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REACTIONS OF ALKYNES, ISOCYANIDES AND CYANIDES AT DINITROGEN-BINDING TRANSITION METAL CENTRES

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CONTENTS

A. INTRODUCTION

Since the discovery of the first dinitrogen complex, about 25 years ago [1], several hundred have been characterized and examples are known for most of the transition elements [2–4]. Although the properties of the transition metal centres which can bind and activate dinitrogen vary widely along the periodic table, rationalizations have started to emerge [2–5].

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Hence, for example, the heavier transition metals of the central groups, in low oxidation states, typically d^6 molybdenum(0), tungsten(0) and rhenium(I) [2,5,6], present a high π-electron releasing ability to N_2, resulting in the maximum known reactivity of the latter towards electrophilic attack in well-defined mononuclear complexes.

These dinitrogen-binding metal centres also provide an opportunity to explore the activation of small molecules related to N_2. Isocyanides, cyanides and alkynes have been selected because they are unsaturated species, isoelectronic with dinitrogen, and also are substrates of nitrogenase, which has molybdenum [7] or vanadium [8] at its active centre; most studies relate to molybdenum nitrogenase since vanadium nitrogenase has only recently been discovered.

Isocyanides are reduced by the enzyme mainly to methane and primary amines with complete cleavage of the unsaturated bond; reductive cleavage of organonitriles may occur to give hydrocarbons and ammonia; dinitrogen is reductively cleaved to ammonia; $6e^-/6H^+$ processes are involved in these reactions. Terminal alkynes are reduced to alkenes through a $2e^-/2H^+$ process and the reduction of C_2H_2 to C_2H_4 has been applied [7–9] as a test of the nitrogen-fixing ability of a biological system (C_2H_6 is also obtained for vanadium nitrogenase).

Isocyanides [10] and alkynes [11–13] present much easier coordination and higher reactivity than dinitrogen, and it is therefore interesting to compare the electronic and chemical properties of these substrates in order to recognize analogies and to propose coordination and reactivity criteria for N_2 itself.

As is well known [14] for carbonyl complexes, both alkyne [15,16] and isocyanide [10,17] compounds may follow nucleophilic pathways to species with metal–carbon multiple bonds. In contrast, in this account we describe the activation of isocyanides and alkynes by N_2-binding electron-rich metal centres, which provides an alternative electrophilic route to metal–carbon multiple-bonded compounds.

B. ACTIVATION OF ISOCYANIDES

(i) Preparation, structure and bonding of isocyanide and mixed dinitrogen–isocyanide complexes

The first step in these studies is to bind the isocyanide (or other substrate, see below) to the metal centre of choice in place of N_2. Typically octahedral binding centres of group VI and VII metals are used, e.g. $[M(N_2)_2L_4]$ (M=Mo or W; L=1/2dppe [18], PMe_2Ph or $PMePh_2$ [19]), *trans*-$[ReCl(N_2)(dppe)_2]$ (dppe=$Ph_2PCH_2CH_2PPh_2$) [20] and *mer*-[Re(η^2-S$\widehat{\text{S}}$)-

$(N_2)L_3]$ ($\widehat{S\,S} = S_2PPh_2$ or S_2CNEt_2; $L = PMe_2Ph$) [21–23]. Displacement reactions give the products shown in reactions (1)–(7) in Scheme 1.

$$[M(N_2)_2L_4] + 2CNR \longrightarrow [M(CNR)_2L_4] + 2N_2 \quad (1)$$

$$trans\text{-}[ReCl(N_2)L_4] \xrightarrow[-N_2]{CNR} trans\text{-}[ReCl(CNR)L_4] \quad (2)$$

$$\widehat{S\,S}^- \;\; -Cl^- \;\; \xrightarrow[-L]{CNMe} mer\text{-}[ReCl(N_2)(CNMe)L_3] \quad (3)$$

$$-L\,(PMe_2Ph) \qquad (L = PMe_2Ph) \quad (4)$$

$$mer\text{-}[Re(\eta^2\text{-}\widehat{S\,S})(N_2)L_3] \xrightarrow[-N_2]{CNMe} [Re(\eta^2\text{-}\widehat{S\,S})(CNMe)L_3] \quad (5)$$

$$CNR \quad (6)$$

$$[Re(\eta^1\text{-}\widehat{S\,S})(N_2)(CNMe)L_3] \xrightarrow[-L]{CNMe} [Re(\eta^1\text{-}\widehat{S\,S})(N_2)(CNMe)_2L_2] \quad (7)$$

Scheme 1. Displacement reactions of dinitrogen complexes with isocyanides.

The displacement of N_2 from $[Mo(N_2)_2L_4]$ with CNR (eqn. (1)) has been monitored by cyclic voltammetry and a dissociative mechanism has been established [19] where dinitrogen loss is rate limiting. The N_2-labilizing order follows the π-acceptor character of the coligands, which suggests that it is the π interaction which determines labilization of N_2, emphasizing the importance of the π component to metal–dinitrogen binding.

However, a labile coligand may be replaced instead of N_2 and, in some cases, mixed dinitrogen–isocyanide complexes have been isolated, e.g. *mer*-$[ReCl(N_2)(CNMe)L_3]$ and $[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNMe)L_3]$ ($L = PMe_2Ph$) (Scheme 1, eqn. (3) and eqn. (6) respectively). The formation of the latter complex involves a dihapto-to-monohapto rearrangement of the dithiophosphinato ligand and further reaction with CNMe affords the dinitrogen–bis(isocyanide) complex $[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNMe)_2L_2]$ (eqn. (7)) [21].

The displacement routes to isocyanide complexes described above require the prior synthesis of the parent N_2 compounds. However, a more direct pathway has also been developed, involving the reaction of isocyanide with a dinitrogen complex precursor, the chelating benzoyl-diazenido species $[ReCl_2(NNCOPh)(PPh_3)_2]$. The N_2 ligand is generated in situ by thermal or nucleophilic (attack by methanol) cleavage of the N–C bond in a monodentate diazenido intermediate, and mixed dinitrogen–isocyanide complexes, $[ReCl(N_2)(CNR)(PPh_3)_xL_{3-x}]$ ($x = 0$; $L = P(OMe)_3$; R = alkyl or aryl. $x = 1$; $L = P(OEt)_3$; R = Me) [24,25], are obtained (eqns. (8) and (9)):

$$[ReCl_2(NNCOPh)(PPh_3)_2] \xrightarrow[C_6H_6,\Delta]{L} [ReCl_2(NNCOPh)(PPh_3)_xL_{3-x}] \quad (8)$$

$$\downarrow \begin{matrix} CNR \\ (MeOH) \end{matrix} \quad (9)$$

$$[ReCl(N_2)(CNR)(PPh_3)_xL_{3-x}] + PhCOCl \text{ (or } PhCOOMe + HCl)$$

This route is similar to that followed [26(a)] in the preparation of mixed carbonyl–dinitrogen compounds, e.g. $[ReCl(N_2)(CO)\{P(OMe)_3\}_3]$. However, such a pathway cannot be applied to the synthesis of mixed alkyne–dinitrogen complexes possibly due, at least in part (see below), to the reaction of the alkyne with the liberated acid.

Isocyanide and analogous dinitrogen complexes can also be prepared by identical routes, carried out in the presence of CNR or N_2 respectively; therefore complexes $[Mo(\eta^6\text{-PhPMePh})L(PMePh_2)_2]$ ($L = CNBu^t$ or N_2), with an η^6-arylphosphine ligand [26(b)], or *trans*-$[FeHL(dppe)_2]^+$ ($L = CNR$ or N_2) [26(c)], have been obtained by replacement of a phosphine or a chloride ligand respectively with the appropriate substrate (L).

The molecular structures of the isocyanide complexes *trans*-$[Mo(CNMe)_2(dppe)_2]$ [27] (Fig. 1), *mer*-$[ReCl(N_2)(CNMe)\{P(OMe)_3\}_3]$ [24,28] (Fig. 2), *mer*-$[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNMe)(PMe_2Ph)_3]$ [21,22] (Fig. 3), *trans*-$[ReCl(CNBu^t)(dppe)_2]$ [29] and $[Mo(\eta^6\text{-PhPMePh})(CNBu^t)(PMePh_2)_2]$ [26(b)] have been determined by X-ray crystallography. They exhibit short metal–carbon bond lengths, e.g. 1.93(1) Å for the diphenyldithiophosphinato complex (Fig. 3), which are well below the value for a single metal–carbon

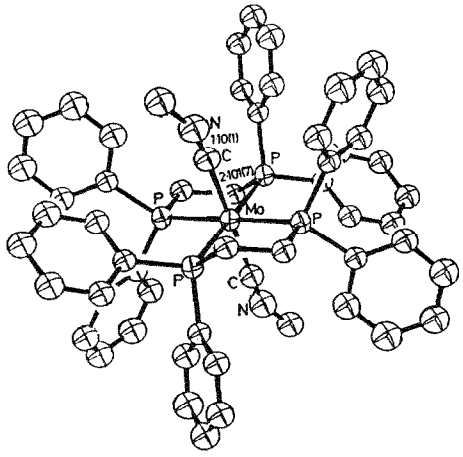


Fig. 1. Molecular structure of *trans*-$[Mo(CNMe)_2(dppe)_2]$ [27]. Selected bond lengths and angles: Mo–C 2.101(7) Å; C–N 1.10(1) Å; Mo–P 2.441(2) or 2.457(3) Å; Mo–C–N 176(1)°; C–N–C 156(1)°.

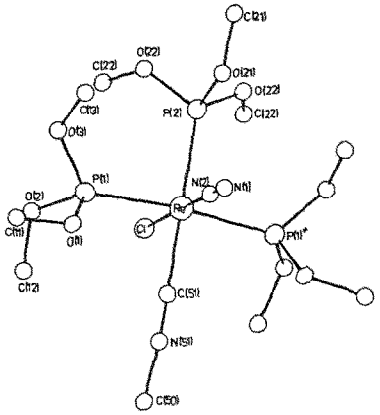


Fig. 2. Molecular structure of *mer*-[ReCl(N_2)(CNMe){$P(OMe)_3$}$_3$] [24,28]. Selected bond lengths and angles: Re–N(2) 1.980(14) Å; Re–C(51) 2.060(16) Å; Re–Cl 2.530(4) Å; N(1)–N(2) 1.038(21) Å; C(51)–N(51) 1.113(21) Å; Re–N(2)–N(1) 179.3(12)°; Re–C(51)–N(51) 179.2(12)°; C(51)–N(51)–C(50) 168.9(14)°; Cl–Re–N(2) 178.4(4)°.

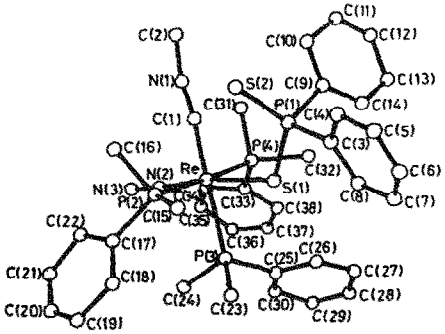


Fig. 3. Molecular structure of *mer*-[Re(η^1-S_2PPh_2)(N_2)(CNMe)(PMe_2Ph)$_3$] [21,22]. Selected bond lengths and angles: Re–S(1) 2.548(2) Å; Re–N(2) 1.829(9) Å; Re–C(1) 1.926(13) Å; N(2)–N(3) 1.126(13) Å; C(1)–N(1) 1.20(2) Å; Re–N(2)–N(3) 174(1)°; Re–C(1)–N(1) 169(1)°; C(1)–N(1)–C(2) 168(1)°; S(1)–Re–N(2) 170.2(3)°.

bond [30,31] and lie towards that expected [32] for a double bond. Therefore the isocyanides behave as strong π-electron acceptors, on account of the extensive π-electron releasing character of the metal centres, and they present relatively low IR ν(CN) values, for example, those observed at 1862 cm^{-1} and 1920 cm^{-1} for *trans*-[Mo(CNMe)$_2$(dppe)$_2$] [18] and *trans*-[ReCl(CNBu^t)(dppe)$_2$] [20] respectively.

A bent geometry at the nitrogen atom (**a**) may be displayed by the isocyanide ligand, as reported [18,27] for *trans*-[Mo(CNMe)$_2$(dppe)$_2$] (Fig. 1) with a C–N–Me angle of 156(1)°; this is much smaller than those quoted for terminal isocyanides with a common linear geometry (**b**):

(a) (b)

These observations are in agreement with simplified π-MO schemes [33–35] which indicate, for example, that the bending could be electronic in origin, thus with a promoting effect on a plausible electrophilic attack at the nitrogen atom (see below). However, the {ReCNR} group is essentially linear in *trans*-[ReCl(CNBu^t)(dppe)$_2$] [29] and bending may not necessarily accompany low ν(CN) values and the reactivity described below.

In the mixed dinitrogen–isocyanide complexes of rhenium (see Figs. 2 and 3), the Re–N_2 bond is stabilized by a strong electron-donor anionic ligand (Cl or S_2PPh_2) in the *trans* position. The dinitrogen ligand is thus retained in spite of the competition of the isocyanide coligand for the available metal *d*-electrons.

Most of the isocyanide complexes which have been cited above, and their dinitrogen parent compounds, show two successive one-electron oxidations at a platinum electrode, in thf–[Bu_4N][BF_4], by cyclic voltammetry. The first is reversible with a relatively low half-wave oxidation potential, e.g. $E^{ox}_{1/2} \approx -0.6$ to -0.4 V for *trans*-[M(CNR)$_2$(dppe)$_2$] (M = Mo or W) [18], and $E^{ox}_{1/2} \approx 0$ to $+0.3$ V vs. the standard calomel electrode (SCE) for *trans*-[ReCl(CNR)(dppe)$_2$] [20]. This is in agreement with the high electron richness of the metal centres. Accordingly, at these sites, the isocyanides present high values of the electrochemical P_L ligand parameter, a proposed [36] measure of the net electron π-acceptor/σ-donor character of the ligand (the stronger this character, the higher is P_L); for example, $P_L \approx -0.17$ V [20,37] for CNMe at the {ReCl(dppe)$_2$} centre, which approaches the values for N_2 and CO ($P_L \approx -0.07$ V and $P_L \approx 0$ V respectively [36]).

(ii) Reactions with electrophiles

(a) Formation of aminocarbyne complexes

In the above-mentioned electron-rich complexes, the isocyanide ligand may present an electronic charge localized at the nitrogen atom (see Section B(i)) which therefore undergoes electrophilic attack (by proton, carbon cation or Lewis acid) to give aminocarbyne species.

The aminocarbyne–isocyanide complexes of molybdenum or tungsten, *trans*-[M(CNR'R)(CNR)(dppe)$_2$]A (R = alkyl; R' = H or alkyl; A = BF_4, FSO_3, HSO_4 etc.) [27,38–43], have been prepared by treatment of a solution of the parent diisocyanide compounds with acid (HA) or an alkylating agent ($MeFSO_3$, Me_2SO_4 or [Et_3O][BF_4]) (eqn. (10)):

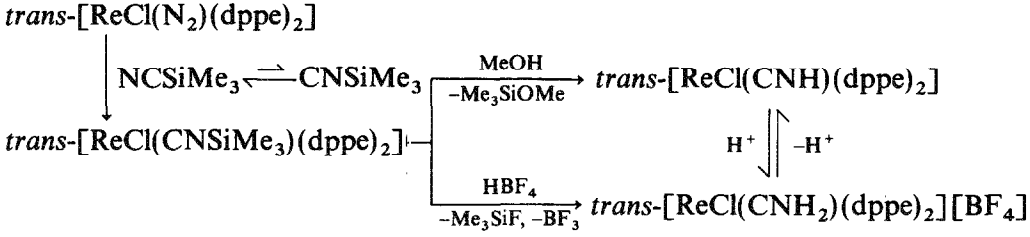
trans-[M(CNR)$_2$(dppe)$_2$] + R'A $\longrightarrow$ *trans*-[M(CNR'R)(CNR)(dppe)$_2$]A (10)

A variety of the aminocarbyne complexes of rhenium, *trans*-[ReCl(CNHR)(dppe)$_2$]A (R = alkyl or aryl; A = BF_4, FSO_3 or HSO_4) [44–46], have been obtained similarly from *trans*-[ReCl(CNR)(dppe)$_2$] (eqn. (11)):

$$\textit{trans}\text{-}[ReCl(CNR)(dppe)_2] + HA \longrightarrow \textit{trans}\text{-}[ReCl(CNHR)(dppe)_2]A \quad (11)$$

The simplest aminocarbyne group, CNH_2, has also been prepared at a rhenium centre by the related pathway shown in Scheme 2, which provides a novel route for carbyne complexes [47]. The starting material, trimethylsilyl cyanide ($NCSiMe_3$), is present in equilibrium with a small percentage (ca. 5%) of the isocyanide isomer; reaction with *trans*-[ReCl(N_2)(dppe)$_2$] affords the isocyanide complex *trans*-[ReCl($CNSiMe_3$)(dppe)$_2$]. The N–Si bond in this compound can be cleaved with an alcohol to give *trans*-[ReCl(CNH)(dppe)$_2$], or with [Et_2OH][BF_4] to form the first example of a ligating primary aminocarbyne group CNH_2, in *trans*-[ReCl(CNH_2)(dppe)$_2$][BF_4]. The CNH and CNH_2 complexes (as well as the CNR and CNHR complexes) are interconverted by addition or removal of a proton.

A single protonation at cyanide occurs on reaction with MeOH, but the stronger acid HBF_4 leads to a double protic attack to generate the carbyne species. In these reactions, the protonation of the isocyanides is conceivably promoted by the formation of an Si–O or an Si–F bond [48].



Scheme 2. Metal-centred synthesis of the aminocarbyne CNH_2 group.

The same route has also been applied to generate CNH_2 at a molybdenum or tungsten centre by methanolysis of *trans*-[M($CNSiMe_3$)$_2$(dppe)$_2$] (M = Mo or W) [47].

In contrast with the mixed aminocarbyne–isocyanide complexes *trans*-[M(CNR'R)(CNR)(dppe)$_2$]$^+$ (M = Mo or W; R' = H or alkyl) (which, in solution, undergo proton migration to the metal (R' = H) [38] or *trans* to *cis* isomerization [43] (eqn. (12) and eqn. (13) respectively))

$$\textit{trans}\text{-}[M(CNHMe)(CNMe)(dppe)_2]^+ \longrightarrow [MH(CNMe)_2(dppe)_2]^+ \quad (12)$$

$$\textit{trans}\text{-}[M(CNR'Me)(CNMe)(dppe)_2]^+ \rightleftharpoons \textit{cis}\text{-}[M(CNR'Me)(CNMe)(dppe)_2]^+ \quad (13)$$

the aminocarbyne complexes of rhenium are fairly stable. They contain a π-electron donor chloride ligand *trans* to the carbyne group, with a resulting stabilizing effect on the multiple metal–carbon bond.

The molecular structures of the CNH_2 [47] and CNHMe [45] complexes of rhenium have been confirmed by X-ray crystallography (Fig. 4) and the data indicate that these aminocarbyne ligands may be represented, in a valence bond formulation, as hybrids of the forms (**c**) and (**d**):

$$\overset{+}{M} \equiv C\text{–}\ddot{N}HR \longleftrightarrow M=C=\overset{+}{N}\begin{matrix} H \\ \diagdown \\ \diagup \\ R \end{matrix}$$

(c) **(d)**

Related compounds, e.g. *trans*-$[CrBr(CO)_4(CNEt_2)]$, are similarly regarded [49,50].

Thus the Re–C bond length (1.802(4) Å or 1.80(3) Å for the CNH_2 or the CNHMe complex respectively) approaches the expected range for an Re≡C bond (1.72–1.75 Å) [45,51–53], whereas the CN distance (1.309(5) Å or 1.35(3) Å respectively) indicates a double-bond character, in accord with the ν(CN) data (1595 cm^{-1} and 1575 cm^{-1} respectively). A roughly planar structure is observed for the CNH_2 ligand, as has been reported [54] for the related $=NNH_2$ group (see below), as a result of the delocalization of the nitrogen lone pair electrons. Moreover, the aminocarbyne bonding may also be interpreted [34] by simplified π-MO schemes.

In the above-mentioned isocyanide complexes, the CNR ligands are also

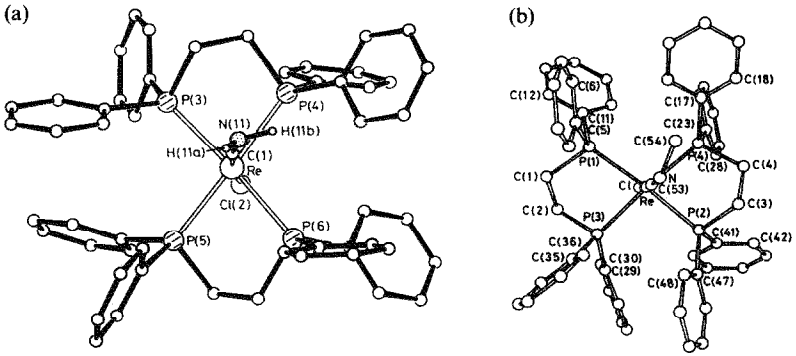


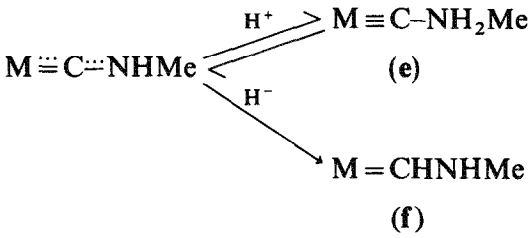
Fig. 4. Molecular structures of (a) *trans*-$[ReCl(CNH_2)(dppe)_2]^+$ [47] and (b) *trans*-$[ReCl(CNHMe)(dppe)_2]^+$ [45]. Selected bond lengths and angles for (a): Re–C(1) 1.802(4) Å; C(1)–N(11) 1.309(5) Å; N(11)–H(11a) 0.71(6) Å; N(11)–H(11b) 0.92(6) Å; Re–Cl(2) 2.485(1) Å; Re–C(1)–N(11) 171.9(3)°; C(1)–N(11)–H(11a) 129(5)°; C(1)–N(11)–H(11b) 113(4)°; H(11a)–N(11)–H(11b) 109(6) Å. Selected bond lengths and angles for (b): Re–C(53) 1.798(30) Å; C(53)–N 1.347(32) Å; N–C(54) 1.422(36) Å; Re–Cl 2.484(6) Å; Re–C(53)–N 175.2(18)°; C(53)–N–C(54) 123.3(22)°; Cl–Re–C(53) 176.3(7)°.

susceptible to electrophilic attack by a Lewis acid such as an organoaluminium compound or an unsaturated transition metal centre, and adducts of the following types have been obtained: $[W\{CN(AlEt_3)Me\}_2(dppe)_2]$ [39] and $[ReCl\{CN(MCl_x)Me\}(dppe)_2]$ ($MCl_x = CoCl_2(thf)$ or $ReOCl_3(PPh_3)$) [55].

The hydrido complexes $[MH(CNMe)_2(dppe)_2]^+$ (M=Mo or W) may undergo further protonation at an isocyanide ligand to give the hydrido–carbyne $[MH(CNHMe)(CNMe)(dppe)_2]^{2+}$ complexes (eqn. (14)):

$$[MH(CNMe)_2(dppe)_2]^+ + H^+ \longrightarrow [MH(CNHMe)(CNMe)(dppe)_2]^{2+} \quad (14)$$

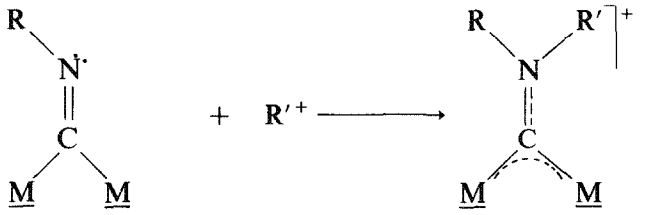
Moreover, the aminocarbyne complexes *trans*-$[M(CNHMe)(CNMe)(dppe)_2]^+$ also react with HBF_4 to give the proposed dicarbene *trans*-$[M(CNHMe)_2(dppe)_2]^{2+}$; in the latter, a CNHMe group appears to be susceptible to protonation at the nitrogen to give CNH_2Me, whereas the α-carbon reacts with a nucleophile ($LiAlH_4$) (as in Fischer's type carbyne species) to afford the ligating carbene CHNHMe [38], as represented by forms (**e**) and (**f**) respectively:



As expected, in the ^{13}C NMR spectra of the aminocarbyne complexes, the resonance of the carbyne carbon, CNHR, is observed at a very low field (δ 195–248 ppm relative to $SiMe_4$, in CD_2Cl_2) [39,42,45,47].

The aminocarbyne ligands and their formation by proton attack at a ligating isocyanide may have some biological relevance in that they may be postulated as intermediates in the reduction of isocyanide or aqueous cyanide at the metallic centre of nitrogenase [7,56].

The above electrophilic attack at isocyanides ligating a single metal site only occurs when the latter presents a high π-electron release ability, and therefore it was not observed at $[Mo(\eta^6\text{-}PhPMePh)(CNBu^t)(PMePh_2)_2]$ [26(b)] or at *trans*-$[FeH(CNR)(dppe)_2]^+$ [26(a)]. Nevertheless, two metal sites without such an electron-rich character may also activate an isocyanide towards electrophilic attack, provided it bridges both centres in a mono-hapto fashion, thus exhibiting a bent geometry at the nitrogen atom (eqn. (15)):



(15)

A bridging aminocarbyne can then be formed, for example, in the protonation or alkylation of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(CNMe)]$ to give $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNR'Me)]^+$ (R' = H or alkyl) [57].

(b) Reductive cleavage of isocyanide ligand to amine and hydrocarbons

The above reactions of isocyanides with electrophiles lead to the formation of aminocarbyne species where the unsaturated NC bond has been considerably weakened, although still without being cleaved.

However, if the binding metal centre carries labile coligands (e.g. monodentate phosphines or phosphites), further protonation may take place until complete cleavage of that bond occurs, to give amine, ammonia and hydrocarbons [28,58]. For example, protonation (by methanol or mineral acid, e.g. HX=HCl, HBF_4 or H_2SO_4) of *trans*-$[MoCNMe)_2L_4]$ (L= PMe_2Ph), *mer*-$[W(CNMe)_3L_3]$ [58] or *mer*-$[ReCl(N_2)(CNR)\{P(OMe)_3\}_3]$ (R = alkyl or aryl) [28] gives RNH_3X, NH_3 and hydrocarbons (although in low yields). Methane is the main hydrocarbon formed, but products (ethylene and ethane in the reduction of CNMe) from C–C bond formation are also observed, as is known [7] to occur in the enzymatic system. Nitrogenase also produces methylamine and traces of ethylene and ethane from CNMe but methane is a major rather than a minor product (eqn. (16)):

$$CNMe + 6e^- + 6H^+ \longrightarrow MeNH_2 + CH_4 \qquad (16)$$

The role of the labile ligand in our systems appears to involve its ready replacement, during the reaction, by a stronger electron donor (X^- or MeO^- from the acid or MeOH respectively) with the expected enhancement of the nucleophilicity of the intermediate carbyne species which then can undergo further protonation.

Reduction of ligating isocyanides to amines and hydrocarbons has previously been reported [17,59] to result from hydridic attack; the isocyanide was then bound to a relatively electron-poor metal centre. However, our results show that the isocyanide reduction can also occur in a protic medium provided the metal is able to supply electrons; the isocyanides then ligate an electron-rich, low valent metal centre, such as can bind dinitrogen. The maximum overall yield of products corresponds to the consumption of the six valence *d* electrons.

C. ACTIVATION OF CYANIDES

The reduction of $NCCH_3$ with crude mutants of nitrogenase to C_2H_6 and NH_3 has been reported [7,60].

Although little is known of the mechanistic details of this reduction, $NCCH_3$ is a relatively poor substrate. By comparison with the foregoing section on reduction of $CNCH_3$, one might expect that $NCCH_3$ would bind to an N_2-binding centre of the type used above and subsequently be attacked by protons.

This appears to be the case for the centre $\{ReCl(dppe)_2\}$. NCR can displace N_2, but the binding of the former is relatively weak, e.g. $NCCH_3$ dissociates from the metal in solution [25]. Nevertheless, in the presence of protons, NCR at this centre is attacked at the β-carbon to give the methylene-imido ligand (N=CHR), e.g. in *trans*-$[ReCl\{NCH(C_6H_4OMe)\}(dppe)_2][BF_4]$ [25] which could represent the first step in a reductive cleavage to give NH_3 and CH_3R. The further steps, which would follow the same pattern as observed for $CNCH_3$ and N_2, will require a more labile metal centre.

In agreement with these expectations, cyanides undergo protonation, e.g. at *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ derived centres, to give (although in low yields) amines and traces of hydrocarbons [61].

Cyanamide ($NCNH_2$) has recently been shown [62] to be a substrate of nitrogenase, being reduced to methane, methylamine and ammonia. Upon reaction with *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W), it undergoes dehydrogenation to give the dicyanoimido(2−) complexes of M(IV), *trans*-$[M(NCN)_2(dppe)_2]$ [63], whose molecular structure (M = Mo) has been established by an X-ray analysis.

The cyanoimido(2−) ligand may well represent an intermediate stage in the reduction of cyanamide to methylamine and ammonia, and its formation provides an example of the tendency of molybdenum or tungsten to form multiple bonds to nitrogen (see below).

D. COMPARISON WITH THE ACTIVATION OF DINITROGEN

(i) Dinitrogen reduction

Dinitrogen, when bound to molybdenum(0) or tungsten(0) centres with labile phosphines, as in *trans*-$[W(N_2)_2(PMePh_2)_4]$ ($\nu(N_2)$=1910 cm^{-1}), is reduced to ammonia on treatment with acid [2,6,64,65]. The metal is again the reducing agent and the mechanism of the reaction has been studied by kinetic methods [66] and by isolation of intermediates as detailed below.

If the metal carries chelating dppe or monodentate ligands which are

relatively basic and strongly held in the higher oxidation states, the intermediate states in the reduction of N_2 can be isolated.

Thus in *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W), protonation of N_2 proceeds under mild conditions through a diazenido ($-N_2H$) step and stops at the hydrazido(2−) (=N−NH_2) stage [2,6], e.g. at $[MX(NNH_2)(dppe)_2]X$ (X = Cl, Br or I). X-ray diffraction analyses have been reported for some of these complexes, such as $[WCl(NNH_2)(dppe)_2][BPh_4]$ (Fig. 5) [67], in which the metal–nitrogen bond length (1.73(1) Å) corresponds to a considerable multiple bond character. That these species are intermediates in reactions of $[W(N_2)_2(PMePh_2)_4]$ and related complexes which give ammonia has been clearly demonstrated in solution by ^{15}N NMR spectroscopy and isolation of hydrazido(2−) complexes from reaction solutions [68].

Protonation beyond the hydrazido(2−) stage to give the hydrazidium ligand has been demonstrated by use of the more basic phosphine PMe_3, the complex $[WCl(=N-NH_3)(PMe_3)_4]Cl_2$ having been isolated and structurally characterized as a hydrogen-bonded dimer (Fig. 6) [69].

Moreover, metallo-imide species, M=NH, as in *trans*-$[M(NH)X(dppe)_2]^+$ (M = Mo, X = Cl [70]; M = W, X = OMe [71]), are known to undergo electrochemical reduction or hydrolysis to give ammonia.

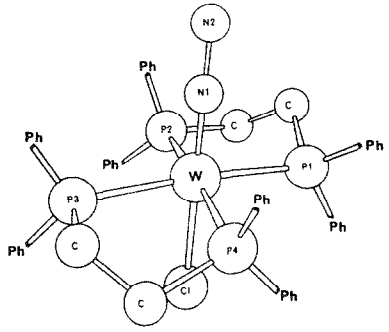


Fig. 5. Molecular structure of *trans*-$[WCl(NNH_2)(dppe)_2]^+$ [67]. Selected bond lengths and angles: W–N(1) 1.73(1) Å; N(1)–N(2) 1.37(2) Å; W–Cl 2.421(4) Å; W–N(1)–N(2) 171(1)°.

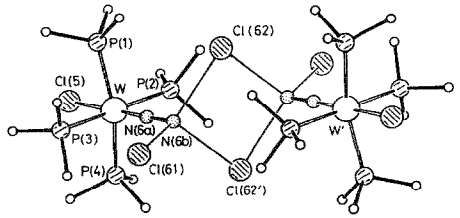
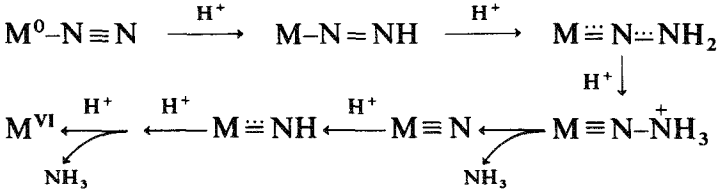


Fig. 6. Molecular structure of $[WCl(NNH_3)(PMe_3)_4]Cl_2$ [69]. Selected bond lengths and angles: W–N(6a) 1.785(15) Å; N(6a)–N(6b) 1.40(2) Å; W–Cl(5) 2.463(4) Å; W–N(6a)–N(6b) 179.2(10)°; N(6a)–N(6b)...Cl 108.9(8)–114.9(8)°; Cl(5)–W–N(6a) 179.5(3)°.

Thus the reductive cleavage of dinitrogen at these centres involves successive β-electrophilic attacks and a combination of the above observations and isolation of species from other systems has led to the proposal of the cycle shown below (Scheme 3) for the formation of ammonia from dinitrogen in these systems [69].



Scheme 3. Dinitrogen reduction to ammonia at an electron-rich group VI d^6 metal centre.

Two essential features of the chemistry of these metal complexes determine the route taken in Scheme 3. The first is the ability of the electron-rich metals to release electron density to the dinitrogen ligand and thus promote the β-electrophilic attack. The second feature is the ability of the metals to form multiple bonds to the ligating atom. Thus at the hydrazide stages of reduction, the metal–nitrogen bond order increases as the N–N bond order decreases, leading inevitably to N–N bond rupture.

This tendency of early transition metals to form multiple bonds to such atoms as nitrogen, carbon and oxygen is a dominant feature of their chemistry and therefore analogies in the behaviour of carbon- or nitrogen-donor ligands at these centres are to be expected as discussed below.

In Scheme 3, the reduction stops after one cycle because the metal is fully oxidized, but an electrochemical method has been discovered [72] which allows the metal to be reduced back to the dinitrogen pick-up stage and thus allows the cycle to continue.

(ii) Analogies in the metal-promoted reactions of isocyanides, cyanides and dinitrogen

As can be seen from the preceding sections, a close analogy exists between the behaviour of isocyanides, cyanides and dinitrogen when they are bound at electron-rich d^6 metal centres.

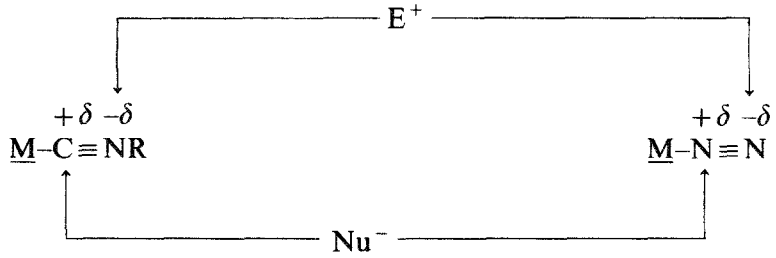
Thus these ligands then show low IR ν(CN) or $\nu(N_2)$ values and they can undergo a sequence of electrophilic attacks at the β position until complete cleavage of the unsaturated bond occurs to afford the enzymatic products. The overall processes require $6e^-/6H^+$ (for tungsten(0) and rhenium(I)) and pass through the intermediate formation of the related multiple-bonded-carbon or multiple-bonded-nitrogen species (e.g. aminocarbyne, M=CNHR, or hydrazido(2−) ligands, $M{=}NNH_2$).

The metal is also susceptible to protonation and hydride species may be involved in the processes.

The above-mentioned basicity of CNR at $\{ReCl(dppe)_2\}$ towards transition metal Lewis acids also finds its counterpart in N_2 bound at the related $\{ReCl(PMe_2Ph)_4\}$ site, since dinitrogen-bridged binuclear or polynuclear complexes have been prepared [73] by interaction of Lewis acid species with the terminal nitrogen atom.

Interestingly, the parallelism of chemical behaviour between N_2 and CNR also appears to occur at a type of metal centre with a much lower electron-rich character than those mentioned previously. Thus in $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2)]$ (with a relatively high $\nu(N_2)$ at 2160 cm^{-1}), the N_2 ligand undergoes nucleophilic attack by a carbanion at the α-nitrogen atom to give a diazenido intermediate which adds an electrophile at the β position to afford an organodiazene (RN=NR') [74]. Similarly, if the isocyanide binds a similar poor π-electron donor centre, as in $[Mn(\eta^5\text{-}C_5H_4Me)(NO)(CO)(CNMe)]^+$, it presents a high $\nu(CN)$ (often higher than that observed in the free ligand) and the ligating isocyanide carbon is susceptible to nucleophilic attack to give an imino species which, upon subsequent β-electrophilic addition, affords an aminocarbene complex [10].

The dinitrogen–isocyanide chemical analogy described may be summarized as follows:



However, a close resemblance between isocyanide and dinitrogen is not always valid, e.g. N_2 is not protonated at $\{ReCl(dppe)_2\}$ although isocyanide undergoes ready protonation at this site. Nevertheless, both substrates are activated to proton attack by the more-electron-rich $\{M(dppe)_2\}$ (M = Mo or W) centres. This has been interpreted [75] (on the basis of the redox properties of the N_2, CNR and CO complexes with these sites) as a consequence of the weaker ability of N_2, compared with CNR or CO, to accommodate the electron release of less-electron-rich sites.

E. ACTIVATION OF ALKYNES

(i) Hydrogen migration reactions

Vinylidene complexes of the type *trans*-[ReCl(C=CHR)(dppe)$_2$] (R= alkyl or aryl) have been prepared by treatment of the dinitrogen complex *trans*-[ReCl(N$_2$)(dppe)$_2$] with the appropriate 1-alkyne (RC≡CH) (eqn. (17)) [76]:

$$\textit{trans}\text{-}[ReCl(N_2)(dppe)_2] + RC{\equiv}CH \longrightarrow \textit{trans}\text{-}[ReCl(C{=}CHR)(dppe)_2] + N_2 \quad (17)$$

The molecular structure of one member of the series, *trans*-[ReCl(C=CHPh)(dppe)$_2$], has been determined by X-ray analysis (Fig. 7) which confirms the double-bond character for both the Re=C and the vinylidene C=C bonds, with corresponding bond lengths of 2.046(8) and 1.308(16) Å [76].

The conversion of 1-alkynes into vinylidene species is promoted by base in some instances [77] and is known to occur, as reported in the literature, for a variety of other centres also capable of binding N$_2$, such as {M(η^5-C$_5$H$_5$)(CO)$_2$} (M=Mn [78] or Re [32]), {FeCl(depe)$_2$}$^+$ [79] and {MCl(PPr$^i_3$)$_2$} (M=Rh or Ir) [80]. At the manganese(I) site, which activates N$_2$ towards nucleophilic attack (see above), methyl propiolate (η^2-HC≡CCO$_2$Me) undergoes a π–σ rearrangement, in the presence of a phosphine (PPh$_3$ or dppe), followed by addition of this nucleophile to give complexes [Mn(η^5-C$_5$H$_5$)(CO)$_2${=C(CO$_2$Me)CH=PPh$_2$R}] (R=Ph or CH$_2$CH$_2$PPh$_2$). This reaction does not proceed through the initially sug-

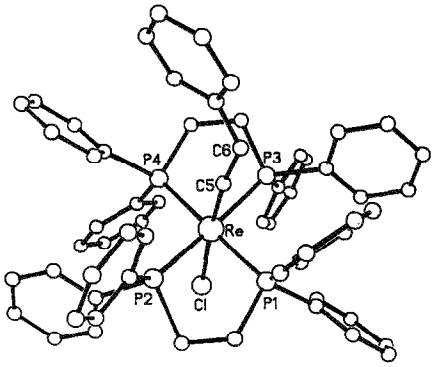
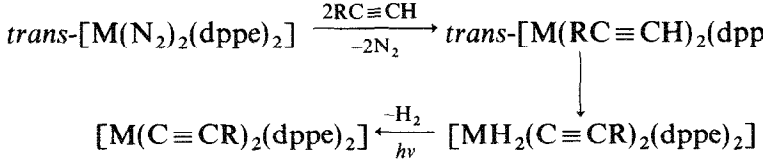


Fig. 7. Molecular structure of *trans*-[ReCl(C=CHPh)(dppe)$_2$] [76]. Selected bond lengths and angles: Re–C(5) 2.046(8) Å; C(5)–C(6) 1.308(16) Å; Re–Cl 2.454(3) Å; Re–C(5)–C(6) 166.6(12)°; C(5)–C(6)–C(91) 125.5(15)°; Cl–Re–C(5) 176.8(4)°.

gested rearrangement of the alkyne into a vinylidene ligand followed by α addition of the phosphine [81].

The 1-alkyne to vinylidene conversion involves a 1,2-hydrogen migration process which has been studied [82] by extended Hückel calculations. These suggest that it involves a dihapto to a monohapto slippage of the ligating alkyne, followed by proton shift from the α to the β carbon. This process corresponds to a lower energy than that involving an intermediate alkynyl–hydrido species, $\underline{M}H(C\equiv CR)$, formed as a result of an oxidative addition of the terminal C–H bond of the alkyne to the metal.

However, alkynyl complexes can also be formed in the reactions of 1-alkynes with *trans*-$[ReCl(N_2)(dppe)_2]$, such as *trans*-$[ReF(C\equiv CPh)(dppe)_2]^+$ [83], obtained in the presence of $TlBF_4$. Moreover, treatment of the complexes *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W) with $RC\equiv CH$ (R = Ph, CO_2Me or CO_2Et) gives, via alkyne adducts, alkynyl-hydride complexes $[MH_2(C\equiv CR)_2(dppe)_2]$ which can eliminate H_2 to give *trans*-$[M(C\equiv CR)_2(dppe)_2]$ (Scheme 4) [84,85].

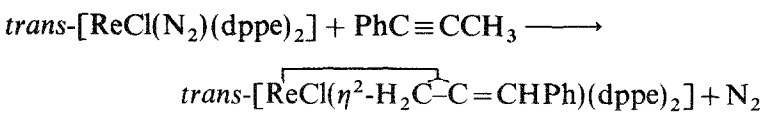


Scheme 4. Formation of alkynyl complexes from the activation of 1-alkynes by molybdenum(0) or tungsten(0) phosphinic centres.

The molecular structure of an alkynyl-hydrido complex, $[WH_2(C\equiv CCO_2Me)_2(dppe)_2]$ (Fig. 8) [84], and of a dialkynyl complex, *trans*-$[Mo(C\equiv CPh)_2(dppe)_2]$ (Fig. 9) [85], have been determined by X-ray analysis. The hydride complex has a square antiprismatic coordination geometry, whereas the dialkynyl compound has *trans* octahedral geometry.

Nevertheless, there is no evidence that any of these alkynyl or alkynyl-hydrido complexes is an intermediate for the conversion of the 1-alkyne into the vinylidene species.

Apart from the above-mentioned 1,2-hydrogen migration and hydrogen shift to the metal, alkynes can undergo other types of hydrogen-transfer reactions at N_2-binding electron-rich metal centres. Thus phenylpropyne ($PhC\equiv CCH_3$) reacts with *trans*-$[ReCl(N_2)(dppe)_2]$ to give the η^2-allene complex *trans*-$[ReCl(\eta^2\text{-}H_2C{-}C{=}CHPh)(dppe)_2]$ (eqn. (18)) [86] derived from a 1,3-hydrogen migration process:



(18)

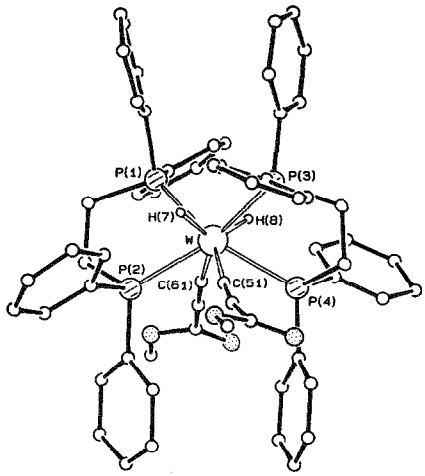


Fig. 8. Molecular structure of $[WH_2(C{\equiv}CCO_2Me)_2(dppe)_2]$ [84]. Selected bond lengths and angles: W–C(51) 2.04(2) Å; W–C(61) 2.04(3) Å; W–H(7) 1.52(12) Å; W–H(8) 1.56(15) Å; C(51)–C(52) 1.22(3) Å; C(61)–C(62) 1.24(4) Å; H(7)–W–C(51) 77(4)°; H(8)–W–C(61) 70(4)°; W–C(51)–C(52) 172.8(16)°; W–C(61)–C(62) 174.5(20)°.

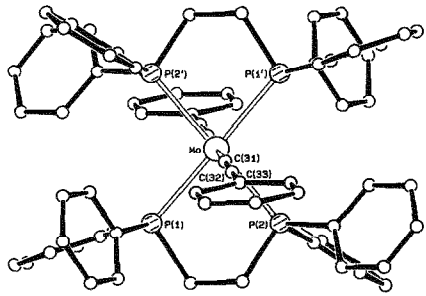


Fig. 9. Molecular structure of *trans*-$[Mo(C{\equiv}CPh)_2(dppe)_2]$ [85]. Selected bond lengths and angles: Mo–C(31) 2.093(8) Å; C(31)–C(32) 1.237(12) Å; C(32)–C(33) 1.422(12) Å; Mo–C(31)–C(32) 175.6(7)°; C(31)–C(32)–C(33) 177.8(9)°.

The molecular structure of the latter complex (Fig. 10) has been authenticated by X-ray analysis [86] which shows, for example, the planarity of the η^2-phenylallene ligand.

This type of metal-centred alkyne-to-allene conversion relates to the known [87] base-catalysed isomerization of alkynes involving an allene intermediate, the role of the base being taken by the metal centre.

Electrophilic alkynes can undergo a similar reaction in $[Mn(\eta^5\text{-}C_5H_4CH_3)(CO)_2(RR'CHC{\equiv}CE)]$ (E=CO_2Me, CO_2Et, CHO or COMe; R,R'=H or alkyl), which is promoted by basic Al_2O_3, whereas a 1,5-hydrogen migration occurs at the vinyl acetylene $RC{\equiv}CCH{=}C(CH_3)_2$ ligating the same metal centre [88].

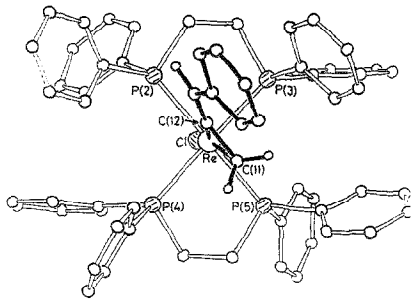


Fig. 10. Molecular structure of *trans*-[ReCl(η^2-H_2C–C=CHPh)(dppe)$_2$] [86]. Selected bond lengths and angles: Re–C(11) 2.181(6) Å; Re–C(12) 2.087(6) Å; C(11)–C(12) 1.41(1) Å; C(12)–C(13) 1.32(1) Å; C(13)–C(14) 1.47(1) Å; Re–Cl 2.469(2) Å; C(11)–C(12)–C(13) 134.5(6)°; C(12)–C(13)–C(14) 127.4(6)°.

In the alkyne reactions at the {ReCl(dppe)$_2$} centre described above, no alkyne complex could be isolated, in accord with the expected destabilizing interaction between the filled $\pi_\perp$ orbital of the alkyne and a filled Re d_π orbital. The alkyne-to-vinylidene or alkyne-to-allene conversion may be promoted by such an interaction, as has been suggested for the former rearrangement, from related studies, at other metal centres [89].

(ii) Protonation reactions

Both the vinylidene [90] and the allene [91] ligands in *trans*-ReCl(C=CHR)(dppe)$_2$] and *trans*-[ReCl(η^2-H_2C–C=CHPh)(dppe)$_2$] respectively, as well as ligating alkynyl at [MH_2(C≡CR)$_2$(dppe)$_2$] (M=Mo or W) [84], can undergo protonation by acid (e.g. HBF_4) at the β position (relative to the metal), as discussed above for the isocyanide ligand at the same metal sites.

Thus the carbyne complexes *trans*-[ReX(CCH_2R)(dppe)$_2$][BF_4] (X=Cl, R=Bu^t or Ph; X=F, R=Bu^t) [90] and the metallacyclopropene (η^2-vinyl) complex *trans*-[ReCl{=C(CH_2Ph)CH_2}(dppe)$_2$][BF_4] [91] are produced from the parent vinylidene and phenylallene compounds respectively, e.g. eqns. (19) and (20):

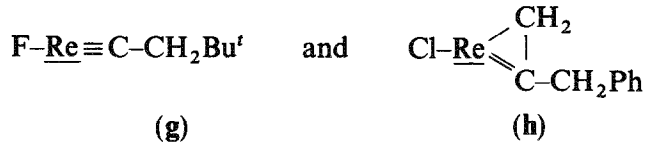
$$\textit{trans}\text{-}[ReCl(C{=}CHR)(dppe)_2] + HBF_4 \longrightarrow \textit{trans}\text{-}[ReCl(CCH_2R)(dppe)_2][BF_4] \quad (19)$$

$$\textit{trans}\text{-}[ReCl(\eta^2\text{-}H_2C{-}C{=}CHPh)(dppe)_2] + HBF_4 \longrightarrow \textit{trans}\text{-}[ReCl\{{=}C(CH_2Ph)CH_2\}(dppe)_2][BF_4] \quad (20)$$

The protonation of the phenylallene ligand at the β position (relative to

the metal) agrees with extended Hückel calculations which indicate, in the HOMO, a high electronic density at the carbon atom in this position [91].

The molecular structures of *trans*-[ReF(CCH_2Bu^t)(dppe)$_2$][BF_4] (Fig. 11) [90] of the metallacyclopropene complex (Fig. 12) [91] have been confirmed by X-ray analyses. The data, in particular the Re–C bond lengths of 1.772(7) Å or 1.947(6) Å respectively, are in agreement with the bonding modes (**g**) and (**h**), where Re stands for *trans*-{Re(dppe)$_2$}:



(**g**) (**h**)

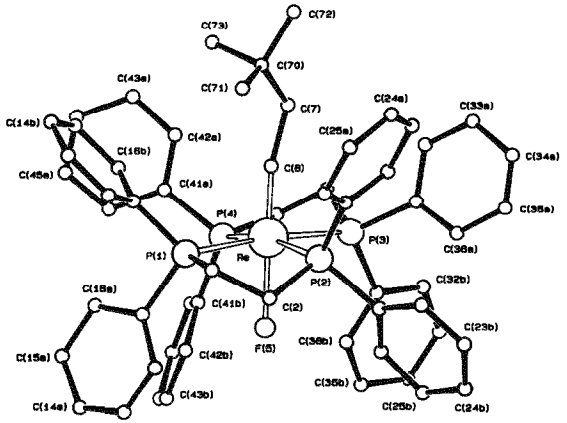


Fig. 11. Molecular structure of *trans*-[ReF(CCH_2Bu^t)(dppe)$_2$]$^+$ [90]. Selected bond lengths and angles: Re–C(6) 1.772(7) Å; C(6)–C(7) 1.505(13) Å; Re–F(5) 2.134(4) Å; Re–C(6)–C(7) 167.9(7)°; C(6)–C(7)–C(70) 125.6(9)°; F(5)–Re–C(6) 174.6(3)°.

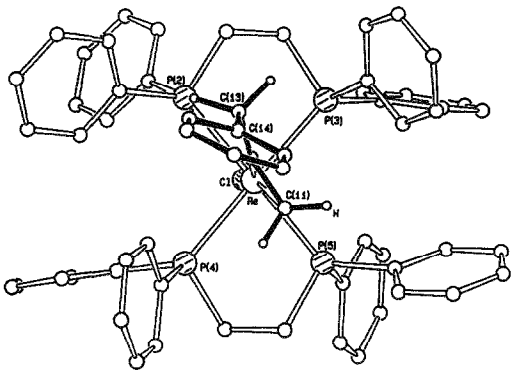


Fig. 12. Molecular structure of *trans*-[ReCl{=C(CH_2Ph)CH_2}(dppe)$_2$]$^+$ [91]. Selected bond lengths and angles: Re–C(11) 2.193(6) Å; Re–C(12) 1.947(6) Å; C(11)–C(12) 1.412(9) Å; C(12)–C(13) 1.500(8) Å; C(13)–C(14) 1.511(9) Å; Re–Cl 2.440(2) Å; C(11)–C(12)–C(13) 130.0(6)°; C(12)–C(13)–C(14) 118.0(5)°.

In both cases, the multiply bonded ligand is stabilized by the π-electron donor halide ligand in the *trans* position.

In contrast with the β-electrophilic addition to a vinylidene ligand, which is an established reaction [89] at a number of metal centres which may bind dinitrogen, for example at $\{Mn(\eta^5\text{-}C_5H_5)(CO)_2\}$ [92], the β protonation of ligating phenylallene, discussed herein, provides a novel synthetic pathway for metallacyclo species based on an electrophilic attack at an alkyne-derived allene ligand. This reaction is promoted by the electron-releasing capacity of the rhenium centre used in this study and it contrasts with the other known methods [15,93,94] of preparation of metallacyclopropenes, based on nucleophilic attack at alkyne ligands.

Moreover, allenes are also substrates of nitrogenase [7], being reduced to propenes, and metallacyclopropene species may correspond to intermediate stages of the reduction.

The use of dinitrogen-binding centres of molybdenum and tungsten has revealed further aspects of alkyne–metal chemistry. Here the dominant reactions, as discussed above, are oxidative additions of the alkyne C–H to the metal to give alkynyl species which can then undergo β-electrophilic attack as shown in reactions of $[WH_2(C{\equiv}CR)_2(dppe)_2]$ with HBF_4 to give $[WF(\equiv CCH_2R)(dppe)_2]$ (R=CO_2Me) or $[WF(=CHCH_2R)(dppe)_2][BF_4]$ (R = Ph) [84] (eqns. (21) and (22)):

$$[WH_2(C{\equiv}CR)_2(dppe)_2] \xrightarrow{HBF_4} \begin{cases} \xrightarrow{(R=CO_2Me)} [WF(\equiv CCH_2R)(dppe)_2] & (21) \\ \xrightarrow{(R=Ph)} [WF(=CHCH_2R)(dppe)_2][BF_4] & (22) \end{cases}$$

Although the protonation of the alkyne fragment stops at the alkylidene stage with these metal centres, it could conceivably continue to the alkyl stage and thence to alkene (via β elimination) or alkane, the products observed for nitrogenases (alkane for the recently discovered vanadium nitrogenase only) [8].

Alkynes can also undergo reductive protonation (which may be catalytic) at less well-defined nitrogen fixing sites [95(a)], namely at aqueous or alcoholic vanadium(II) [95(b)], molybdothiol or molybdoinsulin [95(c)] systems and at the electrochemically reduced form of some double-cubane Mo–Fe–S clusters [96]. However, the mechanisms of these reactions are still poorly understood and the formation of metal–carbon multiple bonds has not been proved.

An alternative approach to the activation of alkynes by N_2-binding sites may result from the synthesis of high oxidation state group V and VI binuclear complexes with bridging N_2, e.g. $[\{MCl_3L_2\}_2(\mu\text{-}N_2)]$ (M = Nb or Ta; L=thf or PR_3) [97(a)], $[\{W(PhC{\equiv}CPh)(OCMe_3)_2\}_2(\mu\text{-}N_2)]$ [97(b)] and $[\{W(\eta^5\text{-}C_5Me_5)Me_3\}_2(\mu\text{-}N_2)]$ [97(c)]. In these complexes, N_2 is regarded as a diimido (or dinitride (4−)) species, N_2^{4-}, possibly as a result of the combined π-electron release from the metal sites. In a similar way, alkynes may also be considered to be in a reduced form when binding suitable centres, for example in $[W(PhC{\equiv}CPh)(OCMe_2CMe_2O)_2]$, which can be viewed as a tungsten(VI) (d^0) complex with a $[PhC{=}CPh]^{2-}$ ligand. This can be protonated with Me_3COH to give $[W(PhC{=}CHPh)(OCMe_3)(OCMe_2CMe_2O)_2]$ [98]; the former compound is analogous to $[W(PhC{\equiv}CPh)((OCMe)_3)_4]$ which by reaction with N_2H_4 gives $[\{W(PhC{\equiv}CPh)(OCMe_3)_2\}_2(\mu\text{-}N_2)]$ in which, however, the charge of the alkyne ligand (0 or 2−) and hence the metal oxidation state (IV or VI) are ambiguous [98].

F. FINAL COMMENTS

This review discusses the application of mononuclear, N_2-binding, electron-rich metal centres to the activation of unsaturated C≡N- and C≡C-containing compounds towards β-electrophilic attack. Such centres are conveniently provided by dinitrogen complexes of the heavier members of the central transition metals (d^6 molybdenum(0), tungsten(0) and rhenium(I)), from which dinitrogen may be displaced.

The unsaturated molecules used in these reactions, isocyanides, nitriles and alkynes, are substrates of nitrogenase and although detailed mechanisms of their reduction by nitrogenase have not yet been elucidated, the chemical studies discussed herein show common features which may pertain to the enzymatic mechanism. Thus the intermediates $M{=}N{=}NH_2$ and $M{\equiv}N{-}\overset{+}{N}H_3$ (in N_2 reduction) and $M{\equiv}C{\cdots}NHR$ and $M{\equiv}C{-}\overset{+}{N}H_2R$ (in CNR and CN reduction) suggest that a common mechanism could be applicable for the reduction of these molecules at metal centres, whether within an enzyme or not. This mechanism may also apply to NCR at these centres.

The formation of species multiply bonded to the metal is the key to reductive cleavage of unsaturated ligands at these metals. It is induced by the high π-electron release from the electron-rich metal centres which also promotes electrophilic attack at the β position of ligating isocyanide, vinylidene, allene or alkynyl species derived from alkynes. Reductive cleavage of alkynes does not occur in this coordination chemistry, nor in the enzymatic reduction of alkynes to alkenes. However, at these mononuclear centres, alkynes can undergo a variety of reactions. The route taken,

whether simple addition of alkyne, isomerization or oxidative addition of the alkyne C–H to the metal, depends upon a number of factors, including the propensity of the metal to form multiple bonds to carbon, the ease of oxidation of the metal centre, steric constraints etc. Clearly more work is necessary before the likely pathway of the reaction of an alkyne at a given metal centre can be accurately predicted.

It is to be expected that this type of activation towards electrophilic attack will be applicable to ligands other than those described above; for example, CO and CO_2 may be induced to yield useful reduced products by use of such systems. Indeed, CO is known to be reduced to methanol by the systems based upon vanadium(II) which reduce dinitrogen [95(b)].

Development of these areas of chemistry, coupled with the mechanistic and theoretical studies outlined above, should lead to the design of new catalytic systems for the synthesis of a range of organic and nitrogenated products, as well as helping to understand nitrogenase function.

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