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Coordination chemistry of nitriles and cyanamide at electron-rich metal centres

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Abstract

The reactions of various nitriles with dinitrogen or isocyanide complexes presenting an electron-rich d^6 transition metal site are described and shown to give the following compounds: the nitrile complexes $[ReCl(NCR)(dppe)_2]$ (R = alkyl or aryl; dppe = $Ph_2PCH_2CH_2PPh_2$), $[Re(NCR)_2(dppe)_2][BF_4]$ or $[Re(N_2)(NCR)(dppe)_2][BF_4]$, derived from the reactions of NCR with *trans*-$[ReCl(N_2)(dppe)_2]$; the cyanamide compounds *trans*-$[Re(CNR)(NCNH_2)(dppe)_2][BF_4]$ (which can undergo deprotonation to the corresponding hydrogen cyanamide, NCNH, complexes), from the reaction of $NCNH_2$ with *trans*-$[ReCl(CNR)(dppe)_2]$; the cyanoimido complexes *trans*-$[M(NCN)_2(dppe)_2]$ (M = Mo or W), from the dehydrogenation reaction of $NCNH_2$ with *trans*-$[M(N_2)_2(dppe)_2]$; and the trimethylsilyl isocyanide species *trans*-$[ReCl(CNSiMe_3)(dppe)_2]$, from the reaction of trimethylsilyl cyanide ($NCSiMe_3$) with *trans*-$[ReCl(N_2)(dppe)_2]$. The neutral organonitrile complexes undergo protonation either at the nitrile ligand or at the metal, to give the methyleneamido or the hydrido complexes $[ReCl(N=CHR)(dppe)_2]^+$ or $[ReHCl(NCR)(dppe)_2]^+$, respectively; further protonation of nitriles to amines and hydrocarbons or coupling with alkynes, although in very low yields, have been detected at some Mo(0) phosphinic centres. Moreover, reaction of the trimethylsilyl isocyanide complex with MeOH or with HBF_4 affords *trans*-$[ReCl(CNH)(dppe)_2]$ or *trans*-$[ReCl(CNH_2)(dppe)_2][BF_4]$, with the simplest isocyanide or aminocarbyne ligands, respectively. The electrochemical behaviour of those complexes is also outlined and shown to involve electroinduced dehydrogenation or deprotonation reactions for the cyanamido methyleneamido or hydrido complexes.

Introduction

Within our interest on the activation of small molecules, particularly C–N and C–C unsaturated substrates of nitrogenase, we have been investigating the coordination chemistry of isocyanides, alkynes and derived species, such as allenes and vinylidenes, at electron-rich N_2-binding metal centres [1].

Methyl isocyanide is reduced by the enzyme until complete cleavage of the unsaturated bond ($6e^-/6H^+$ process) to give mainly methylamine and methane (although reduction to the secondary amine also occurs via a $4e^-/4H^+$ process) whereas 1-alkynes generate alkenes (and, in the case of V-nitrogenase, also alkanes) and allene is reduced to propene [2].

The mechanisms are not known, but we have obtained derived species in our systems which may suggest possible pathways of biological significance for the understanding of the natural process.

Multiple metal–carbon bonded species have been prepared through a β-electrophilic attack at the activated substrate or at a derived ligand, which, in some cases, constituted an unprecedent route for such a type of organic compound.

In particular, aminocarbynes are obtained by β-electrophilic attack (by proton [3], carbocation [4] or a transition metal Lewis acid [5]) at the N atom of the metal ligating isocyanide (eqn. (1) where $\underline{M}$ = $ReCl(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) or a related site with the $\{M(dppe)_2\}$ (M = Mo or W) centre), whereas carbynes and carbenes are formed upon β-protonation + alkyne-derived vinylidene (eqn. (2)) [6] or alkynyl (eqns. (3) and (4)) [7] ligands. An η^2-vinyl (cyclic carbene) has been prepared by an analogous route from an alkyne-derived allene (eqn. (5)) [8].

$$\underline{M}\text{–CNR} \xrightarrow{E} \underline{M} \equiv C - N\begin{matrix}E\\R\end{matrix} \quad (E = H^+, R^+ \text{ or Lewis acid}) \tag{1}$$

$$\underline{M} = C = C\begin{matrix}\diagup\\\diagdown\end{matrix} \xrightarrow{H^+} \underline{M} \equiv C - C\begin{matrix}\diagup\\\diagdown\end{matrix}H \tag{2}$$

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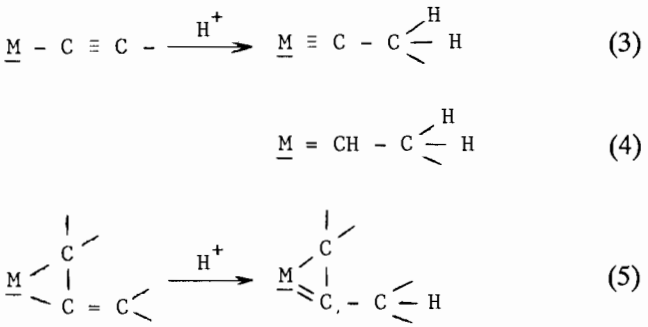


(3)

(4)

(5)

In contrast, the coordination chemistry of nitriles (N≡CR), which are isoelectronic with dinitrogen, isocyanides and alkynes, has not been explored at electron-rich dinitrogen-binding metal sites. This is somewhat surprising since some nitriles have been recognized [2] as substrates of nitrogenase – organic cyanides (which, however, with the exception of acrylonitrile, appear to be reductively cleaved to alkanes only by crude nitrogenase rather than by the purified enzyme [2c]) and aqueous cyanide, apart from cyanamide [9] – and in view of the widespread use of nitrile complexes as starting materials and the known reactivity (e.g. towards nucleophiles) [10] of nitrile ligands at less electron-rich metal sites.

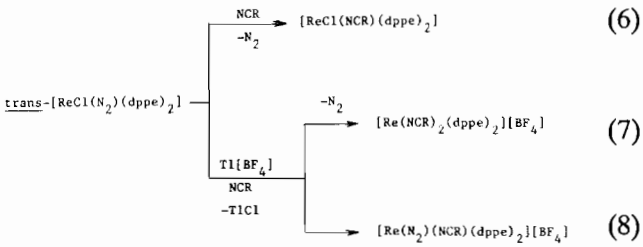
We have been interested in comparing the reactivity of nitriles with those exhibited by the other above-mentioned substrates and, in particular, in finding out if a nitrile, upon coordination, could also be susceptible to activation towards electrophiles and, if so, which would be the favourable site for such an attack, e.g. the unsaturated C or N atom. The effect of the R group of the nitrile should also be investigated and, as shown below, quite different patterns of reactivity are observed when one considers a silyl or an amide group (in $N{\equiv}C{-}SiMe_3$ or $N{\equiv}C{-}NH_2$, respectively) instead of the common alkyl or aryl moieties.

This review contains, to a considerable extent, work which is still unpublished.

Organonitriles

Syntheses of mono- and di-nitrile complexes of rhenium(I)

The main strategies applied for the entries into electron-rich nitrile complexes of rhenium(I) are summarized by eqns. (6)–(8), where the dinitrogen complex *trans*-$[ReCl(N_2)(dppe)_2]$ ($dppe = Ph_2PCH_2CH_2PPh_2$) is the starting material.



(6)

(7)

(8)

Displacement of N_2 or of the chloride ligand by nitrile (in the latter case in the presence of a thallium(I) salt, $Tl[BF_4]$, as a halide abstractor) is commonly a clean route for the neutral chloro–mononitrile $[ReCl(NCR)(dppe)_2]$ [11, 12] or the dinitrile $[Re(NCR)_2(dppe)_2][BF_4]$ [12, 13] complexes, respectively. Series of these compounds have been prepared for a variety of alkyl and aryl-nitrile species (R = Me, Et, Bu^t, Ph, C_6H_4X-4 (X = NEt_2, OMe, Me, F, Cl or NO_2), $CH_2C_6H_4Cl$-4, etc.) and either the *trans* or the *cis* isomer can be obtained, depending on the experimental conditions, e.g. for the dinitrile complexes, the use of refluxing solvent favours the *trans* isomers whereas the *cis* ones are formed in milder conditions; moreover, upon heating, the latter convert into the former [12]. This is consistent with some MO theoretical studies [14] for related carbonyl or dinitrogen 18-electron complexes of a Group VI transition metal (Cr, Mo or W) which indicate that the *cis* isomer should be thermodynamically more stable than the *trans* one. Moreover, the relative redox behaviour [12] of the *trans* and *cis* isomers of the dinitrile complexes also corroborate these considerations (see below).

In addition, the mixed dinitrogen–nitrile complexes $[Re(N_2)(NCR)(dppe)_2][BF_4]$ (R = Bu^t, Ph or C_6H_4X-4 (X = OMe, F, Cl or NO_2) [12]) have also been obtained by simple replacement of the chloride ligand at $[ReCl(N_2)(dppe)_2]$ (eqn. (8)), as quoted by others [15] for the identical dinitrogen–acetonitrile and for the benzonitrile member of the series.

The mononitrile complexes $[ReCl(NCR)(dppe)_2]$ present ν(NC) in their IR spectra at wavenumbers which are considerably below those observed for the free ligands (by *c.* 140–20 cm^{-1}) in agreement with the expected strong π-electron releasing ability of the Re(I) neutral centre to the NC–π^* orbitals of the ligating nitrile. This is also consistent with the X-ray structure analysis of the acetonitrile complex *trans*-$[ReCl(NCMe)(dppe)_2]$ (Fig. 1) [11] which indicates an unusually short Re–N bond, 1.978(5) Å.

For the dinitrile complexes $[Re(NCR)_2(dppe)_2]^+$, ν(NC) occurs at values which, although still somewhat below those for the free nitriles (usually by *c.* 90–20 cm^{-1}), are higher than those observed in the corresponding chloro–mononitrile compounds in view of the less extensive π-electron acceptance of a ligating nitrile

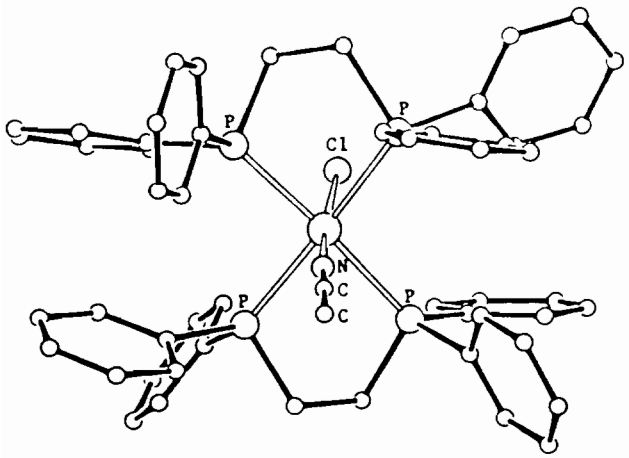


Fig. 1. Molecular structure of *trans*-[ReCl(NCMe)(dppe)$_2$] [11].

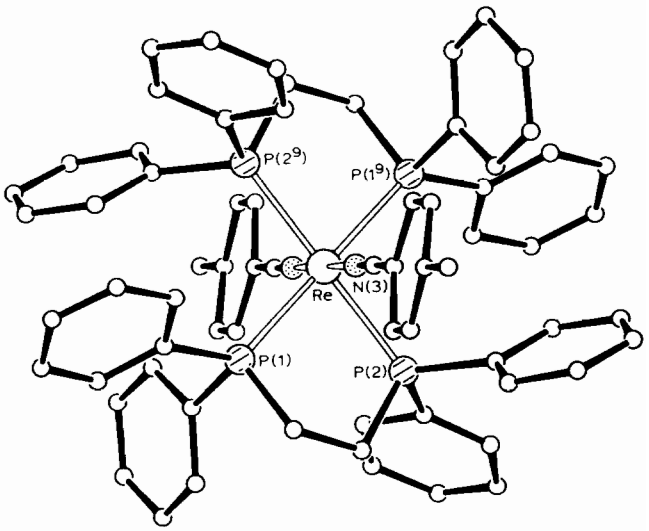


Fig. 2. Molecular structure of the *trans*-[Re(NCC$_6$H$_4$Me-4)$_2$(dppe)$_2$]$^+$ moiety. Selected dimensions (with e.s.d.s in parentheses): Re(1)–N(3) 2.063(7), N(3)–C(30) 1.102(13), C(30)–C(31) 1.417(14), Re(1)–P(1) 2.392(3), Re(1)–P(2) 2.409(2) Å. Re(1)–N(3)–C(30) 178.6(6), N(3)–C(30)–C(31) 177.2(12), P(1)–Re(1)–N(3) 85.8(2), P(2)–Re(1)–N(3) 85.6(2)° [13].

at the former cationic metal centre. This also agrees with some X-ray data (see below) for an orange crystalline dinitrile species derived from the reaction of NCC$_6$H$_4$Me-4 with *trans*-[ReCl(N$_2$)(dppe)$_2$] in refluxing THF and in the presence of Tl[BF$_4$]. Its molecular structure has been determined by single crystal X-ray diffraction analysis [13] which, interestingly, indicates that the crystal is also formed, apart from the expected cation *trans*-[Re(NCC$_6$H$_4$Me-4)$_2$(dppe)$_2$]$^+$ and BF$_4^-$ anions, by discrete moieties of the difluoro complex cation *trans*-[ReF$_2$(dppe)$_2$]$^+$ which constitutes a rare example of a mononuclear rhenium compound with only halide and phosphine ligands. Therefore, the species can be formulated as the complex double salt *trans*-[Re(NCC$_6$H$_4$Me-4)$_2$(dppe)$_2$][BF$_4$]·*trans*-[ReF$_2$-(dppe)$_2$][BF$_4$] [13]. Both complex cations show a distorted octahedral coordination and the Re–N distance for the virtually linear nitrile ligands in the *trans*-dinitrile complex, 2.063(7) Å (Fig. 2), is a little longer than the 1.978(5) Å observed [11] for the above-mentioned compound *trans*-[ReCl(NCMe)(dppe)$_2$] where there is a *trans* influence of the π-donor chloride ligand. The crystal structure of the *cis*-dinitrile isomer, *cis*-[Re(NCC$_6$H$_4$Me-4)$_2$(dppe)$_2$][BF$_4$] has very recently been authenticated by an X-ray study [16].

Although the route for the intriguing formation of the difluoro–Re(III) species has not yet been elucidated, it can formally be derived via a reductive coupling of two ligating nitriles (with metal oxidation) and replacement of the resulting postulated di(methyleneamido)(2−) ligand by two fluorides originated from BF$_4^-$ ions.

The redox properties of the nitrile complexes have been studied by cyclic voltammetry (CV) and controlled potential electrolysis (CPE), at a Pt electrode, in an aprotic solvent [12, 17].

They undergo a first single-electron reversible oxidation at half-wave oxidation potential values ($E_{1/2}^{ox}$ (V) versus SCE) in the following order: [ReCl(NCR)(dppe)$_2$] (*c.* −0.4 to 0 V) < [Re(NCR)$_2$(dppe)$_2$]$^+$ (0.3–0.6 V) < [Re(N$_2$)(NCR)(dppe)$_2$]$^+$ (0.9–1.0 V). For the neutral chloro–nitrile complexes [17], the oxidation occurs at a considerably low oxidation potential in agreement with the high electron-richness of the metal centre, as discussed, and the observed order of $E_{1/2}^{ox}$ values follows the increase of the net electron-acceptor character of the ligand *trans* to the ligating nitrile (chloride < nitrile < dinitrogen), a stronger net electron-acceptance resulting in a decrease of the electron-rich character of the binding metal centre, in a stabilization of the HOMO and therefore in the expected anodic shift of the oxidation potential. Related electronic arguments can also rationalize the observed [12, 17] gross linear correlations between $E_{1/2}^{ox}$ and the IR ν(N≡C) frequency (for each of the series of the nitrile complexes) and between $E_{1/2}^{ox}$ and the Hammett's σ_p substituent constant within a series of substituted benzonitrile complexes.

Interestingly, the *cis*-dinitrile complexes are oxidized at significantly higher oxidation potentials (by *c.* 0.1–0.2 V) than the corresponding *trans* isomers [12] thus indicating that the former present the HOMO with a lower energy in accord with some theoretical calculations [14] and experimental observations (see above) which suggest that the *cis* isomers should be thermodynamically more stable than the *trans* ones.

In addition, by comparing the values of the oxidation potential of the rhenium nitrile complexes with those

presented by the analogous dinitrogen, isocyanide and alkyne-derived complexes with the common {ReCl(dppe)$_2$} metal site, it was possible to order the various substrates according to their net electron donor ability (see 'Conclusions').

Protonation reactions

Formation of methyleneamido and hydrido complexes

As a result of the strong π-electron releasing ability of the {ReCl(dppe)$_2$} site, as discussed above, the nitrile ligands might be expected to undergo electrophilic attack and this was demonstrated for [ReCl(NCR)(dppe)$_2$] (R = Ph or C_6H_4X-4 (X = MeO, Me, F or Cl)) which upon protonation by [Et$_2$OH][BF$_4$], in CH_2Cl_2, give the corresponding monosubstituted methyleneamido complexes [ReCl(N=CHR)(dppe)$_2$][BF$_4$] (eqn. (9)) [12, 18]. In the ^{13}C NMR spectrum (for R = C_6H_4OMe-4), the methyleneamido-C resonates as a singlet at δ = 113.9 ppm which splits into a doublet (J(C–H) = 164 Hz), as expected, in the ^{1}H-coupled spectrum. The C–*H* proton of the methyleneamido ligand has a high field ^{1}H ABCDX-type resonance centred at $\delta = -7$ ppm due to coupling to N and to the four non-equivalent phosphorus nuclei which, in turn, show a complex ABCD-type ^{31}P resonance pattern.

$$[ReCl(NCR)(dppe)_2] + HBF_4 \longrightarrow [ReCl(N{=}CHR)(dppe)_2][BF_4] \quad (9)$$

This protonation reaction is distinct from the previously known coordination chemistry of nitriles and therefore corresponds to a novel type of reactivity of ligating nitriles. It also provides an unprecedented route for methyleneamido ligands and may represent the first step in the enzymatic reductive cleavage of the unsaturated bond of the nitriles which are substrates of nitrogenase.

Moreover, this reaction extends to nitriles the mode of the above-mentioned (eqns. (1)–(5)) ligation-induced reactivity which we have previously observed for isocyanides and alkyne-derived vinylidene and allene species.

However, it is noteworthy to mention that there is another case where such a type of reaction is conceivably involved, although it was not recognized initially. In fact, the imido complexes [Re(NCH$_2$R)X$_3$(dppbe)] (R = alkyl; X = Cl or Br; dppbe = 1,2-bis(diphenylphosphino)benzene) were initially obtained in very low yield by refluxing a solution of [Bu$_4$N]$_2$[Re$_2$X$_8$] in nitrile, in the presence of an excess of the phosphine [19]; however, a substantial increase of the yield was observed upon deliberate addition of acid (HX) which suggests the possible involvement of protonation steps, of the type we have described, at the nitrile ligand. The authors [19] indicate that the reaction occurs via the dirhenium(II) species [Re$_2$X$_4$(dppbe)$_2$] which would undergo a postulated disproportionation to Re(III) and Re(I), the latter providing the nitrile-reducing site.

We have discussed the protonation of nitrile ligands activated by electron-rich Re(I) centres, but it should also be mentioned that the metal site itself is also susceptible to protic attack and the hydride complexes [ReHCl(NCR)(dppe)$_2$][BF$_4$] (R = Ph or C_6H_4X-4 (X = NEt$_2$, MeO, Me, F or Cl)) have been obtained as alternative products of the reactions of [ReCl(NCR)(dppe)$_2$] with [Et$_2$OH][BF$_4$] (eqn. (10)) [12, 20]. However, the factors determining the preference of the protic attack have not yet been clearly established.

$$[ReCl(NCR)(dppe)_2] + HBF_4 \longrightarrow [ReClH(NCR)(dppe)_2][BF_4] \quad (10)$$

Both the methyleneamido [12, 21] and the hydrido [12, 22] complexes undergo anodic processes at much higher oxidation potentials ($E_{1/2}^{ox}$ *c.* 0.7–0.9 V versus SCE, for the first anodic wave, as measured by CV at sufficiently high scan rates to observe reversibility) than those of the parent nitrile complexes (see above). Moreover, by preparative scale electrolysis at this anodic wave, ligand [21] or metal [22] deprotonation occurs, respectively, to give *trans*-[ReCl(NCR)(dppe)$_2$]$^{2+}$ in a two-electron process which obeys the overall eqn. (11) or (12).

$$[ReCl(NCHR)(dppe)_2]^+ \xrightarrow{-2e^-/-H^+} \underline{trans}\text{-}[ReCl(NCR)(dppe)_2]^{2+} \quad (11)$$

$$[ReClH(NCR)(dppe)_2]^+ \xrightarrow{-2e^-/-H^+} \underline{trans}\text{-}[ReCl(NCR)(dppe)_2]^{2+} \quad (12)$$

Therefore, an anodically-induced C–H or metal–H heterolytic bond cleavage is observed, in agreement with the expected increase of the acidity character of such groups as a result of the oxidation of the metal centre. Related anodic deprotonations are known to occur, e.g. at the methylene groups adjacent to amino groups in various diaminocarbene complexes of Pd(II) or Pt(II), such as *cis*-[PtCl$_2${CN(Bu^t)CH$_2$CH$_2$NH}(L)] (L = PPh$_3$ or CNBu^t) [23], or at the hydrido–isocyanide complexes *trans*-[FeH(CNR)(dppe)$_2$][BF$_4$] [24].

Moreover, the hydride–nitrile complexes [ReClH(NCR)(dppe)$_2$]$^+$ also undergo cathodic processes (at *c.* -1.0 to -1.2 V) which involve metal dehydrogenation (homolytic Re–H bond cleavage) to afford the neutral nitrile compounds *trans*-[ReCl(NCR)(dppe)$_2$] [22].

The investigation of the mechanisms of these redox processes is under way by using fast CV with (ultra)microelectrodes and simulation methods [25].

Reduction to amines and hydrocarbons. Coupling with alkynes

We have been discussing the protonation of the neutral $[ReCl(NCR)(dppe)_2]$ complexes with a robust metal centre presenting two chelating phosphines. They can undergo a single protonation and no further protic attack is observed.

However, at an electron-rich metal centre with labile ligands, further reactivity can occur. In fact, treatment of the molybdenum phosphinic complex *cis*-$[Mo(N_2)_2L_4]$ ($L = PMe_2Ph$) with an alkyl or an aromatic nitrile results in replacement of dinitrogen or phosphine by this substrate and the products undergo protonation by $[Et_2OH][BF_4]$ in methanol to afford, although generally in low yields, amines, ammonia and hydrocarbons [26].

For acetonitrile, ethylamine was the main detected product which was found in a considerable yield (*c.* 50% relatively to the metal). However, for the other nitriles, amines and ammonia were only detected in much lower yields. Methane and heavier hydrocarbons were also formed and the results suggest that reductive cleavage of the N≡C unsaturated bond has occurred, as well as, possibly, nitrile coupling processes [26]. The yields are commonly low but, in any case, very high yields would not be expected since the metal itself behaves as the reducing agent, the reaction proceeding without further addition of any other electron source.

These reactions parallel those observed [27, 28] for isocyanides when ligating related electron-rich and labile metal sites, e.g. at $[Mo(CNMe)_2L_4]$ and $[W(CNMe)_3L_3]$ [27], which, by treatment with mineral acid, give methylamine, ammonia and methane, apart from traces of higher hydrocarbons. The latter reactions involve the formation of aminocarbyne intermediates, e.g. $[W_2(CNMe)_4(\mu\text{-}CNHMe)_2L_4]^{2+}$, upon β-protonation at the isocyanide ligand, whereas, in the case of the nitriles, the reactions conceivably proceed via methyleneamido intermediates of the type indicated above, derived from β-protic attack at the metal ligating nitrile (eqn. (13)).

$$M\text{–}N{\equiv}CR \xrightarrow{H^+} M\text{–}N{=}C\begin{matrix}H\\R\end{matrix} \xrightarrow{H^+} M^{ox} + H_2NCH_2R \qquad (13)$$

Apart from the above-mentioned conceivable nitrile coupling reactions, we have also observed [29] coupling between nitriles and alkynes induced by the same molybdenum(0) metal site to give, although in very low yields, 2-substituted pyridines derived from co-cyclization of two molecules of alkyne with one of nitrile. However, the main detected organic products are alkyne cyclic trimers and linear oligomers, i.e. do not appear to involve nitrile activation.

Therefore, these systems cannot compete with those already developed [30] for such co-cyclization reactions.

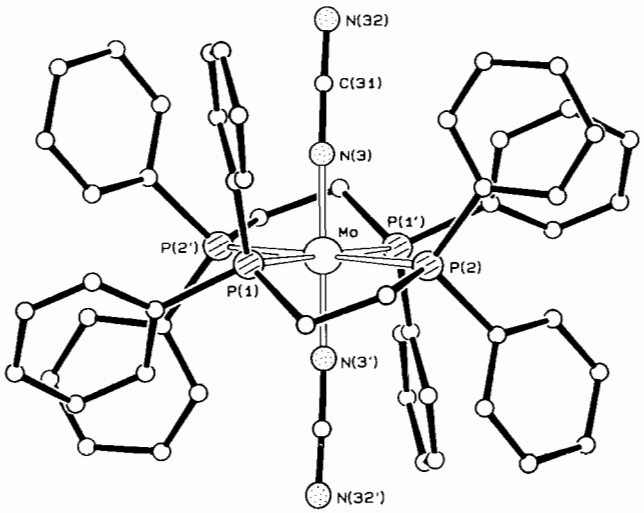


Fig. 3. Molecular structure of *trans*-$[Mo(NCN)_2(dppe)_2]$. Selected dimensions (with e.s.d.s in parentheses): Mo–N(3) 1.860(11), N(3)–C(31) 1.297(20), C(31)–N(32), 1.167(19), Mo–P(1) 2.509(3), Mo–P(2) 2.514(4) Å. Mo–N(3)–C(31) 173.8(10), N(3)–C(31)–N(32) 177.8(16), N(3)–Mo–P(1) 95.9(3), N(3)–Mo–P(2) 95.9(3), P(1)–Mo–P(2) 79.3(1)° [31].

Cyanamide

Cyanamide ($N{\equiv}C\text{–}NH_2$) has recently been recognized [9] as a substrate of nitrogenase, being reduced to methylamine and ammonia (six-electron pathway) or to methane and ammonia (eight-electron pathway), and this has prompted our interest in the investigation of its coordination chemistry which is virtually unexplored, in particular at N_2-binding metal sites.

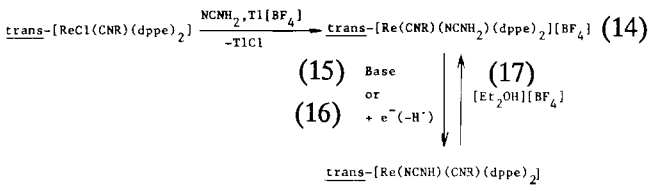
From the reaction of cyanamide with *trans*-$[M(N_2)_2(dppe)_2]$ ($M = Mo$ or W) we have isolated dark red crystalline solids which, by ^1H NMR or IR spectroscopy, do not appear to contain any NH_x group, although a strong band at *c.* 2050 cm^{-1}, assigned to $\nu(N{\equiv}C)$, has been observed in their IR spectra [31]. The spectroscopic and microanalytical data suggested the formulation *trans*-$[M(NCN)_2(dppe)_2]$ which has been unambiguously proved by single crystal X-ray diffraction for the molybdenum complex (Fig. 3), thus confirming the presence of two cyanoimido(2−), NCN^{2-}, ligands in *trans* position in a centrosymmetrical arrangement [31]. To our knowledge, this provided the first example of a cyanoimido transition-metal complex to be structurally characterized by X-rays.

The apical Mo–NCN group is almost linear and presents a Mo–N bond length, 1.860(11) Å, considerably short, whereas the N_α–C bond length, 1.297(20) Å, suggests a bond order greater than one. Therefore, the cyanoimido(2−) ligand is thus best represented by the following linear forms:

$$M \rightleftharpoons N\text{–}C{\equiv}N \longleftrightarrow \overset{+}{M} \rightleftharpoons N{=}C{=}\bar{N}$$

The formation of the cyanoimido(2−) ligand agrees with the known ability [32] of Mo and W to form multiple bonds to N, and involves dehydrogenation of cyanamide, a reaction which can be related with the synthesis of the salts MgNCN or Na_2NCN by reaction of cyanamide with Mg or Na metal. In our system, the electron-rich and readily oxidizable neutral d^6 molybdenum or tungsten centre conceivably plays the role of such reducing metals.

In contrast, cyanamide does not undergo dehydrogenation by the less electron-rich cationic rhenium centre derived from chloride abstraction from the isocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$] (R = Me or Bu^t) which, by reaction with $NCNH_2$ in the presence of Tl[BF_4], form the cyanamide–isocyanide complexes *trans*-[Re(CNR)($NCNH_2$)(dppe)$_2$][BF_4] (eqn. (14)) [32]. These products are yellow and their IR spectra show ν(N≡C) at *c.* 2250 cm^{-1} which are considerably higher (by *c.* 100 cm^{-1}) than those observed for the free



cyanamide, in agreement with the η^1-coordination through the cyano group, behaving mainly as a σ-donor.

Upon treatment with a base, such as Bu^{t}OK or Et_3N, these cyanamide complexes undergo reversible deprotonation to give the corresponding hydrogen cyanamide compounds *trans*-[Re(NCNH)(CNR)(dppe)$_2$] (eqn. (15)) in which, on the basis of IR data (ν(N≡C) of the $NCNH^-$ ligand is observed at *c.* 2150 cm^{-1})), the coordination through the amido nitrogen (**a**) is favoured relatively to that of the cyano group (**b**) [33].

The hydrogen cyanamide complexes are also formed upon cathodically-induced dehydrogenation of the parent cyanamide compounds (eqn. (16)) [33].

Trimethylsilyl cyanide

The chemical behaviour of trimethylsilyl cyanide (N≡C–$SiMe_3$), due to its peculiarities (see below), should be considered separately from the other nitriles. In fact, this cyanosilane is present in equilibrium with a small percentage (*c.* 5%) of the isocyanide isomer (C≡N–$SiMe_3$) and they react with *trans*-[ReCl(N_2)(dppe)$_2$] to afford the isocyanide complex *trans*-[ReCl(CNSiMe_3)(dppe)$_2$] rather than the nitrile

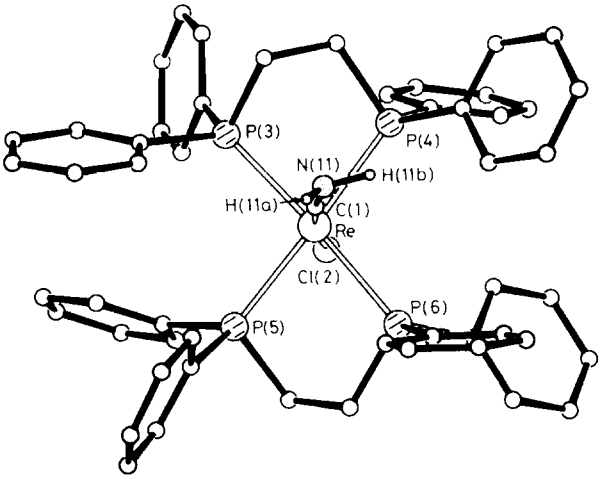
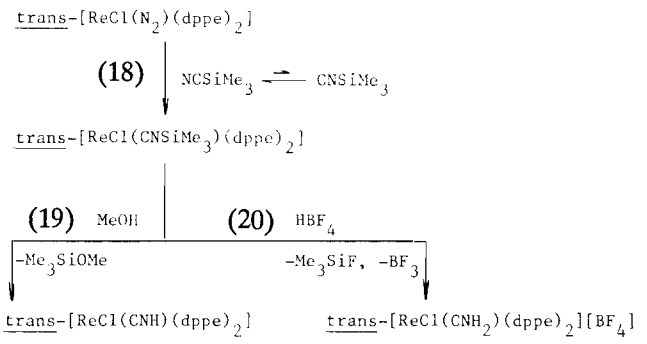


Fig. 4. Molecular structure of *trans*-[ReCl(CNH_2)(dppe)$_2$]$^+$. Selected dimensions (with e.s.d.s in parentheses): Re–C(1) 1.802(4), C(1)–N(11) 1.309(5), N(11)–H(11a) 0.71(6), N(11)–H(11b) 0.92(6), Re–Cl(2) 2.485(1), Re–P range of 2.433(1)–2.478(1) Å; Re–C(1)–N(11) 171.9(3), C(1)–N(11)–H(11a) 129(5), C(1)–N(11)–H(11b) 113(4), H(11a)–N(11)–H(11b) 109(6)° [34].

compound (eqn. (18)) [34], in accord with the expected higher π-acceptance of the coordinated isocyanide relative to the nitrile isomer, with resulting more efficient stabilization of the electron-rich Re(I) centre.

The N–Si bond can be cleaved by an alcohol to give the isocyanide complex *trans*-[ReCl(CNH)(dppe)$_2$] upon single proton attack at the cyanide group (eqn. (19)) [34]. Moreover, by reaction with [Et_2OH][BF_4], double protonation occurs to yield *trans*-[ReCl(CNH_2)(dppe)$_2$][BF_4] (eqn. (20)) the X-ray structure of which has been determined (Fig. 4) [34]. This provided the first example of synthesis of the simplest aminocarbyne CNH_2 at a single metal centre and also a novel route for the preparation of carbyne-type complexes. The CNH_2 group, as well as CHNH and NCH_2, can be viewed as partially reduced cyanide, postulated as intermediates in the reduction of aqueous cyanide (to methylamine, methane and ammonia) by nitrogenase, and the aminocarbyne (CNH_2) has been the first of them to be structurally characterized [34].



We have also attempted the activation of trimethylsilyl cyanide by a dinitrogen-binding Fe(II) centre by investigating its reaction with *trans*-[FeHCl(dppe)$_2$] and Tl[BF_4], which, followed by addition of MeOH or HBF_4, appears to lead to the formation of *trans*-[FeH(NCH)(dppe)$_2$]$^+$ or *trans*-[FeH(CNH)(dppe)$_2$]$^+$ [35].

Interestingly, as a result of a single-electron oxidation of this isocyanide complex, CNH appears to isomerize to NCH, a better net electron donor ligand [35]. The dependence of such isomerization on the redox state of the binding metal may be of some biological significance to the enzymatic reduction of aqueous cyanide.

Conclusions

The versatility of nitriles in coordination chemistry, when activated by electron-rich metal centres, has been illustrated in this work.

A short metal-nitrogen (M–N) bond with a concomitant wakening of the unsaturated N≡C bond is then observed for the organonitrile ligands which undergo β-protonation at the unsaturated carbon to give a methyleneamido species, M–N=C(H)R, a possible intermediate in the reduction to amines, ammonia and hydrocarbons. Such an unprecedent electrophilic addition reaction at an activated nitrile is analogous to that observed at an isocyanide (and other related unsaturated species) when activated by an electron-rich metal centre (see 'Introduction') and occurs in spite of the fact that nitriles are considerably weaker π-acceptors than isocyanides (see below); moreover, it contrasts with the well documented [10] susceptibility of nitriles to nucleophilic addition when binding less electron-rich metal sites.

Different products are obtained from trimethylsilyl cyanide, N≡C–$SiMe_3$, by taking advantage of its isomerization to the isocyanide species and the lability of the $SiMe_3$ group which is susceptible to ready abstraction by an oxygenating or a fluorinating agent (MeOH or BF_4^-, respectively): hydrogen cyanide (NCH) or the isocyanide isomer (CNH) are then formed, as well as, for the first time, the simplest aminocarbyne group, CNH_2^+, upon protonation of the latter species.

Cyanamide (N≡C–NH_2) is also particularly interesting and, apart from simple coordination, it can convert into novel types of ligands upon dehydrogenation (induced by a high electron-rich and readily oxidizable metal centre or by cathodic reduction, to give metal ligating cyanoimido(2−), NCN^{2-}, or hydrogen cyanamide, $NCNH^-$, respectively) or deprotonation by base (to afford $NCNH^-$).

Reduction of nitriles to amines, ammonia and hydrocarbons, as well as coupling reactions of nitriles with alkynes, have also been detected, at metal centres with labile ligands, but they occur only in very low yields.

However, some of the above-mentioned products of activation can be of significance for the understanding of the enzymatic reduction of cyanide, cyanamide and organocyanides (when behaving as nitrogenase substrates), although clear pathways for their conversion into the enzymatic products have still to be established. Moreover, they can be potentially valuable for synthesis of organo- or inorgano-nitrogenated compounds.

Electrochemical methods appear particularly promising for the study of the electronic properties of nitriles and derived ligands, and for their activation towards deprotonation or dehydrogenation with possible interconversion.

In fact, from the knowledge of the first oxidation potential of their complexes with the {ReCl(dppe)$_2$} site, it has been possible to estimate [12, 36, 37], for such ligands, the electrochemical P_L ligand parameter, a proposed [38] measured of the net electron π-acceptor minus σ-donor character of a ligand. Within this approach, those ligands can be ordered as follows in terms of such a net electron-acceptor ability: aminocarbyne CNH_2 [36] ≳ methyleneamido NC(H)R [21] > CO [38] > N_2 [38] > isocyanides [37] > phenylallene [36] > nitriles [12] > vinylidenes C=CHR [36] > cyanamide [33] > alkynyl C≡CR [7] > hydrogen cyanamide NCNH (the strongest net electron donor, within these species, even somewhat more effective than chloride) [33].

Nevertheless, the application of electrochemical techniques for the activation of nitriles towards further reactivity (involving, for example, electrophilic or nucleophilic additions) and for mechanistic studies has not yet been conveniently explored.

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