the apical nitrogen ligands (consistent with sp-hybridized N$_\alpha$ atoms) is evident [Mo–N$_\alpha$–C bond angles of 179.6(9) (A) and 174.1(11)° (A′)].

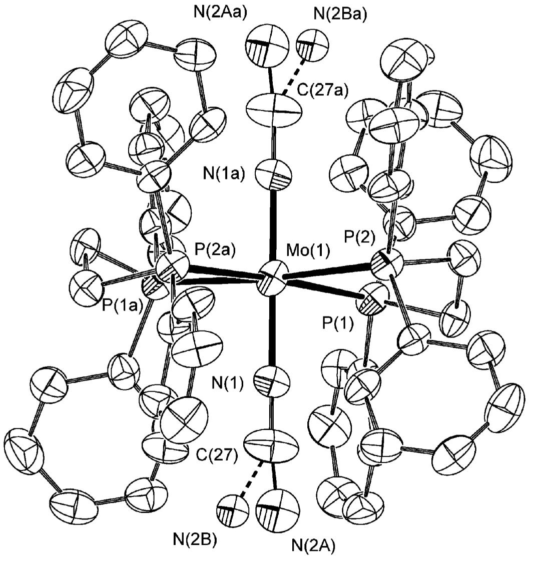


Fig. 1 Molecular structure of the complex cation A of *trans*-[Mo(NCN)(NCNH)(dppe)$_2$][BF$_4$] **2** with ellipsoids at the 30% probability level.

Only marginal structural alterations have resulted from the single protonation of **1**, as shown by comparing its molecular structure[17] with that of **2**. Hence, a slight stretching of the Mo–N$_\alpha$ bond [from 1.860(11) (**1**) to 1.906(9) (**2**, A) or 1.903(9) (**2**, A′) Å] with a concomitant shortening of the N$_\alpha$–C distance [from 1.297(20) (**1**) to 1.189(18) (**2**, A) or 1.176(19) (**2**, A′) Å] appears to occur, although the differences are within 3σ standard deviations. Hence, in complex **2**, the canonical form **c** (Scheme 2), which corresponds to form **a** in complex **1**, is the most likely VB representation of the NCNH and NCN ligands, both behaving as π-electron donors to the high oxidation state molybdenum atom, although conceivably in not a so effective way as the cyanoimide ligands in the parent compound **1**.

The small structural and electronic changes resulting from the single proton addition to the cyanoimide ligand are also corroborated by a concomitant small ^{13}C NMR higher field shift [from δ 125.78 (N*C*N) in **1** to 124.96 (N*C*NH) in **2**]. This shift is enhanced upon the second protonation [δ 121.75 (N*C*NH$_2$) in **3**] and parallels a lower field shift for the non-protonated N*C*N ligand [δ 125.78 (**1**), 126.17 (**2**) or 128.46 (**3**)]. Corresponding higher field and lower field shifts are similarly observed on addition of other electrophiles to **1** (see below).

Complex **3** displays two sets of dppe-phenyl rings as shown by the corresponding pairs of sets of aromatic proton and carbon resonances observed in the ^{1}H and ^{13}C-{^{1}H} NMR spectra, as detected for other octahedral *trans*-bis(dppe) complexes with quite different axial ligands, *e.g.* *trans*-[Re(CN)(L)(dppe)$_2$] (L = organonitrile or vinylidene)[49] or *trans*-[ReCl(CNH$_2$)(dppe)$_2$][BF$_4$].[35h] This has been accounted for by considering one set of four aromatic rings on the side of the equatorial plane of the molecule with one of the axial ligands, and the other set on the opposite side. However, this observation is not expected to correspond to a general rule since fluxional behaviour can change the situation.

Other electrophilic additions

The cyanoimide ligand in *trans*-[Mo(NCN)$_2$(dppe)$_2$] **1** is also susceptible to electrophilic attack by various organic electrophiles (E$^+$), namely on treatment of a CH$_2$Cl$_2$ solution with [Et$_3$O][BF$_4$], EtC(O)Cl, PhC(O)Cl or Me$_3$SiI (added in a stoichiometric amount or in a 1 : 2 molar ratio), to give *trans*-[Mo(NCN)(NCNE)(dppe)$_2$]X [E = Et, X = BF$_4$ **4**; E = EtC(O), X = Cl **5a**, E = PhC(O), X = Cl **5b**; E = Me$_3$Si, X = I **6**] [Scheme 1, reactions (4), (5) or (6), respectively]. These complexes, isolated in good to moderate yields (71–32%), as golden brown (**4**), green (**5a**, **5b**) or greenish brown (**6**) solids have been characterized by IR and multinuclear NMR spectroscopies, FAB-MS and, in the case of **4**, also by an X-ray diffraction analysis, although the rather poor quality of the crystal prevented an accurate structure determination.

In their IR spectra (KBr pellets), the strong bands exhibited in the 2150–2120 and 2117–2100 cm^{-1} ranges are assigned to ν_{as}(N=C=N) of the organocyanoimide (NCNE) and the cyanoimide (NCN) ligands, respectively. Hence, as observed for protonation, the alkylation, acylation, aroylation or silylation of the latter ligand results in a shift of the corresponding IR stretching vibration to higher wavenumbers. The strong bands at 1290–1280 cm^{-1} are ascribed to ν_s(N=C=N) and/or ν(MoN), as for the above complexes, whereas for complexes **5a** and **5b** ν(C=O) of the propionyl and benzoyl groups, respectively, appears at 1619 and 1599 cm^{-1} (strong bands). In the case of complex **6**, ν(SiN)[50] is detected as a medium intensity band at 840 cm^{-1}.

In the ^{13}C NMR spectra, electrophilic attack at the cyanoimide ligand (similar to what is observed in the case of protonation) results in a shift to higher field (δ 121.7–125.1 for N*C*NE *vs.* 125.8 in complex **1**), whereas an opposite shift occurs for the unreacted cyanoimide ligand (δ 126.6–128.5). In addition, two sets of ^{1}H and ^{13}C NMR phosphinic aromatic resonances are observed for complexes **4**, **5a** and **5b**, as for complex **3** (see above), and the NCN*C*(O)R resonances occur at δ 176.95 (**5a**) or 174.56 (**5b**). The *trans* geometry of all the complexes is

Table 1 Selected bond lengths (Å) and angles (°) for the two independent complex cations A and A′ of *trans*-[Mo(NCN)(NCNH)(dppe)$_2$][BF$_4$] **2**, with e.s.d.s in parentheses

Cation A			
Mo(1)–N(1)	1.906(9)	N(1)–Mo(1)–P(2a)	88.7(2)
Mo(1)–P(1)	2.548(3)	P(1)–Mo(1)–P(2)	79.54(9)
Mo(1)–P(2)	2.551(3)	P(2)–Mo(1)–P(2a)	100.36(9)
N(1)–C(27)	1.189(18)	P(1a)–Mo(1)–P(2a)	79.54(9)
C(27)–N(2A)	1.19(3)	P(1)–Mo(1)–P(1a)	100.81(9)
C(27)–N(2B)	1.39(4)	P(1)–Mo(1)–P(2a)	176.23(9)
N(1)–Mo(1)–N(1a)	180.00	P(1a)–Mo(1)–P(2)	176.23(10)
N(1)–Mo(1)–P(1)	87.6(2)	Mo(1)–N(1)–C(27)	179.6(9)
N(1)–Mo(1)–P(2)	91.3(2)	N(1)–C(27)–N(2A)	173.6(18)
N(1)–Mo(1)–P(1a)	92.4(2)	N(1)–C(27)–N(2B)	150(2)
Cation A′			
Mo(1′)–N(1′)	1.903(9)	N(1′)–Mo(1′)–P(2′b)	91.0(3)
Mo(1′)–P(1′)	2.527(3)	P(1′)–Mo(1′)–P(2′)	79.81(9)
Mo(1′)–P(2′)	2.551(3)	P(1′b)–Mo(1′)–P(2′)	100.19(9)
N(1′)–C(27′)	1.176(19)	P(1′b)–Mo(1′)–P(2′b)	79.81(9)
C(27′)–N(1#)	1.24(3)	P(1′)–Mo(1′)–P(2′b)	100.19(9)
C(27′)–N(2#)	1.42(4)	P(1′)–Mo(1′)–P(1′b)	180.00
N(1′)–Mo(1′)–N(1′b)	180.00	P(2′)–Mo(1′)–P(2′b)	180.00
N(1′)–Mo(1′)–P(1′)	86.9(2)	Mo(1′)–N(1′)–C(27′)	174.1(11)
N(1′)–Mo(1′)–P(2′)	89.0(3)	N(1′)–C(27′)–N(1#)	164(2)
N(1′)–Mo(1′)–P(1′b)	93.1(2)	N(1′)–C(27′)–N(2#)	163(2)

indicated by the observed singlets in their ^{31}P-{^{1}H} NMR spectra, whereas their FAB-MS spectra clearly show the positive (for the complexes) and negative (for the counter-ions) molecular ions, with the expected isotopic patterns, as well as, for **5a** and **5b**, the corresponding NCNC(O)R$^-$ fragments.

The occurrence of electrophilic addition at the *exo*-N atom of the cyanoimide ligand in complex **1** would be expected in terms of electronic and stereochemical arguments (see above), as well as in view of the similarity of spectroscopic properties of the obtained products in comparison with those derived from protonation (complex **2**). This has been confirmed by the X-ray crystal structural analysis of the ethylated complex *trans*-[Mo(NCN)(NCNEt)(dppe)$_2$][BF$_4$] **4** whose molecular structure (complex cation) is depicted in Fig. 2, and selected bond lengths and angles are given in Table 2.

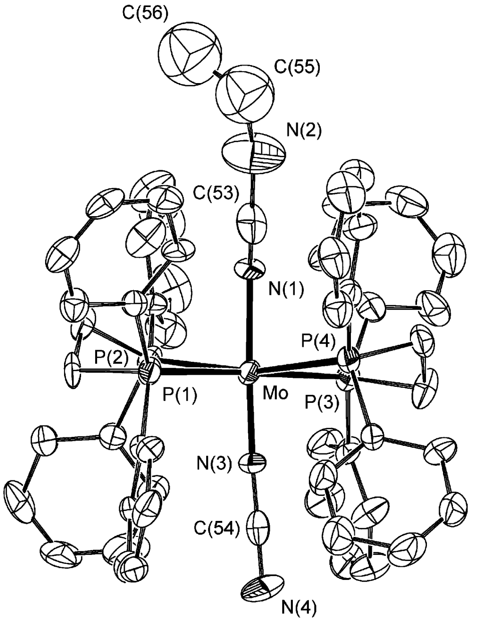


Fig. 2 Molecular structure of the complex cation of *trans*-[Mo(NCN)(NCNEt)(dppe)$_2$][BF$_4$] **4** with ellipsoids at the 30% probability level.

The essentially linear coordination modes of both the NCNEt and NCN ligands [Mo–N$_\alpha$–C angles of 173(3) and 177.0(13)°, respectively] are evident and the alkylation of the cyanoimide ligand resulted in the elongation of the Mo–N$_\alpha$ bond [2.050(17) Å (NCNEt) *vs.* 1.801(13) Å (NCN) in **4** or 1.860(11) Å (NCN) in **1**] which is much longer than the average Mo–N(imide) triple bond, 1.729 Å,[51] although still being significantly shorter than the average Mo–N(nitrile) single bond length, 2.147 Å.[51]

Table 2 Selected bond distances (Å) and angles (°) for the complex cation of *trans*-[Mo(NCN)(NCNEt)(dppe)$_2$][BF$_4$] **4**, with e.s.d.s in parentheses

Mo–N(1)	2.050(17)	N(3)–Mo–P(2)	98.7(4)
Mo–N(3)	1.801(13)	N(3)–Mo–P(3)	87.5(4)
Mo–P(1)	2.580(4)	N(3)–Mo–P(4)	92.9(4)
Mo–P(2)	2.551(4)	P(1)–Mo–P(2)	79.12(14)
Mo–P(3)	2.560(4)	P(2)–Mo–P(3)	100.96(14)
Mo–P(4)	2.542(4)	P(3)–Mo–P(4)	79.37(15)
N(2)–C(55)	1.54(4)	P(1)–Mo–P(4)	100.92(15)
C(55)–C(56)	1.42(5)	P(1)–Mo–P(3)	178.18(15)
N(3)–C(54)	1.29(2)	P(2)–Mo–P(4)	168.41(15)
C(54)–N(4)	1.20(3)	Mo–N(1)–C(53)	173(3)
N(1)–Mo–N(3)	177.5(6)	N(1)–C(53)–N(2)	170(3)
N(1)–Mo–P(1)	91.6(5)	C(53)–N(2)–C(55)	133(3)
N(1)–Mo–P(2)	82.7(4)	N(2)–C(55)–C(56)	108(3)
N(1)–Mo–P(3)	90.2(5)	Mo–N(3)–C(54)	177.0(13)
N(1)–Mo–P(4)	85.7(4)	N(3)–C(54)–N(4)	179(2)
N(3)–Mo–P(1)	90.7(4)		

The comparative features suggest that the electrophilic attack at one of the cyanoimide ligands in **1** results (i) in a decrease of the π-electron donor character of one of the nitrogen ligands (NCNE is a weaker π-donor than NCN), (ii) in a tendency towards the basic form of the corresponding organocyanamide (N≡C–NE$^-$) rather than towards an organoimide ligand, and (iii) in an enhancement of the π-electron release from the other unreacted cyanoimide (NCN) ligand, thus somehow compensating electronically the metal for the former effect.

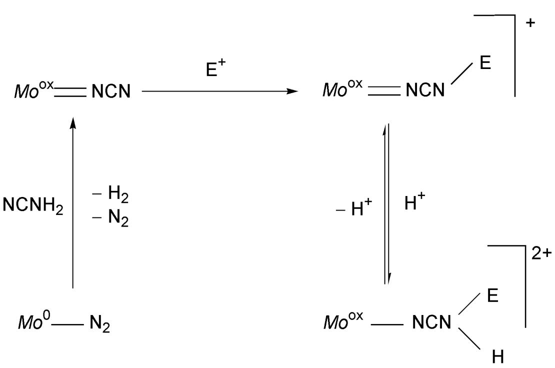
The alkylated cyanoimide ligand (NCNEt$^-$) in complex **4** can undergo further electrophilic attack by acid (HBF$_4$) which, as observed for NCNH$^-$ in the complex *trans*-[Mo(NCN)(NCNH)(dppe)$_2$][BF$_4$] **2** (see above), also occurs at the *exo*-N atom to afford [reaction (7), Scheme 1] a cyanamide product, the ethylcyanamide complex *trans*-[Mo(NCN)(NCNHEt)(dppe)$_2$][BF$_4$]$_2$ **7** that was isolated in high yield (81%) as a pale green solid. The protonation reaction (7) is also reversible [like reaction (3)] and complex **7** reverts to the parent compound **4** on treatment with NEt_3. Complex **7** is also formed, although in a less convenient way, by treatment of a CH_2Cl_2 solution of the bis(cyanoimide) complex **1** with an excess (1 : 4 to 1 : 8 molar ratio) of $[Et_3O][BF_4]$, followed by work-up of the reaction solution, but the product is contaminated with the oxonium salt and its purification requires repeated recrystallisations.

Complex **7** presents spectroscopic properties comparable with those of the related cyanamide complex *trans*-$[Mo(NCN)(NCNH_2)(dppe)_2][BF_4]_2$ **3** (see above), and in particular the N*C*NHEt and N*C*N carbon-atom resonances in the ^{13}C NMR spectrum of **7** (δ 122.06 and 126.99, respectively) exhibit the corresponding shifts to higher and lower field upon protonation of the parent NCNEt complex **4**. In the IR spectrum, $\nu(N{\equiv}C)$ of the ethyl cyanamide ligand is observed at 2210 cm^{-1} (strong band), a value considerably higher than that of the parent NCNEt ligand which in turn is higher than those of the NCN ligand.

The regular spectroscopic trends, discussed above, along the NCN (**1**), NCNE (**2**, **4**–**6**) and NCNHE (**3** and **7**) series of complexes, suggest that the cyanoimide and derived ligands can be ordered as follows according to their π-electron releasing character to the Mo(IV) centre: NCN (cyanoimide) > NCNE (hydrogen- or organo-cyanoimides) > NCNHE (cyanamides).

Final comments

This study provides a contribution towards the emergence of the virtually unexplored field of the activation of cyanamide ($N{\equiv}C{-}NH_2$) upon coordination to a transition metal centre, by showing (Scheme 3) that it can undergo reductive dehydrogenation by an electron-rich and easily oxidizable metal centre to give a ligated cyanoimide (NCN^{2-}) that displays further reactivity towards a variety of electrophiles (E^+) which add to the *exo*-nitrogen atom: (i) reversible stepwise double protonation ($E^+ = H^+$) to hydrogen cyanamide (or hydrogen cyanoimide) ($NCNH^-$) and cyanamide itself ($NCNH_2$), (ii) alkylation, (iii) acylation, (iv) aroylation, and (v) silylation, to form the corresponding organocyanoimide ($NCNE^-$) [E^+ = Et^+, $C(O)Et^+$, $C(O)Ph^+$, $SiMe_3{}^+$] which (vi) can be further protonated to give a monoorganocyanamide ($N{\equiv}C{-}NHE$). The cyanoimide ligand (or its cyanamide precursor) is thus susceptible to further functionalization which opens up the possibility of their application in the metal-mediated synthesis of organo-nitrogen species that may not be easily accessible by conventional organic processes. Moreover, the stepwise electrophilic addition to the ligated cyanoimide results in a corresponding decrease of the ligands' π-electron donor character which may be of significance towards the control of further reactivity.



[$E^+ = H^+$, Et^+, $C(O)Et^+$, $C(O)Ph^+$, $SiMe_3{}^+$]

Scheme 3

Experimental

General

Solvents were dried and degassed by using standard techniques. All reactions were performed under an inert atmosphere (argon). *trans*-$[Mo(N_2)_2(dppe)_2]$ was prepared according to a published method.[52] Before use, the acid chlorides EtC(O)Cl and PhC(O)Cl were dried over K_2CO_3 and then distilled, in an inert atmosphere (dinitrogen) and under vacuum, respectively, from the same desiccant material. The other reagents were used as purchased (Aldrich).

Infrared spectra were recorded on a Bio-Rad Excalibur FTS 3000MX FTIR spectrometer; wavenumbers are in cm^{-1}. Abbreviations: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. NMR spectra were acquired on a Varian Unity 300 spectrometer; 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 $^{13}C\text{-}\{^1H\}$ NMR spectra are not repeated. Coupling constants are in Hz. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, m = complex multiplet, br = broad, dd = doublet of doublets, dt = doublet of triplets, dm = doublet of complex multiplets, tq = triplet of quartets, tqnt = triplet of quintets, tm = triplet of complex multiplets, qt = quartet of triplets, qm = quartet of complex multiplets. The FAB-MS spectra were run on a Trio 2000 mass spectrometer. The samples were dispersed in a 3-nitrobenzyl alcohol (NBA) liquid matrix and then bombarded with an 8 keV (*ca.* 1.28×10^{-15} J) xenon fast atoms beam. Data system acquisition was calibrated with CsI. The calculation of the theoretical isotopic patterns was performed by using a computer program[53] taking into account the natural abundances of the various isotopes. The *m*/*z* values were calculated using the ^{98}Mo isotope. The elemental analyses were done by the Laboratório de Análises of the Instituto Superior Técnico.

Preparation of the complexes

***trans*-$[Mo(NCN)_2(dppe)_2]$ 1.** A thf solution (30 cm^3) of *trans*-$[Mo(N_2)_2(dppe)_2]$ (0.500 g, 0.527 mmol) was treated with cyanamide (0.044 g, 1.05 mmol) which had been dried under vacuum at room temperature, and left stirring. A dark brown suspension gradually formed and the maximum amount of the precipitated solid (complex **1**) was obtained after *ca.* three days. Concentration *in vacuo* followed by addition of *n*-pentane (or *n*-hexane) led to the precipitation of an additional amount of the complex as a violet solid which was then filtered-off, washed with an *n*-pentane (or *n*-hexane)–thf mixture and dried *in vacuo* (0.282 g, 55% yield of spectroscopically pure product **1**). Analytical purity was obtained after recrystallisation from CH_2Cl_2/Et_2O (yields not higher than 85%, depending on the levels of contamination of the crude product). IR (KBr pellet): 2043 [vs, sharp, $\nu_{as}(N{=}C{=}N)$], 1279 [vs, sharp, $\nu_s(N{=}C{=}N)$ and/or $\nu(MoN)$]. NMR (298 K): ^1H (CD_2Cl_2), δ 7.36 [t, 8 H, $^3J_{HH}$ 7.0, H_p (dppe)], 7.22 [t, 16 H, $^3J_{HH}$ 7.5, H_m (dppe)], 7.20 [m, 16 H, H_o (dppe)], 2.72 [t, 8 H, virtual J_{HP} 8.4, CH_2 (dppe)]; $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2), δ −102.7 s; $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), δ 134.50 [qnt, virtual J_{CP} 8.5, C_i (dppe)], 133.45 [qnt, virtual J_{CP} 2.8, C_o (dppe)], 130.26 [s, C_p (dppe)], 128.78 [qnt, virtual J_{CP} 2.1, C_m (dppe)], 125.78 (s, N*C*N), 28.36 [qnt, virtual J_{CP} 9.3, CH_2 (dppe)]; ^{13}C (CD_2Cl_2), δ 134.50, 133.45 (dm, J_{CH} 161.2), 130.26 (dt, J_{CH} 161.2, $^2J_{CH}$ 6.7), 128.78 (dm, J_{CH} 161.1), 125.78, 28.36 (tqnt, J_{CH} 133.7, virtual J_{CP} 7.9). FAB$^+$-MS: *m*/*z* 974 ($[M]^+$). (Found: C, 65.1; H, 4.9; N, 5.4%. $C_{54}H_{48}N_4MoP_4{\cdot}1/3CH_2Cl_2$ requires C, 65.2; H, 4.9; N, 5.6%).

***trans*-$[Mo(NCN)(NCNH)(dppe)_2][BF_4]$ 2.** CH_2Cl_2 (25 cm^3) was added to crude *trans*-$[Mo(NCN)_2(dppe)_2]$ (0.150 g, *ca.* 0.154 mmol) and the resulting suspension was vigorously stirred and then filtered through celite, whereafter a 1 : 11 Et_2O

diluted solution of 85% [Et$_2$OH][BF$_4$] was slowly added dropwise (0.235 cm^3, 0.123 mmol). The solution colour turned immediately yellowish olive green and its concentration *in vacuo*, followed by the slow addition of Et$_2$O, resulted in the deposition of compound **2** as a microcrystalline olive green solid which was filtered-off, washed with Et$_2$O and dried *in vacuo* (0.111 g, 68% yield). IR (KBr pellet): 3270 [w, br, ν(NH)], 2082 [vs, ν_{as}(N=C=N)], 1624 [m, δ(NH)], 1280 [vs, ν_{s}(N=C=N) and/or ν(MoN)], 1120–1000 [vs, br, ν(BF)]. NMR (298 K): ^{1}H (CD$_2$Cl$_2$), δ 7.48 [t, 8 H, $^3J_{\mathrm{HH}}$ 7.3, H_p (dppe)], 7.30 [t, 16 H, $^3J_{\mathrm{HH}}$ 7.6, H_m (dppe)], 7.08 [m, 16 H, H_o (dppe)], 2.96 [t, 8 H, virtual J_{HP} 8.4, CH_2 (dppe)]; ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ −100.6 s; ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 132.84 [qnt, virtual J_{CP} 2.7, C_o (dppe)], 131.73 [s, C_p (dppe)], 130.93 [qnt, virtual J_{CP} 9.1, C_i (dppe)], 129.60 [qnt, virtual J_{CP} 2.1, C_m (dppe)], 126.17 (s, N*C*N), 124.96 (s, N*C*NH), 27.62 [qnt, virtual J_{CP} 9.4, *C*H$_2$ (dppe)]; ^{13}C (CD$_2$Cl$_2$), δ 132.84 (dm, J_{CH} 162.9), 131.73 (dt, J_{CH} 156.9, $^2J_{\mathrm{CH}}$ 6.7), 130.93, 129.60 (dm, J_{CH} 159.3), 126.17, 124.96, 27.62 (tm, J_{CH} 134.0). FAB$^+$-MS: *m/z* 975 ([M]$^+$), 953 ([M − NCNH + F]$^+$). FAB$^-$-MS: *m/z* 87 ([BF$_4$]$^-$). (Found: C, 56.6; H, 4.7; N, 4.6%. $C_{54}H_{49}N_4BF_4MoP_4\cdot 4/3CH_2Cl_2$ requires C, 56.6; H, 4.4; N, 4.8%).

***trans*-[Mo(NCN)(NCNH$_2$)(dppe)$_2$][BF$_4$]$_2$ 3.** A suspension of crude *trans*-[Mo(NCN)$_2$(dppe)$_2$] (0.100 g, *ca.* 0.103 mmol) in CH$_2$Cl$_2$ (30 cm^3), after vigorous stirring, was filtered through celite and the filtered solution was treated with a 1 : 11 Et$_2$O diluted solution of 85% [Et$_2$OH][BF$_4$] (0.410 cm^3, 0.215 mmol) which was added slowly and dropwise. The colour of the reaction solution turned immediately light green. Concentration of this solution *in vacuo* followed by the slow addition of Et$_2$O resulted in the precipitation of compound **3** as a microcrystalline light green solid which was filtered-off, washed with Et$_2$O and dried *in vacuo* (0.089 g, 75% yield). IR (KBr pellet): 3255 [w, br, ν_{as}(NH$_2$)], 3199 [w, br, ν_{s}(NH$_2$)], 2250 [vs, ν(N≡C)], 2086 [vs, sharp, ν_{as}(N=C=N)], 1624 [m, δ(NH$_2$)], 1290 [s, ν_{s}(N=C=N) and/or ν(MoN)], 1150–1000 [vs, br, ν(BF)]. NMR (298 K): ^{1}H (CD$_2$Cl$_2$), δ 7.60 [t, 4 H, $^3J_{\mathrm{HH}}$ 7.2, H_p (dppe)], 7.50 [t, 4 H, $^3J_{\mathrm{HH}}$ 7.3, H_p' (dppe)], 7.42 [t, 8 H, $^3J_{\mathrm{HH}}$ 7.6, H_m (dppe)], 7.32 [t, 8 H, $^3J_{\mathrm{HH}}$ 7.6, H_m' (dppe)], 7.22 [m, 8 H, H_o (dppe)], 6.96 [m, 8 H, H_o' (dppe)], 5.42 [s, br, 2 H, disappears on addition of D$_2$O, NCNH_2], 3.31 [m, 4 H, CH_2 (dppe)], 3.02 [m, 4 H, CH_2 (dppe)]; ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ −97.7 s; ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 132.72 [s, C_p (dppe)], 132.66 [s, C_p' (dppe)], 132.46 [qnt, virtual J_{CP} 2.9, C_o (dppe)], 132.34 [qnt, virtual J_{CP} 2.7, C_o' (dppe)], 130.98 [qnt, virtual J_{CP} 9.7, C_i (dppe)], 130.40 [qnt, virtual J_{CP} 2.3, C_m (dppe)], 130.07 [qnt, virtual J_{CP} 2.4, C_m' (dppe)], 128.46 (s, N*C*N), 128.16 [qnt, virtual J_{CP} 11.3, C_i' (dppe)], 121.75 (s, N*C*NH$_2$), 26.97 [qnt, virtual J_{CP} 9.8, *C*H$_2$ (dppe)]; ^{13}C (CD$_2$Cl$_2$), δ 134.2–128.0 [m, C_6H_5 (dppe)], 128.46, 121.75, 26.97 (tm, J_{CH} 133.3). FAB$^+$-MS: *m/z* 976 ([M]$^+$). FAB$^-$-MS: *m/z* 87 ([BF$_4$]$^-$). (Found: C, 53.2; H, 3.9; N, 4.5%. $C_{54}H_{50}N_4B_2F_8MoP_4\cdot 6/5CH_2Cl_2$ requires C, 53.0; H, 4.2; N, 4.5%).

***trans*-[Mo(NCN)(NCNEt)(dppe)$_2$][BF$_4$] 4.** To a suspension of crude *trans*-[Mo(NCN)$_2$(dppe)$_2$] (0.150 g, *ca.* 0.154 mmol) in CH$_2$Cl$_2$ (20 cm^3) was added [Et$_3$O][BF$_4$] (0.030 g, 0.158 mmol). The mixture was left stirring for *ca.* 24 h and then filtered through celite. Concentration *in vacuo* of the resulting yellowish brown filtrate followed by slow addition of Et$_2$O led to the precipitation of compound **4** as a microcrystalline golden brown solid which was filtered-off, washed with Et$_2$O and dried *in vacuo* (0.119 g, 71% yield). IR (KBr pellet): 2120 and 2100 [vs, sharp, ν_{as}(N=C=N)], 1280 [vs, ν_{s}(N=C=N) and/or ν(MoN)], 1120–1000 [vs, br, ν(BF)]. NMR (298 K): ^{1}H (CD$_2$Cl$_2$), δ 7.51 [t, 4 H, $^3J_{\mathrm{HH}}$ 7.2, H_p (dppe)], 7.47 [t, 4 H, $^3J_{\mathrm{HH}}$ 7.2, H_p' (dppe)], 7.34 [t, 8 H, $^3J_{\mathrm{HH}}$ 7.6, H_m (dppe)], 7.25 [t, 8 H, $^3J_{\mathrm{HH}}$ 7.5, H_m' (dppe)], 7.18 [m, 8 H, H_o (dppe)], 7.01 [m, 8 H, H_o' (dppe)], 2.92 [m, 8 H, CH_2 (dppe)], 2.62 [q, 2 H, $^3J_{\mathrm{HH}}$ 7.2, CH_2 (NCNEt)], 0.75 [t, 3 H, $^3J_{\mathrm{HH}}$ 7.2, CH_3 (NCNEt)]; ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ −101.3 s; ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 133.00 [qnt, virtual J_{CP} 2.7, C_o (dppe)], 132.84 [qnt, virtual J_{CP} 2.9, C_o' (dppe)], 132.20 [qnt, virtual J_{CP} 9.2, C_i (dppe)], 131.70 [s, C_p (dppe)], 131.48 [s, C_p' (dppe)], 131.25 [qnt, virtual J_{CP} 10.2, C_i' (dppe)], 129.58 [qnt, virtual J_{CP} 2.3, C_m (dppe)], 129.43 [qnt, virtual J_{CP} 2.2, C_m' (dppe)], 126.57 (s, N*C*N), 122.78 (s, N*C*NEt), 40.20 [s, *C*H$_2$ (NCNEt)], 27.58 [qnt, virtual J_{CP} 9.3, *C*H$_2$ (dppe)], 17.16 [s, *C*H$_3$ (NCNEt)]; ^{13}C (CD$_2$Cl$_2$), δ 133.00 (dm, J_{CH} 161.8), 132.84 (dm, J_{CH} 161.2), 132.20, 131.70 (dt, J_{CH} 154.7, $^2J_{\mathrm{CH}}$ 7.3), 131.48 (dt, J_{CH} 154.7, $^2J_{\mathrm{CH}}$ 7.4), 131.25, 129.58 (dm, J_{CH} 164.8), 129.43 (dm, J_{CH} 164.8), 126.57, 122.78, 40.20 (tq, J_{CH} 143.4, $^2J_{\mathrm{CH}}$ 4.5), 27.58 (tm, J_{CH} 134.9), 17.16 (qt, J_{CH} 127.3, $^2J_{\mathrm{CH}}$ 3.7). FAB$^+$-MS: *m/z* 1003 ([M]$^+$), 974 ([M − Et]$^+$), 953 ([M − NCNEt + F]$^+$). FAB$^-$-MS: *m/z* 87 ([BF$_4$]$^-$). (Found: C, 59.9; H, 4.8; N, 4.9%. $C_{56}H_{53}N_4BF_4MoP_4\cdot 1/2CH_2Cl_2$ requires C, 60.0; H, 4.8; N, 5.0%).

***trans*-[Mo(NCN){NCNC(O)R}(dppe)$_2$]Cl (R = Et 5a or Ph 5b).** A suspension of crude *trans*-[Mo(NCN)$_2$(dppe)$_2$] (0.150 g, *ca.* 0.154 mmol) in CH$_2$Cl$_2$ (20 cm^3) was treated with a 1 : 11 CH$_2$Cl$_2$ diluted solution of the acid chloride RC(O)Cl [0.148 cm^3 (R = Et) or 0.197 cm^3 (R = Ph), 0.154 mmol]. The reaction mixture was left stirring for *ca.* 24 h, the suspension was then filtered through celite and the dark green solution was concentrated *in vacuo*, whereupon Et$_2$O was added leading to the formation of compound **5a** or **5b** as a green solid which was separated by filtration, washed with Et$_2$O and dried *in vacuo* [0.054 g, 33% yield (**5a**); 0.086 g, 50% yield (**5b**)]. Subsequent fractions, obtained by concentration of the mother liquors *in vacuo* and addition of Et$_2$O, revealed a mixture of the acylated or aroylated complexes with free dppe.

*Complex **5a***. IR (KBr pellet): 2143 (sh) and 2117 (s) [ν_{as}(N=C=N)], 1619 [s, ν(C=O)], 1284 [s, sharp, ν_{s}(N=C=N) and/or ν(MoN)]. NMR (298 K): ^{1}H (CD$_2$Cl$_2$), δ 7.53 [t, 4 H, $^3J_{\mathrm{HH}}$ 7.2, H_p (dppe)], 7.45 [t, 4 H, $^3J_{\mathrm{HH}}$ 7.5, H_p' (dppe)], 7.35 [t, 8 H, $^3J_{\mathrm{HH}}$ 7.8, H_m (dppe)], 7.22 [t, 8 H, $^3J_{\mathrm{HH}}$ 7.6, H_m' (dppe)], 7.12 [m, 16 H, $H_o + H_o'$ (dppe)], 3.09 [m, 4 H, CH_2 (dppe)], 3.03 [m, 4 H, CH_2 (dppe)], 2.47 {q, 2 H, $^3J_{\mathrm{HH}}$ 7.5, CH_2 [NCNC(O)Et]}, 1.07 {t, 3 H, $^3J_{\mathrm{HH}}$ 7.5, CH_3 [NCNC(O)Et]}; ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ −103.0 s; ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 176.95 [s, NCN*C*(O)Et], 133.26 [qnt, virtual J_{CP} 2.7, C_o (dppe)], 132.93 [qnt, virtual J_{CP} 10.8, C_i (dppe)], 132.53 [qnt, virtual J_{CP} 2.7, C_o' (dppe)], 131.96 [s, C_p (dppe)], 131.64 [s, C_p' (dppe)], 130.52 [qnt, virtual J_{CP} 10.8, C_i' (dppe)], 129.70 [qnt, virtual J_{CP} 2.1, C_m (dppe)], 129.15 [qnt, virtual J_{CP} 2.1, C_m' (dppe)], 128.22 (s, N*C*N), 121.67 [s, N*C*NC(O)Et], 29.30 {s, *C*H$_2$ [NCNC(O)Et]}, 27.19 [qnt, virtual J_{CP} 9.6, *C*H$_2$ (dppe)], 9.12 {s, *C*H$_3$ [NCNC(O)Et]}; ^{13}C (CD$_2$Cl$_2$), δ 176.95, 133.26 (dm, J_{CH} 162.3), 132.93, 132.53 (dm, J_{CH} 161.2), 131.96 (dt, J_{CH} 163.6, $^2J_{\mathrm{CH}}$ 7.0), 131.64 (dt, J_{CH} 163.6, $^2J_{\mathrm{CH}}$ 7.0), 130.52, 129.70 (dm, J_{CH} 162.9), 129.15 (dm, J_{CH} 163.5), 128.22, 121.67, 29.30 (tq, J_{CH} 130.0, $^2J_{\mathrm{CH}}$ 4.8), 27.19 (tm, J_{CH} 135.8), 9.12 (qt, J_{CH} 128.0, $^2J_{\mathrm{CH}}$ 4.3). FAB$^+$-MS: *m/z* 1031 ([M]$^+$), 974 {[M − C(O)Et]$^+$}, 969 {[M − NCNC(O)Et + Cl]$^+$}. FAB$^-$-MS: *m/z* 97 [NCNC(O)Et$^-$], 35 (Cl$^-$). (Found: C, 60.6; H, 4.9; N, 5.0%. $C_{57}H_{53}N_4OClMoP_4\cdot CH_2Cl_2$ requires C, 60.6; H, 4.8; N, 4.9%).

*Complex **5b***. IR (KBr pellet): 2140 and 2115 [vs, ν_{as}(N=C=N)], 1599 [s, ν(C=O)], 1284 [s, sharp, ν_{s}(N=C=N) and/or ν(MoN)]. NMR (298 K): ^{1}H (CD$_2$Cl$_2$), δ 8.07 {d, 2 H, $^3J_{\mathrm{HH}}$ 6.9, H_o [NCNC(O)Ph]}, 7.52 [t, 4 H, $^3J_{\mathrm{HH}}$ 7.3, H_p (dppe)], 7.44 [t, 4 H, $^3J_{\mathrm{HH}}$ 7.3, H_p' (dppe)], 7.34 [t, 8 H, $^3J_{\mathrm{HH}}$ 7.3, H_m (dppe)], 7.20 [t, 8 H, $^3J_{\mathrm{HH}}$ 7.5, H_m' (dppe)], 7.11 [m, 16 H, $H_o + H_o'$ (dppe)], 3.08 [m, 4 H, CH_2 (dppe)], 3.02 [m, 4 H, CH_2 (dppe)]; ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ −103.1 s; ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 174.56 [s, NCN*C*(O)Ph], 133.31 [qnt, virtual J_{CP} 2.6, C_o (dppe)], 132.95 [qnt, virtual J_{CP} 10.9, C_i (dppe)], 132.58 [qnt, virtual J_{CP} 2.7, C_o' (dppe)], 131.94 [s, C_p (dppe)], 131.87 {s, C_i [NCNC(O)Ph]}, 131.63 [s, C_p' (dppe)], 130.55 [qnt, virtual J_{CP} 10.8, C_i' (dppe)], 130.40 {s, C_p [NCNC(O)Ph]}, 129.71 [qnt, virtual J_{CP} 2.2, C_m (dppe)], 129.18 [qnt, virtual J_{CP} 2.3, C_m' (dppe)], 129.02 {s, C_m

[NCNC(O)Ph]}, 128.49 (s, N*C*N), 127.79 {s, C_o [NCNC(O)-Ph]}, 121.72 [s, N*C*NC(O)Ph], 27.19 [qnt, virtual J_{CP} 9.6, *C*H_2 (dppe)]; ^{13}C (CD_2Cl_2), δ 174.56, 133.31 (dm, J_{CH} 163.0), 132.95, 132.58 (dm, J_{CH} 161.8), 131.94 (dt, J_{CH} 163.6, $^2J_{CH}$ 7.0), 131.87 (m), 131.63 (dt, J_{CH} 163.5, $^2J_{CH}$ 7.0), 130.55, 130.40 (dm, J_{CH} 163.1), 129.71 (dm, J_{CH} 162.3), 129.18 (dm, J_{CH} 161.1), 129.02 (dm, J_{CH} 160.5), 128.49, 127.79 (dd, J_{CH} 159.1, $^2J_{CH}$ 7.0), 121.72, 27.19 (tm, J_{CH} 137.6). FAB$^+$-MS: *m*/*z* 1079 ([M]$^+$), 974 {[M − C(O)Ph]$^+$}, 969 {[M − NCNC(O)Ph + Cl]$^+$}. FAB$^-$-MS: *m*/*z* 145 [NCNC(O)Ph$^-$], 35 (Cl$^-$). (Found: C, 62.9; H, 4.4; N, 5.2%. $C_{61}H_{53}N_4OClMoP_4\cdot 3/4CH_2Cl_2$ requires C, 63.0; H, 4.7; N, 4.8%).

***trans*-[Mo(NCN)(NCNSiMe$_3$)(dppe)$_2$]I 6.** Me_3SiI (0.045 cm^3, 0.307 mmol) was added to a suspension of crude *trans*-[Mo(NCN)$_2$(dppe)$_2$] (0.150 g, *ca.* 0.154 mmol) in CH_2Cl_2 (20 cm^3). The mixture was left stirring for *ca.* 24 h, then filtered and the resulting yellowish brown solution was concentrated *in vacuo*, whereafter addition of Et_2O led to the precipitation of a greenish brown solid which was filtered-off, washed with Et_2O and dried *in vacuo*. It was shown to be a mixture of compound **6** contaminated with the monoprotonated derivative *trans*-[Mo(NCN)(NCNH)(dppe)$_2$]I, the main contaminant, and other unidentified species. Concentration of the filtrate *in vacuo* followed by addition of Et_2O and cooling to *ca.* −20 °C led to the precipitation, after a few days, of the pure compound **6** as an olive green solid which was isolated by filtration, washed with Et_2O and dried *in vacuo* (0.058 g, 32% yield). IR (KBr pellet): 2150 and 2100 [vs, ν_{as}(N=C=N)], 1290 [vs, ν_s(N=C=N) and/or ν(MoN)], 840 [m, ν(SiN)]. NMR (298 K): ^{1}H (CD_2Cl_2), δ 7.47 [t, 8 H, $^3J_{HH}$ 6.7, H_p (dppe)], 7.30 [m, 16 H, H_m (dppe)], 7.11 [m, 16 H, H_o (dppe)], 2.94 [t, 8 H, virtual J_{HP} 8.4, C*H_2* (dppe)], −0.029 [s, 9 H, C*H_3* (NCNSiMe$_3$)]; ^{31}P-{^{1}H} (CD_2Cl_2), δ −101.4 s; ^{13}C-{^{1}H} (CD_2Cl_2), δ 132.94 [m, C_o or C_m (dppe)], 131.38 [s, C_p (dppe)], 129.44 [m, C_m or C_o (dppe)], 126.84 (s, N*C*N), 125.14 (s, N*C*NSiMe$_3$), 27.89 [qnt, virtual J_{CP} 9.2, *C*H_2 (dppe)], 1.17 [s, *C*H_3 (NCNSiMe$_3$)]; ^{13}C (CD_2Cl_2), δ 132.94 (dm, J_{CH} 159.4), 131.38 (dm, J_{CH} 163.0), 129.44 (dm, J_{CH} 161.8), 126.84, 125.14, 27.89 (tm, J_{CH} 137.4), 1.17 (q, J_{CH} 120.5). FAB$^+$-MS: *m*/*z* 1061 ([M − NCNSiMe$_3$ + I]$^+$), 1047 ([M]$^+$), 974 ([M − SiMe$_3$]$^+$). FAB$^-$-MS: *m*/*z* 127 (I$^-$). (Found: C, 55.5; H, 4.6; N, 4.3%. $C_{57}H_{57}N_4SiIMoP_4\cdot CH_2Cl_2$ requires C, 55.4; H, 4.7; N, 4.4%).

***trans*-[Mo(NCN)(NCNHEt)(dppe)$_2$][BF$_4$]$_2$ 7.** To a stirred CH_2Cl_2 solution (30 cm^3) of *trans*-[Mo(NCN)(NCNEt)(dppe)$_2$]-[BF$_4$] **4** (0.070 g, 0.064 mmol) was added, slowly and dropwise, a 1 : 11 Et_2O diluted solution of 85% [Et$_2$OH][BF$_4$] (0.125 cm^3, 0.066 mmol). The solution colour turned immediately greenish yellow and its concentration *in vacuo*, followed by the slow addition of *n*-pentane, resulted in the formation of a green oil whereafter the supernatant solution was decanted off. Further addition of *n*-pentane to the oily residue, with vigorous stirring, followed by freezing in liquid nitrogen and subsequent slow warming up to room temperature (freeze–thaw technique), with moderate stirring, resulted in the formation of a pale green microcrystalline solid of complex **7** which was filtered-off, washed with *n*-pentane and dried *in vacuo* (0.061 g, 81% yield). Alternatively, complex **7** could be obtained, in a less convenient way, by treating a CH_2Cl_2 solution of *trans*-[Mo(NCN)$_2$(dppe)$_2$] **1** with an excess (4 : 1 to 8 : 1 molar ratio) of [Et$_3$O][BF$_4$], followed by work-up of the reaction solution, but the product was then rather contaminated with the triethyloxonium salt and its purification required repeated recrystallisations. IR (KBr pellet): 2210 [m, ν(N≡C)], 2110 (s, sharp) and 2090 (vs, sharp) [ν_{as}(N=C=N)], 1280 [s, ν_s(N=C=N) and/or ν(MoN)], 1150–1000 [vs, br, ν(BF)]. NMR (298 K): ^{1}H (CD_2Cl_2), δ 7.59 [t, 4 H, $^3J_{HH}$ 7.5, H_p (dppe)], 7.55 [t, 4 H, $^3J_{HH}$ 7.3, H_p' (dppe)], 7.42 [t, 8 H, $^3J_{HH}$ 7.5, H_m (dppe)], 7.35 [t, 8 H, $^3J_{HH}$ 7.5, H_m' (dppe)], 7.19 [m, 8 H, H_o (dppe)], 6.98 [m, 8 H, H_o' (dppe)], 4.37 [br, 1 H, disappears on addition of D_2O, NCN*H*Et], 3.41 [m, 4 H, C*H_2* (dppe)], 3.14 [m, 4 H, C*H_2* (dppe)], 1.82 [q, 2 H, $^3J_{HH}$ 7.3, C*H_2* (NCNHEt)], 0.52 [t, 3 H, $^3J_{HH}$ 7.3, C*H_3* (NCNHEt)]; ^{31}P-{^{1}H} (CD_2Cl_2), δ −98.0 s; ^{13}C-{^{1}H} (CD_2Cl_2), δ 132.76 [m, C_o or C_m (dppe)], 132.64 [m, C_o' or C_m' (dppe)], 132.34 [s, C_p + C_p' (dppe)], 131.94 [qnt, virtual J_{CP} 9.4, C_i (dppe)], 131.39 [m, C_i' (dppe)], 130.39 [m, C_m or C_o (dppe)], 130.13 [m, C_m' or C_o' (dppe)], 126.99 (s, N*C*N), 122.06 (s, N*C*NHEt), 41.79 [s, *C*H_2 (NCNHEt)], 27.82 [qnt, virtual J_{CP} 9.0, *C*H_2 (dppe)], 14.57 [s, *C*H_3 (NCNHEt)]; ^{13}C (CD_2Cl_2), δ 132.76 (dm, J_{CH} 171.5), 132.64 (dm, J_{CH} 170.9), 132.34 (dm, J_{CH} 164.8), 131.94, 131.39, 130.39 (dm, J_{CH} 163.6), 130.13 (dm, J_{CH} 165.4), 126.99, 122.06, 41.79 (tm, J_{CH} 145.3), 27.82 (tm, J_{CH} 136.7), 14.57 (qm, J_{CH} 130.0). FAB$^+$-MS: *m*/*z* 1004 ([M]$^+$), 975 ([M − Et]$^+$). FAB$^-$-MS: *m*/*z* 87 ([BF$_4$]$^-$). (Found: C, 52.9; H, 4.5; N, 4.5%. $C_{56}H_{54}N_4B_2F_8MoP_4\cdot 3/2CH_2Cl_2$ requires C, 53.0; H, 4.4; N, 4.3%).

Crystal structure determinations

The poor quality of the crystals of both complexes prevented accurate structure determinations. The PROFIT program[54] was used for cell refinement and data reduction. Structures were solved by direct methods by using the SHELXS-97 package.[55] The structure refinements were carried out with SHELXL-97.[56] ORTEP representations were performed using the PLATON99 program.[57] Crystallographic data are summarised in Table 3 and selected bond lengths and angles in Tables 1 and 2.

***trans*-[Mo(NCN)(NCNH)(dppe)$_2$][BF$_4$]·CH$_2$Cl$_2$ (2·CH$_2$Cl$_2$).** Crystals of **2** were obtained by spontaneous crystallisation of this compound during its preparation, after the step of slow addition of Et_2O to the concentrated reaction solution. X-Ray diffraction data were collected on a Nicolet P3 diffractometer equipped with a beta-monochromator and using Cu-K$_\alpha$ radiation. An extinction correction was applied. All non-hydrogen atoms were treated anisotropically. Both N(2) and N(2′) could be split into two positions with occupancy factors of 63 and 37%. As a consequence, hydrogens around these atoms could not be found. The hydrogen atoms of the solvent of crystallisation molecule could also not be located. All other hydrogen atoms were constrained to have identical *U*.

***trans*-[Mo(NCN)(NCNEt)(dppe)$_2$][BF$_4$]·H$_2$O (4·H$_2$O).** Crystals of **4** were grown spontaneously and slowly from the supernatant solution which was decanted when compound **7** was prepared. X-Ray diffraction data were collected on a Enraf-Nonius CAD4 diffractometer equipped with a niobium-monochromator and using Mo-K$_\alpha$ radiation. All non-hydrogen atoms were treated anisotropically except C(55) and C(56) which have strong thermal vibrations. The atoms of the NCNEt group, particularly N(1) and C(53), are not well resolved, their positions could not be satisfactorily refined and, as a consequence, the N(1)–C(53) bond length is not precise. Hydrogen atoms were constrained to have identical *U*. The hydrogen atoms of the crystallisation water molecule could not be located and the oxygen atom was disordered in two positions which were refined with 0.70 and 0.30 isotropic displacement parameters. A disorder model was applied to each of the fluorine atoms of the tetrafluoroborate anion which were then refined with occupancy factors of 63 and 37%.

CCDC reference numbers 171672 and 171673.

See http://www.rsc.org/suppdata/dt/b1/b108165a/ for crystallographic data in CIF or other electronic format.

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Table 3 Crystallographic data for *trans*-[Mo(NCN)(NCNH)(dppe)$_2$][BF$_4$]·CH$_2$Cl$_2$ (**2**·CH$_2$Cl$_2$) and *trans*-[Mo(NCN)(NCNEt)(dppe)$_2$][BF$_4$]·H$_2$O (**4**·H$_2$O)

	2	**4**
Chemical formula	$C_{55}H_{48}BCl_2F_4MoN_4P_4$	$C_{56}H_{53}BF_4MoN_4OP_4$
Formula weight	1142.50	1104.65
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2$_1$/*n*
a/Å	22.450(4)	11.778(2)
b/Å	12.196(2)	21.290(4)
c/Å	39.540(8)	22.115(4)
α/°	90	90
β/°	98.93(3)	90.85(3)
γ/°	90	90
V/Å^3	10695(3)	5544.8(17)
T/K	293	293
Z	8	4
μ^a/mm^{-1}	4.511	0.406
Total reflections collected	4006	7930
Independent reflections	4004 (R_{int} = 0.0000)	2003 (R_{int} = 0.0155)
Observed reflections [$I > 2\sigma(I)$]	3931	2003
R indices (all data)	$R1 = 0.0742$ $wR2 = 0.1964$	$R1 = 0.0468$ $wR2 = 0.1210$
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0729$ $wR2 = 0.1938$	$R1 = 0.0468$ $wR2 = 0.1210$

[a] μ(Cu-K$_\alpha$) for **2** and μ(Mo-K$_\alpha$) for **4**.

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References

1 C. Ponnamperuma and E. Peterson, *Science*, 1965, **147**, 1572.

2 C. Ponnamperuma, R. D. Brown, A. G. Cairns-Smith, S. P. S. Andrew and M. D. Braiser, *Chem. Br.*, 1979, 560.

3 R. W. Miller and R. R. Eady, *Biochim. Biophys. Acta*, 1988, **952**, 290.

4 U. H. Maier-Greiner, B. M. M. Obermaier-Skrobranek, L. M. Estermaier, W. Kammerloher, C. Freund, C. Wülfing, U. I. Burkert, D. H. Matern, M. Breuer, M. Eulitz, Ö. I. Küfrevioglu and G. R. Hartmann, *Proc. Natl. Acad. Sci. USA*, 1991, **88**, 4260.

5 C. B. McColl, *Aust. J. Exp. Agric.*, 1988, **264**, 505.

6 (*a*) V. H. Michaud, W. Goll, B. Hammer, J. von Seyerl, W. Sturm, S. Weiss and R. Youngman, *Chem. Ztg.*, 1988, **112**, 287; (*b*) *Cyanamide*, Cyanamid Canada Inc., Montreal, Canada.

7 (*a*) C. H. Kwon, H. T. Nagasawa, E. G. DeMaster and F. N. Shirota, *J. Med. Chem.*, 1986, **29**, 1922; (*b*) R. Obach, R. A. Menargues, J. Valles, J. M. Valles and J. A. Garcia-Sevilla, *Eur. J. Pharmacol.*, 1986, **127**, 225; (*c*) C. J. P. Eriksson, *Biochem. Pharmacol.*, 1985, **34**, 3979.

8 A. J. L. Pombeiro, *New J. Chem.*, 1994, **18**, 163 and references therein.

9 L. M. D. R. S. Martins, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, R. A. Henderson, D. J. Evans, F. Benetollo, G. Bombieri and R. A. Michelin, *Inorg. Chim. Acta*, 1999, **291**, 39.

10 M. T. A. R. S. Costa, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, R. A. Michelin, G. Bombieri and F. Benetollo, *Inorg. Chim. Acta*, 1998, **280**, 308.

11 L. M. D. R. S. Martins, M. F. C. Guedes da Silva, I. Marques, J. J. R. Fraústo da Silva, M. C. N. Vaz and A. J. L. Pombeiro, *Rapid Commun. Mass Spectrom.*, 1996, **10**, 447.

12 M. F. C. Guedes da Silva, E. M. P. R. P. Branco, Y. Wang, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, R. Bertani, R. A. Michelin, M. Mozon, F. Benetollo and G. Bombieri, *J. Organomet. Chem.*, 1995, **490**, 89.

13 F. Meyer, I. Hyla-Kryspin, E. Kaifer and P. Kircher, *Eur. J. Inorg. Chem.*, 2000, 771.

14 D. B. Mitzi, K. Liang and S. Wang, *Inorg. Chem.*, 1998, **37**, 321.

15 K. Zusai, T. Katayama, T. Ishida and T. Nogami, *Mol. Cryst. Liq. Cryst.*, 2000, **343**, 121.

16 M. F. N. N. Carvalho and A. J. L. Pombeiro, *J. Organomet. Chem.*, 1991, **410**, 347.

17 A. J. L. Pombeiro, M. F. C. Guedes da Silva, D. L. Hughes and R. L. Richards, *J. Organomet. Chem.*, 1989, **371**, C45.

18 W. Sacher, U. Nagel and W. Beck, *Chem. Ber.*, 1987, **120**, 895.

19 M. H. Chisholm, F. A. Cotton, M. W. Extine and L. A. Rankel, *J. Am. Chem. Soc.*, 1978, **100**, 807.

20 W. Beck, H. Bock and R. Schlodder, *Z. Naturforsch. B*, 1974, **29**, 75.

21 R. J. Balahura and R. B. Jordan, *J. Am. Chem. Soc.*, 1971, **93**, 625.

22 J. K. Bera, M. Nethaji and A. G. Samuelson, *Inorg. Chem.*, 1999, **38**, 1725.

23 P. Desjardins, E. P. A. Yap and R. J. Crutchley, *Inorg. Chem.*, 1999, **38**, 5901.

24 M.-N. Ohnet, M. Jouan, G. Ménard, A. Spasojević-de Biré, N. Q. Dao, H. Fischer and D. Reindl, *Spectrochim. Acta, Part A*, 1996, **51**, 505.

25 M.-N. Ohnet, A. Spasojević-de Biré, N. Q. Dao, P. Schweiss, M. Braden, H. Fischer and D. Reindl, *J. Chem. Soc., Dalton Trans.*, 1995, 665.

26 H. Fischer and C. Troll, *J. Organomet. Chem.*, 1992, **427**, 77.

27 M. H. Chisholm, J. C. Huffman and N. S. Marchant, *Polyhedron*, 1988, **7**, 919.

28 M. H. Chisholm, J. C. Huffman and N. S. Marchant, *Organometallics*, 1987, **6**, 1073.

29 M. H. Chisholm, K. Folting, J. C. Huffman and N. S. Marchant, *Organometallics*, 1986, **5**, 602.

30 M. H. Chisholm, K. Folting, J. C. Huffman and N. S. Marchant, *Polyhedron*, 1984, **3**, 1033.

31 E. O. Fischer, W. Kleine, U. Schubert and D. Neugebauer, *J. Organomet. Chem.*, 1978, **149**, C40.

32 C. E. B. Evans, D. Ducharme, M. L. Naklicki and R. J. Crutchley, *Inorg. Chem.*, 1995, **34**, 1350.

33 R. J. Crutchey and M. L. Naklicki, *Inorg. Chem.*, 1989, **28**, 1955.

34 For reviews see: (*a*) A. J. L. Pombeiro, M. F. C. Guedes da Silva and R. A. Michelin, *Coord. Chem. Rev.*, 2001, **218**, 43; (*b*) A. J. L. Pombeiro and M. F. C. Guedes da Silva, *J. Organomet. Chem.*, 2001, **617–618**, 65; (*c*) A. J. L. Pombeiro, M. F. C. Guedes da Silva and M. A. N. D. A. Lemos, *Coord. Chem. Rev.*, 2001, **219–221**, 53; (*d*) A. J. L. Pombeiro, *Inorg. Chem. Commun.*, 2001, **4**, 585; (*e*) A. J. L. Pombeiro, *J. Organomet. Chem.*, 2001, **632**, 215; (*f*) V. Yu. Kukushkin and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 1999, **181**, 147; (*g*) A. J. L. Pombeiro and R. L. Richards, *Coord. Chem. Rev.*, 1990, **104**, 13.

35 For recent papers see: (*a*) M. Kopylovich, V. Yu. Kukushkin, M. F. C. Guedes da Silva, M. Haukka, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 2001, 1569; (*b*) G. Wagner, M. Haukka, J. J. R. Fraústo da Silva, A. J. L. Pombeiro and V. Yu. Kukushkin, *Inorg. Chem.*, 2001, **40**, 264; (*c*) L. Zhang, M. F. C. Guedes da Silva, M. L. Kuznetsov, M. P. Gamasa, J. Gimeno, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *Organometallics*, 2001, **20**, 2782; (*d*) G. Wagner, T. B. Pakhomova, N. A. Bokach, J. J. R. Fraústo da Silva, J. Vicente, A. J. L. Pombeiro and V. Yu. Kukushkin, *Inorg. Chem.*, 2001, **40**, 1683; (*e*) M. L. Kuznetsov, A. J. L. Pombeiro and A. I. Dement'ev, *J. Chem. Soc.,*

Dalton Trans., 2000, 4413; (*f*) M. F. N. N. Carvalho, A. M. Galvão and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 2000, 3393; (*g*) P. M. Reis, J. A. L. Silva, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *Chem. Commun.*, 2000, 1845; (*h*) M. F. C. Guedes da Silva, M. A. N. D. A. Lemos, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, M. A. Pellinghelli and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 2000, 373; (*i*) G. Wagner, A. J. L. Pombeiro and V. Yu. Kukushkin, *J. Am. Chem. Soc.*, 2000, **122**, 3106.

36 M. F. N. N. Carvalho, A. J. L. Pombeiro, A. Hills, D. L. Hughes and R. L. Richards, *J. Organomet. Chem.*, 1993, **469**, 179.

37 C. M. P. Ferreira, M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, V. Yu. Kukushkin and R. A. Michelin, *Inorg. Chem.*, 2001, **40**, 1134.

38 M. F. C. Guedes da Silva, C. M. P. Ferreira, E. M. P. R. P. Branco, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, R. A. Michelin, U. Belluco, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo and V. Yu. Kukushkin, *Inorg. Chim. Acta*, 1997, **265**, 267.

39 J. Chatt, C. T. Kan, G. J. Leigh, C. J. Pickett and D. R. Stanley, *J. Chem. Soc., Dalton Trans.*, 1980, 2032.

40 Chemische Fabrik A.-G. von Heyden, *Br. Pat.,* 5,051, 1913 (*Chem. Abstr.*, 1914, **8**, 407); *Ger. Pat.,* 265,892, 1914 (*Chem. Abstr.*, 1914, **8**, 409).

41 (*a*) N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, London, UK, 1964; (*b*) F. Kurzer and K. Douraghi-Zadeh, *Chem. Rev.*, 1967, **67**, 107.

42 S. T. King and J. H. Strope, *J. Chem. Phys.*, 1971, **54**, 1289.

43 (*a*) W. A. Nugent, *Coord. Chem. Rev.*, 1980, **31**, 123; (*b*) W. A. Nugent., *Inorg. Chem.*, 1983, **22**, 965 and references therein.

44 M. H. Chisholm and I. P. Rothwell, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, UK, 1987, vol. 2, ch. 13.4, pp. 161–188.

45 (*a*) T. Uchida, Y. Uchida, M. Hidai and T. Kodama, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2883; (*b*) T. Uchida, Y. Uchida, M. Hidai and T. Kodama, *Acta Crystallogr., Sect. B*, 1975, **31**, 1197.

46 (*a*) D. L. Hughes, S. K. Ibrahim, C. J. Macdonald, H. Mohd.-Ali and C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 1992, 1762; (*b*) S. A. Fairhurst, D. L. Hughes, S. K. Ibrahim, M.-L. Abasq, J. Talarmin, M. A. Queiros, A. Fonseca and C. J. Pickett, *J. Chem. Soc., Dalton Trans.*, 1995, 1973.

47 H. M. M. Shearer and J. D. Sowerby, *J. Chem. Soc., Dalton Trans.*, 1973, 2629.

48 F. A. L. Anet and I. Yavari, *Org. Magn. Reson.*, 1976, **8**, 327.

49 M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, M. A. Pellinghelli and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1996, 2763.

50 K. Komori, S. Sugiura, Y. Mizobe, M. Yamada and M. Hidai, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2953.

51 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.

52 (*a*) T. A. George and M. E. Noble, *Inorg. Chem.*, 1978, **17**, 1678; (*b*) L. J. Archer, T. A. George and M. E. Noble, *J. Chem. Educ.*, 1981, **58**, 727.

53 http://www.shef.ac.uk/chemistry/chemputer/isotopes.html.

54 V. A. Strel'tsov and V. E. Zavodnick, *Kristallografiya*, 1989, **34**, 1369.

55 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

56 G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.

57 A. L. Spek, PLATON, version 240698, Utrecht University, The Netherlands, 1998.