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Aminocarbyne complexes derived from isocyanides activated towards electrophilic addition

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Abstract

When binding a low-valent electron-rich metal centre, isocyanides can be activated towards β-electrophilic attack at the N atom to give aminocarbyne complexes. The syntheses, structural and electronic properties of these compounds are reviewed, as well as their reactions, in particular, proton-induced C–C coupling to form diaminoacetylene complexes, deprotonation, dehydrogenation and addition of electrophiles across the metal–carbon triple bond. The kinetic and mechanistic studies performed on these systems are also described.

Keywords: Aminocarbyne complexes; Isocyanide complexes; Protonation reactions; Electrophilic addition reactions; Carbon–carbon coupling; Diaminoacetylene complexes; Molybdenum; Tungsten; Rhenium

1. Introduction

Isocyanides (C≡NR) are versatile reagents in organic [1] and coordination [2] chemistries and their reactivity (often determined by the electron lone pair at the terminal carbon atom — as shown, e.g. by the canonical form $:\bar{C}\equiv\overset{+}{N}R$ — , the unsaturated unsymmetric bond and the properties of the group R) can be modulated by coordination to a transition metal centre.

Two opposite modes of activation can result on coordination, depending on the electronic properties of the binding metal site: (i) activation towards electrophilic attack which occurs at the N-atom to give an aminocarbyne species, ≡CNER (E, electrophile), when the coordination centre bears a low-valent metal and is sufficiently electron-rich, exhibiting a high π-electron releasing ability to the isocyanide ligand; and (ii) activation towards nucleophilic addition at the ligated C-atom, in particular by a protic nucleophile (NuH) or by another nucleophilic reagent which also bears an electrophilic centre (without cleavage along the reaction), to form an aminocarbene, =C(Nu)NHR, or an heterocyclic aminocarbene, =C(Nu ENR) respectively, when the binding site is not an appreciable π-electron donor and behaves as a good σ-electron acceptor (efficient Lewis acid) from the ligated isocyanide. This dichotomy of behaviour is represented by Scheme 1 in which M stands for the coordinated metal centre.

These two limiting forms of activation, which result in distinct structural, electronic, spectroscopic and chemical properties of the isocyanide ligand, are induced typically: (i) by low-valent Group 6 (Mo and W) or 7 (Re) centres; or (ii) by Group 10 (Pt or Pd) metal sites in middle or high oxidation states.

It is the purpose of this review to describe the former type of coordination behaviour of isocyanides at mononuclear transition metal centres, whereas the latter type is the object of a subsequent review [2a]. The description is based on the research of the authors, but the works of the other teams active in the field will also be described. The review will focus mainly on the literature published during the last decade, but older reports are also taken into consideration when appropriate for the discussion.

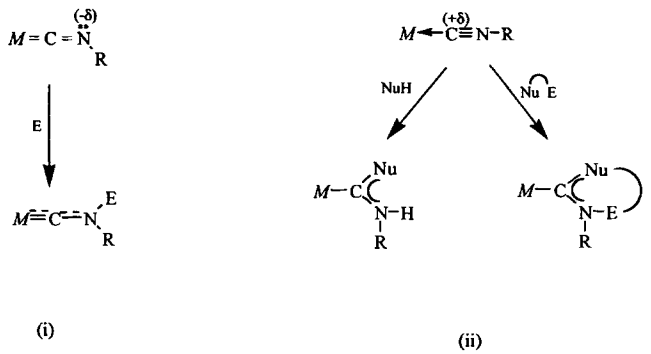
2. Rhenium complexes

2.1. Synthesis, structure and bonding

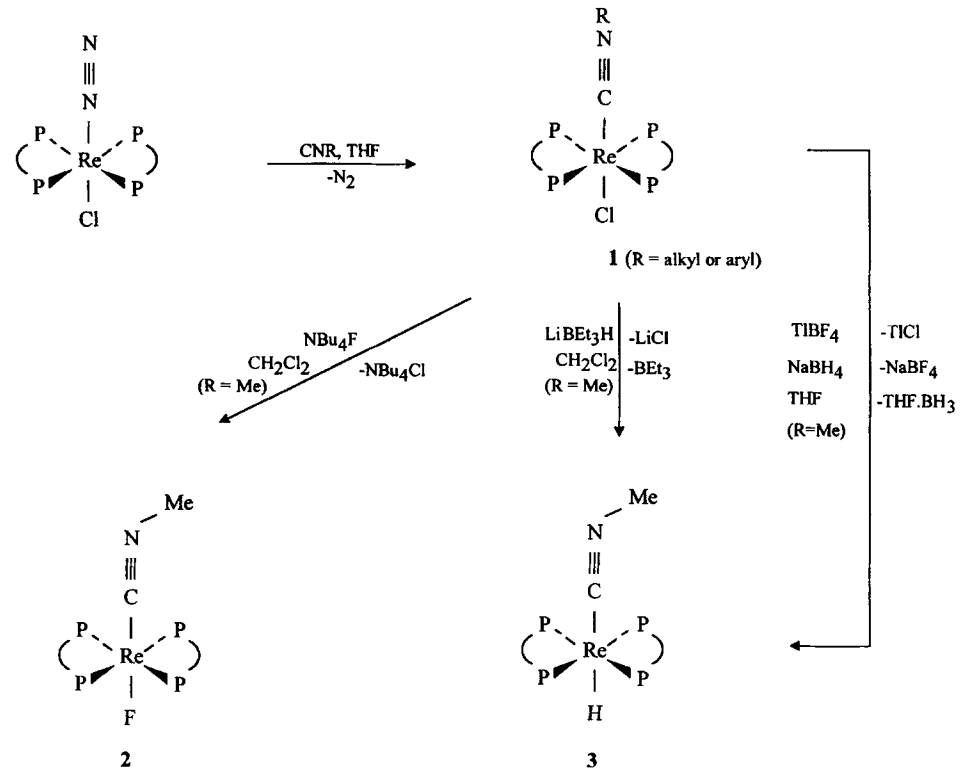
Isocyanides displace dinitrogen from *trans*-[ReCl(N_2)(dppe)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) in THF to form the corresponding isocyano-chloro complexes of Re^I *trans*-[ReCl(CNR)(dppe)$_2$] (**1**, R = alkyl or aryl, e.g. Me, ^{t}Bu, C_6H_4Me-4, C_6H_4Me-2, C_6H_4Cl-4, C_6H_4OMe-4 or $C_6H_3Cl_2$-2,6) [3,4] (Scheme 2), as they do from *trans*-[M(N_2)$_2$(dppe)$_2$] (M = Mo or W) to give *trans*-[M(CNR)$_2$(dppe)$_2$] (see below), but the Re–dinitrogen complex is more inert to substitution and more drastic conditions have to be used, i.e. longer refluxing times under argon and/or irradiation. The displacement of N_2 is promoted by light in accord with some simplified π-MO schemes [5,6] which indicate that the HOMO in the N_2 complex has a M–N_2 bonding character; thus, photochemical electron removal from this orbital should promote the labilisation of the ligating N_2.

The analogous fluoride and hydride complexes, *trans*-[ReX(CNMe)(dppe)$_2$] (X = F (**2**) or H (**3**)), can be prepared by replacement of the chloride ligand from the chloro-isocyanide complex [7,8] (Scheme 2) on treatment of a CH_2Cl_2 solution with NBu_4F (for complex **2**) or $LiBEt_3H$ (for **3**) or of a THF solution with $TlBF_4$ in the presence of $NaBH_4$ (for complex **3**).

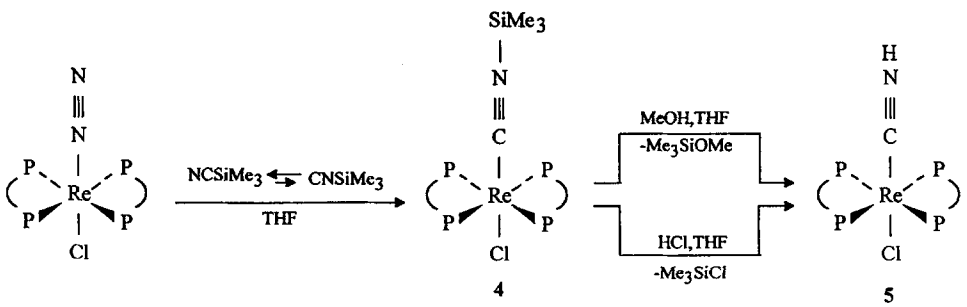
The related trimethylsilylisocyanide and the hydrogen isocyanide complexes *trans*-[ReCl(CNSiMe$_3$)(dppe)$_2$] (**4**) and *trans*-[ReCl(CNH)(dppe)$_2$] (**5**), respectively, have been prepared [9,10] by using, as a convenient starting material, trimethylsilyl cyanide, $NCSiMe_3$, which is known to contain a small amount (ca. 5%) of the isocyanide isomer. The former isocyanide complex is obtained by displacement (promoted by sunlight) of N_2 in *trans*-[ReCl(N_2)(dppe)$_2$] (Scheme 3). The coordination of the isocyanide $CNSiMe_3$, in preference to the predominant cyanide isomer $NCSiMe_3$, shifts the isomeric equilibrium towards the former which is thus further generated; it is in agreement with the expected more effective stabilisation of the



Scheme 1. Activation of isocyanide towards (i) electrophilic and (ii) nucleophilic additions: *M* — transition metal coordination centre; E — electrophile; NuH — protic nucleophile; Nu⌒E — nucleophile which also bears an electrophilic centre.



Scheme 2. Syntheses of alkyl- and aryl-isocyanide diphosphinic complexes of Re(I) [3,4,7,8]. P⌒P dppe = $Ph_2PCH_2CH_2PPh_2$.



Scheme 3. Syntheses of the $CNSiMe_3$ and CNH diphosphinic complexes of Re(I) [9,10].

electron-rich $\{ReCl(dppe)_2\}$ centre by the stronger net π-acceptor/σ-donor isocyanide in comparison with the cyanide isomer.

The CNH complex **5** is derived (Scheme 3) from *trans*-$[ReCl(CNSiMe_3)(dppe)_2]$ (**4**), on treatment of a THF solution with MeOH or with a stoichiometric amount of HCl which leads to desilylation of the $CNSiMe_3$ ligand [9,10].

Those isocyanide complexes exhibit strong and broad bands assigned to ν(C≡N) at very low values (in the 1930–1760 cm^{-1} range) in the IR spectra, well below those of the free ligands. Hence, e.g. for the ligated CNMe in the chloro- and fluoro-complexes, ν(C≡N) occurs at 1830 and 1800 cm^{-1} (whereas in the free ligand it is observed at 2150 cm^{-1}). Similar large lowering of ν(CN) is exhibited by *trans*-[M(CNR)$_2$(dppe)$_2$] (M = Mo or W) (see below) and it reflects the effective electron-releasing character of these electron-rich metal sites. This is also accounted for by the single-crystal X-ray diffraction analyses of the abovementioned isocyanide complexes (**1**, R = Me) [7], **3** [7], **4** [10] and **5** [10] (Table 1).

The Re atom exhibits octahedral-type coordination and the Re–C_α (ligated terminal C atom of the isocyanide) bond length [1.86(1)–2.01(4) Å range] is much shorter than the expected [11] Re–C single bond length, 2.13 Å [for (**1**, R = Me) the value 1.861(12) Å is even shorter than that estimated [12] for an Re=C double bond, 1.91 Å], whereas the unsaturated C_α–N bond is usually elongated beyond the average value, 1.14 Å, quoted in Ref. [13] for a C≡N triple bond [e.g. C_α–N = 1.210(15) Å for **1**, R = Me]. The related isocyanide complexes *trans*-[ReCl(CN^{t}Bu)(dppe)$_2$] [14], *mer*-[ReCl(N$_2$)(CNMe){P(OMe)$_3$}$_3$] [15a] and *mer*-[Re(η^1-S$_2$PPh$_2$)(N$_2$)(CNMe)(PMe$_2$Ph)$_3$] [16], derived from reactions of the appropriate isocyanide with *trans*-[ReCl(N$_2$)(dppe)$_2$], [ReCl$_2$(NNCOPh){P(OMe)$_3$}$_3$] or [Re(η^2-S$_2$PPh$_2$)(N$_2$)(PMe$_2$Ph)$_3$], respectively, also exhibit short Re–C_α corresponding distances [1.926(9), 2.07(2) or 1.93(1) Å].

Moreover, the isocyanide ligand can exhibit a clearly bent geometry, if steric effects are not dominating. Hence, although the bulky CNSiMe$_3$ and CN^{t}Bu isocyanides in the above complexes are essentially linear [C_α–N–R angle in the 172(2)–174(2)° range], the CNMe ligand in *trans*-[ReCl(CNMe)(dppe)$_2$] (**1**, R = Me) and *trans*-[ReH(CNMe)(dppe)$_2$] is markedly bent, with angles at the N atom of 139.4(10) or 147.7(7)° [7], even shorter than that, 156(1)°, known [17] for *trans*-[Mo(CNMe)$_2$(dppe)$_2$] (see below).

This bending of the isocyanide ligating the electron-rich {ReCl(dppe)$_2$} site is electronic in origin but can be overcome by steric hindrances. It is expected on the basis of electronic arguments associated with an extensive π-electron release from the metal centre to a π*(C≡N) orbital [strong π-backbonding component of the coordination bond — Fig. 1(a)]. This would result in strengthening of the metal–carbon bond (which then presents a carbene character) with concomitant weakening of the unsaturated C–N bond and a localisation of electronic charge at the N atom as shown by the significant weight of the canonical carbene from, Fig. 1(b), in the valence-bond representation of the isocyanide ligand. These features can also be rationalised by extended Hückel calculations [18] and by qualitative simplified π-MO schemes [5,6] which comprise filled Re–C_α bonding and C_α–N antibonding valence π-MOs.

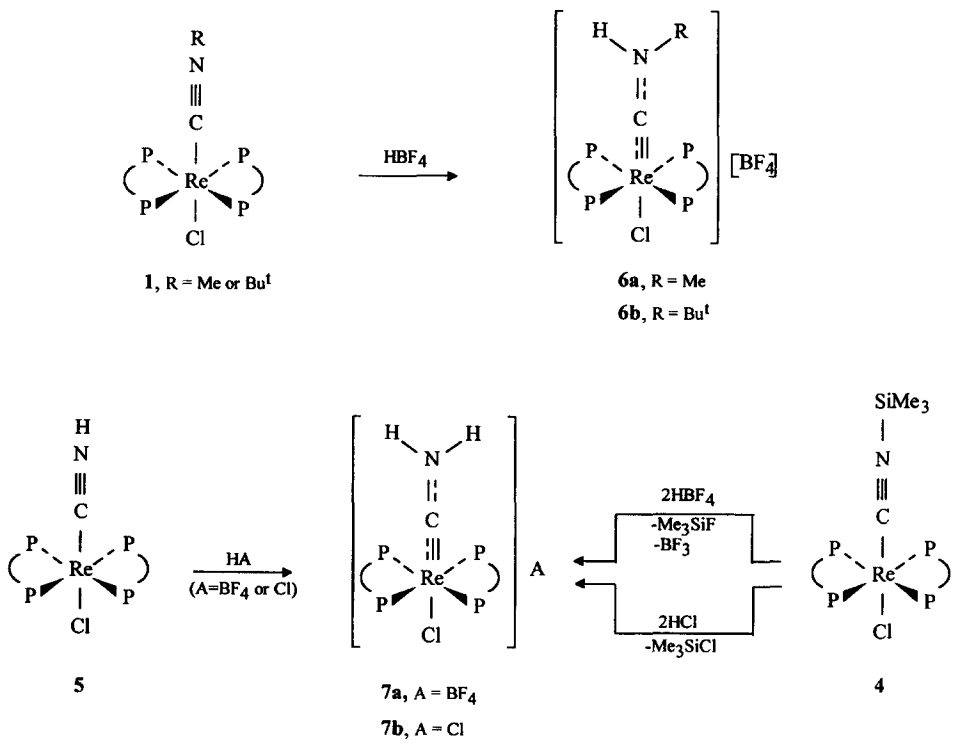
In agreement with the above features, the isocyanide ligand is activated towards β-electrophilic attack which occurs at the N-atom. Hence, e.g. the aminocarbyne complexes *trans*-[ReCl(CNHR)(dppe)$_2$][BF$_4$] (**6a**, R = Me; **6b**, R = ^{t}Bu) [3] and *trans*-[ReCl(CNH$_2$)(dppe)$_2$]A [**7a**, A = BF$_4$ (the first CNH$_2$ complex to be reported [9,10]); **7b**, A = Cl [10]] are readily obtained by protonation, with HBF$_4$ or HCl, of

Table 1
Selected bond lengths (Å) and angles (°) for isocyanide phosphinic complexes of Re(I) and isocyanide-derived aminocarbynes

Complex	Re–C_α	C_α–N	Re–Cl	Re–P(av)	C_α–N–R	Other	References
trans-[ReCl(CNMe)(dppe)$_2$] (**1**, R = Me)	1.861(12)	1.210(15)	2.607(5)	2.40	139.4(10)		[7]
trans-[ReCl(CNSiMe$_3$)(dppe)$_2$] (**4**)							
A	1.950(22)	1.128(28)	2.524(6)	2.400(6)	171.9(18)		[10]
B	1.833(23)	1.232(29)	2.520(6)	2.394(6)	174.4(19)		
trans-[ReCl(CN^{t}Bu)(dppe)$_2$] (**1**, R = ^{t}Bu)	1.926(9)	1.154(10)	2.520(2)	2.401(2)	174.0(9)		[14]
trans-[ReCl(CNH)(dppe)$_2$] (**5**)	2.007(38)	1.157(43)	2.532(9)	2.426(2)			[10]
trans-[ReH(CNMe)(dppe)$_2$] (**3**)	1.947(8)	1.207(9)	–	2.36	147.7(7)	1.54(7) (Re–H)	[7]
trans-[ReCl(CN^{t}Bu)$_2$(PMe$_3$)$_3$]	2.004(7)	1.128(9)	2.570(2)	2.348(2)	175(1)		[20]
	2.003(7)	1.151(9)			159(1)		
mer-[ReCl(N$_2$)(CNMe){P(OMe$_3$}$_3$]	2.07(2)	1.12(2)	2.530(4)	2.372(4)	169(1)	1.98(1) (Re–N)	[15a]
						1.04(2) (N–N)	
mer-[Re(η^1-S$_2$PPh$_2$)(N$_2$)(CNMe)(PMe$_2$Ph)$_3$]	1.93(1)	1.20(2)	–		168(1)	1.83(1) (Re–N)	[16]
						1.13(1) (N–N)	
trans-[ReCl(CNHMe)(dppe)$_2$][BF$_4$] (**6a**)	1.80(3)	1.35(3)	2.484(6)	2.457(7)	123.3(22)		[3]
trans-[ReCl(CNH$_2$)(dppe)$_2$][BF$_4$] (**7a**)	1.802(4)	1.309(5)	2.485(1)	2.456(1)	113(4)		[9]
					129(5)		
trans-[ReCl(CNH^{t}Bu)(CN^{t}Bu)$_2$(PMePh$_2$)$_2$][SbF$_6$]	1.82(1)	1.30(1)	2.497(3)	2.441(3)	127.6(9)	2.05(1) (Re–C(CN^{t}Bu))	[19]
						2.07(1) (Re–C(CN^{t}Bu))	

the parent isocyanide compounds (**1**, R = Me or ^{t}Bu) and **5** (Scheme 4). The latter aminocarbyne complexes **7** can also be prepared in a more direct way from protic desilylation of *trans*-[ReCl(CNSiMe$_3$)(dppe)$_2$] (**4**) [Scheme 4(a)] on treatment of a toluene solution with HBF_4 or HCl in a twofold molar ratio.

(a)



1, R = Me or Bu^t

6a, R = Me

6b, R = Bu^t

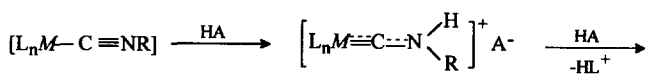
5

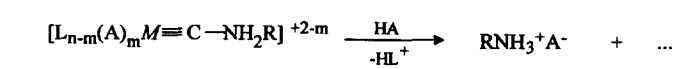
7a, A = BF_4

7b, A = Cl

4

(b)





Scheme 4. (a) Protonation reactions of isocyanide phosphinic complexes of Re(I) to give aminocarbyne products [3,8–10]. (b) Protic cleavage of an isocyanide to a primary amine at a Mo, W or Re centre with labile phosphine or phosphite ligands [15].

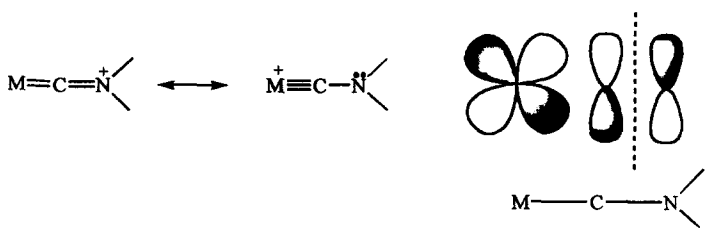
The Re–aminocarbyne complexes *trans*-[ReCl(CNHR)(CNR)$_2$(PMePh$_2$)$_2$][SbF$_6$] (R = Me or ^{t}Bu) were obtained by reduction of the seven-coordinate [ReCl$_2$(CNR)$_3$(PMePh$_2$)$_2$]$^+$ cations with Zn or Al in refluxing THF containing ca. 1% H_2O [19]. The molecular structure of the CNHMe complex has been authenticated by X-ray diffraction [19] (Table 1) and the reaction is believed to proceed via a two-electron reduction of the Re(III) starting complex to form a postulated Re(I) intermediate which then undergoes protonation by H_2O with increased acidity owing to coordination to Zn(II) or Al(III).

The related aminocarbyne complexes [ReCl(CNH^{t}Bu)(CN^{t}Bu)$_n$(PMe$_3$)$_{4-n}$][BF$_4$] (n = 1 or 2) were obtained by N-protonation of the Re(I)-isocyanide complexes [ReCl(CN^{t}Bu)$_{n+1}$(PMe$_3$)$_{4-n}$] (Table 1, for n = 1) by HBF_4 [20].

The formation of a Re–aminocarbyne complex derived from the reaction of *mer*-[ReCl$_3$(PMePh$_2$)$_3$] with 2-(trimethylsiloxy)phenylisocyanide, i.e. *mer*-[ReCl{CN(H)C$_6$H$_4$(OSiMe$_3$)-2}L$_3$] (L = 2,3-dihydrobenzoxazol-2-ylidene), has also been reported [2b] although without details.

β-Electrophilic attack, at an activated isocyanide, by a transition metal Lewis acid is also known and it leads to the formation of the dinuclear adducts [ReCl{CN(M)R}(dppe)$_2$] [R = Me or ^{t}Bu; M = CoCl$_2$(THF), ReOCl$_3$(PPh$_3$), WCl$_4$(PPh$_3$) or WCl$_4$(PEtPh$_2$)] on treatment of *trans*-[ReCl(CNR)(dppe)$_2$] with CoCl$_2$(THF)$_{1.5}$, [ReOCl$_3$(PPh$_3$)$_2$], [WCl$_4$(PPh$_3$)$_2$] or [WCl$_4$(PEtPh$_2$)$_2$], respectively [18]. The isocyanide bridges the two metals and the Re-ligated CN(M)R species is believed to be of the aminocarbyne type.

The aminocarbyne ligands in *trans*-[ReCl(CNHMe)(dppe)$_2$][BF$_4$] (**6a**) and *trans*-[ReCl(CNH$_2$)(dppe)$_2$][BF$_4$] (**7a**) exhibit, in the ^{13}C–{^{1}H}-NMR spectra, a low-field *C*NHR resonance centred at δ 222.7 (R = Me) [3] or 222.38 (R = H) [10], the latter being resolved as a quintet [^2J(CP) = 13.4 Hz]. In the IR spectra, the medium-strong bands in the range 1530–1575 cm^{-1} (CNHMe and CNH^{t}Bu) or at 1585 cm^{-1} (CNH$_2$) are assigned to ν(C=N), indicating that the canonial carbene-type form **a** (iminomethylenium or 2-azavinylidene) has a significant weighting in the VB representation in which **b** represents the aminocarbyne form. This can be accounted for [5,6] by simplified π-MO bond schemes with filled valence π-MOs having M–C$_\alpha$ bonding and C$_\alpha$–N antibonding characters, i.e. **c** and the related one in the perpendicular plane.



a **b** **c**

Such a description is also corroborated by the X-ray diffraction analyses (Table 1) e.g. of *trans*-[ReCl(CNHMe)(dppe)$_2$][BF_4] (**6a**) [3] and *trans*-[ReCl(CNH_2)-(dppe)$_2$][BF_4] (**7a**) [9] which show that the CNHR (R = Me or H) ligand is roughly planar owing to the delocalisation of the nitrogen lone pair electrons, as it is known [21] for the related hydrazide(2-), $=NNH_2$, ligand derived from double protonation of ligating N_2 at a {M(dppe)$_2$} (M = Mo or W) centre. Moreover, the Re–C_α bond length of 1.80(3) or 1.802(4) Å is somewhat longer than that estimated, 1.721–1.751 Å [3], for a Re≡C triple bond, and the C_α–N distance, 1.35(3) or 1.309(5) Å, is shorter than a N–C single bond [e.g. 1.42(4) Å for N–CH_3 in **6**, R = Me].

Comparison of the structural data of these aminocarbyne compounds with those of their isocyanide precursors, *trans*-[ReCl(CNMe)(dppe)$_2$] (**1**, R = Me) [7] and *trans*-[ReCl(CNH)(dppe)$_2$] (**5**) [10] allows one to observe the structural rearrangements resulting from the β-protonation of the isocyanide, i.e. from its conversion into the corresponding aminocarbyne: shortening of the Re–C_α bond length [from 1.86(1)–2.01(4) to 1.80(3)–1.802(4) Å] and of the Re–Cl distance [from 2.607(5)–2.532(9) to 2.484(6)–2.485(1) Å], with concomitant elongation of the C_α–N [from 1.210(15)–1.157(43) to 1.35(3)–1.309(5) Å] and Re–$P_{(av)}$ [from 2.40–2.426(2) to 2.457(7)–2.456(1) Å] bond lengths. These alterations can be accounted for by considering that the aminocarbyne ligands behave as much stronger π-electron acceptors than the isocyanides, thus leading to an increase of the σ- and π-electron donor character of the chloro-ligand to compensate electronically the metal, and to a decrease of the π-electron releasing ability of the rhenium site to the phosphine ligands.

The stronger π-electron acceptance of the aminocarbyne compared with the isocyanide is also indicated by electrochemical studies, in particular by the much higher oxidation potentials of the aminocarbyne complexes compared with those of the isocyanide compounds [22,23]. The value of the electrochemical P_L ligand parameter (a measure [24] of the net π-electron acceptor minus σ-donor character of a ligand) estimated [22,25] for the CNH_2 ligand, + 0.09 V, is higher than those of isocyanides (− 0.07 to − 0.44 V range) [4,25] or even CO (P_L = 0 V), although being lower than those (ca. 0.27 V) [22,26] of the carbynes ≡C–CH_2R.

The above structural and electronic CNR → CNHR arrangements are also consistent with some theoretical calculations [18,27] and simplified π-MO schemes [6,28] which show that an increase in both the π- and σ-overlap populations of the Re–C_α bond and a decrease in such populations for the C_α–N bond result from the β-electrophilic attack at the ligating isocyanide to give the aminocarbyne ligand.

2.2. Reactivity

The aminocarbyne groups CNHR and CNH_2 can be considered as partially reduced isocyanides or cyanide and may be postulated [5,29] as intermediates in the reduction of these substrates to alkylamine, methane and ammonia by nitrogenase. This hypothesis gains some support (although the postulated aminocarbyne intermediates have not been isolated) from the known protic cleavage to primary amines

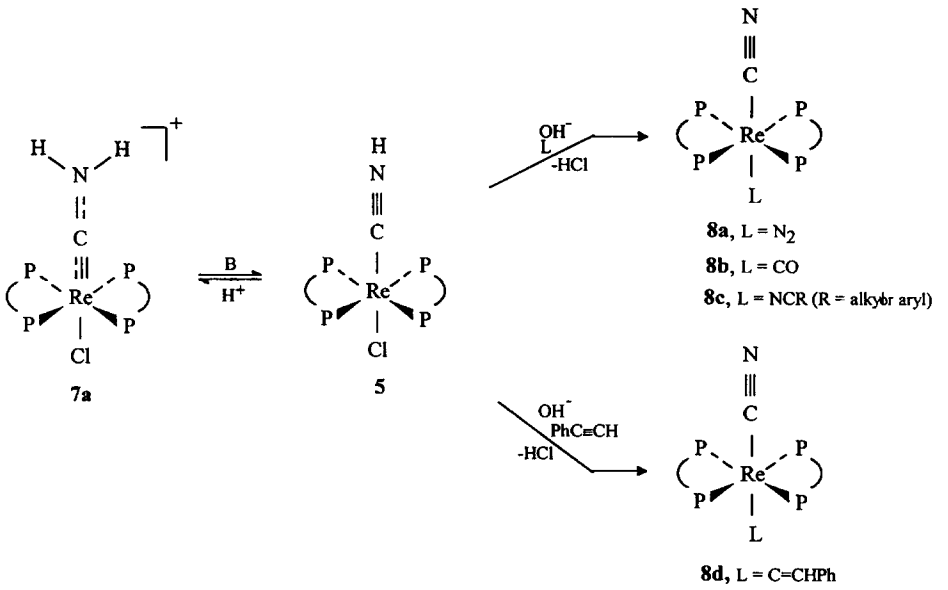
of the isocyanide ligands in *mer*-[ReCl(N_2)(CNR){$P(OMe)_3$}$_3$] [15a] and related Mo and W [15b] complexes (see also Section 3.4) with labile co-ligands (monodentate phosphines or phosphites). Such ligands are easily replaced, along the isocyanide protonation reaction with HA (mineral acid), by the more effective electron-donor anion A^- with a further protonation promoting effect on the aminocarbyne intermediate [Scheme 4(b)]. The protonation of the latter can result in the complete C≡N bond cleavage with formation of the ammonium salt $RNH_3^+A^-$ (and methane, although in low yield). In that respect, the study of the interconversion of the CNH_x ($x = 0–2$) species would also be of significance and this has been accomplished by chemical and electrochemical means.

The aminocarbyne ligands present some acidic character in the usual organic solvent solutions of their complexes and can be deprotonated by a base such as NEt_3 or NBu_4OH to regenerate the parent isocyanide or cyanide and this reaction can be used in the synthesis of new compounds. Moreover, the acidity can be dramatically increased by oxidation leading to a spontaneous deprotonation. Hence, the acidity constant (K_a) of *trans*-[ReCl(CNH_2)(dppe)$_2$][BF_4] (**7a**) in NCMe increases by nearly ten orders of magnitude (pK_a decrease from 8.2 to −1.4) as a result of single-electron oxidation of the complex to give (on spontaneous anodically induced H^+ loss) the isocyanide compound *trans*-[ReCl(CNH)(dppe)$_2$]$^+$ which, in turn, by oxidation undergoes a related deprotonation to form the cyanide complex *trans*-[ReCl(CN)(dppe)$_2$]$^+$ via a mechanism that was established by digital simulation of cyclic voltammetry [10,23].

The aminocarbyne ligands can also convert into the corresponding isocyanide ones in reductive conditions. Hence, the cathodic reduction of a solution of *trans*-[ReCl(CNH_2)(dppe)$_2$][BF_4] (**7a**) leads to the formation, at least in part, of the isocyanide complex *trans*-[ReCl(CNH)(dppe)$_2$] (**5**) [23]. A detailed cyclic voltammetric study indicates that the dehydrogenation of CNH_2 occurs not by direct reduction of its complex, but simply by the reduction of liberated H^+ (due to the acidity character of the CNH_2 ligand) with resulting shift of the dissociation equilibrium of the aminocarbyne complex to give the isocyanide one [23].

Treatment of an acetonitrile solution of the aminocarbyne complex *trans*-[ReCl(CNHMe)(CNMe)$_2$($PMePh_2$)$_2$][SbF_6] with Zn leads to its dehydrochlorination to give the trisisocyanide compound [Re(NCMe)(CNMe)$_3$($PMePh_2$)$_2$][SbF_6], and the reaction is believed to proceed also by first reduction of H^+ (liberated on partial protic dissociation of the CNHMe ligand) [19].

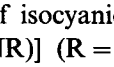
A chemical route for the conversion of the aminocarbyne complex *trans*-[ReCl(CNH_2)(dppe)$_2$][BF_4] (**7a**) into a variety of derived cyano species was also devised [30] (Scheme 5). It involves a stepwise deprotonation of CNH_2 by base to form the isocyanide *trans*-[ReCl(CNH)(dppe)$_2$] (**5**) and the postulated cyano-complex *trans*-[ReCl(CN)(dppe)$_2$]$^-$ with concomitant labilisation of the Re–Cl bond, thus inducing a ready replacement of the chloride ligand by a suitable π-electron acceptor (e.g. N_2, NCR, CO or an alkyne derivative) which can stabilise the low metal oxidation state centre [Re(I)] [30]. Hence, treatment of *trans*-[ReCl(CNH_2)(dppe)$_2$][BF_4] (**7a**) with NBu_4OH, under N_2 or CO, leads to deprotonation followed by dehydrochlorination to form the cyano-dinitrogen or -carbonyl



Scheme 5. Conversion of the aminocarbyne complex **7a** into Re cyano-complexes of dinitrogen, carbonyl, organonitriles or phenylvinylidene: B = NEt_3 or NBu_4OH [30].

complexes *trans*-[Re(CN)L(dppe)$_2$] (**8a**, L = N_2; **8b**, L = CO), respectively, whereas in the presence of an organonitrile NCR (R = alkyl or aryl) or of phenylacetylene, under argon, the nitrile or vinylidene complexes *trans*-[Re(CN)L(dppe)$_2$] (**8c**, L = NCR; **8d**, L = C=CHPh) are the obtained products (the crystal structure of the cyano-acetonitrile complex has been determined) [30].

This chemical route to aminocarbyne-derived isocyano- or cyano-complexes leads to products in low metal oxidation state, i.e. Re(I), whereas the electrochemical one, discussed previously, gives derived CNH or CN complexes in medium metal oxidation states, i.e. Re(II) or Re(III).

An aminocarbyne species has been postulated as an intermediate in the protic conversion, in the presence of water, of isocyanide ligands into carbonyl, in the reactions of [Re{η^4-N(CH_2CH_2S)$_3$}(CNR)] (R = ^{t}Bu, CH_2CH_2 or ) [complexes with the tripodal tetradentate NS_3-type 2,2′,2″-nitrilotris(ethanethiolate) ligand] with HCl, in a two-phase toluene–water medium, to give [Re{η^4-N(CH_2CH_2S)$_3$}(CO)] [31]. In agreement with a strong π-electron-releasing ability of the Re–NS_3 binding centre (in spite of the medium oxidation state of the metal, Re(III)), its isocyanide complexes exhibit IR ν(C≡N) at considerably low wavenumbers (1976–1940 cm^{-1} range) and a significantly bent geometry [C–N–C angles of 150.8(9) and 154.0(10)° for R = CH_2COOMe or ^{t}Bu, respectively], and N-protonation by HCl is proposed [31] to give an aminocarbyne ligand, =CNHR, which would hydrolyse, via postulated –C(OH)=NHR and –C(=O)–NH_2R intermediates, to give the carbonyl product.

3. Groups 6 and 5 metal complexes

3.1. Complexes with the {M(dppe)$_2$} (M = Mo or W) centres

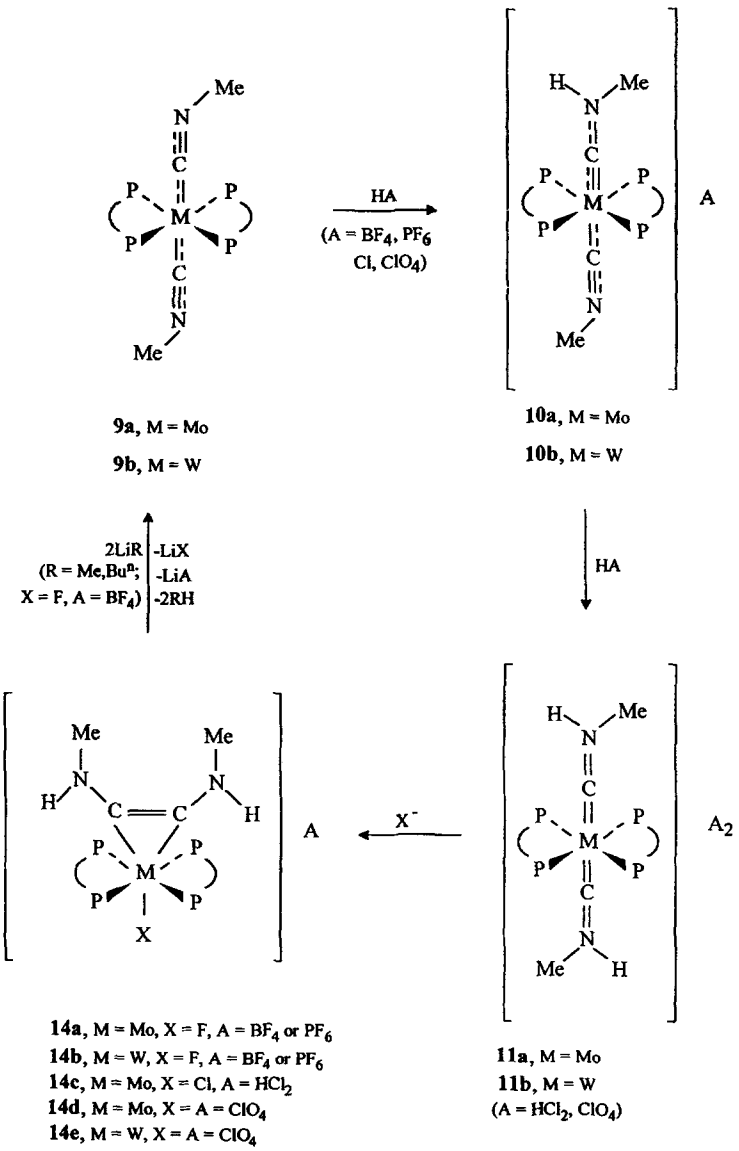
3.1.1. Synthesis, reactivity and protic C–C coupling

The first examples of activation of ligated isocyanides towards β-protonation to form [17] aminocarbyne complexes started to be reported in 1975 by one of us (with R.L. Richards and J. Chatt) and were provided by the reactions of the diisocyanide compounds *trans*-[M(CNR)$_2$(dppe)$_2$] (**9a**, M = Mo, R = Me; **9b**, M = W, R = Me; **9c**, M = Mo, R = ^{t}Bu; **9d**, M = W, R = ^{t}Bu) with mineral acids to give a variety of products: the mono- and di-aminocarbynes *trans*-[M(CNHR)(CNR)(dppe)$_2$]$^+$ (**10a**, M = Mo, R = Me; **10b**, M = W, R = Me; **10c**, M = Mo, R = ^{t}Bu; **10d**, M = W, R = ^{t}Bu) and *trans*-[M(CNHR)$_2$(dppe)$_2$]$^{2+}$ (**11a**, M = Mo, R = Me; **11b**, M = W, R = Me) (Scheme 6), the hydrides [MH(CNR)$_2$(dppe)$_2$]$^+$ (**12a**, M = Mo, R = Me; **12b**, M = W, R = Me; **12c**, M = Mo, R = ^{t}Bu; **12d**, M = W, R = ^{t}Bu) and the hydride-aminocarbynes [MH(CNHR)(CNR)(dppe)$_2$]$^{2+}$ (**13a**, M = Mo, R = Me; **13b**, M = W, R = Me) [17,32–35].

The CNMe ligand in *trans*-[Mo(CNMe)$_2$(dppe)$_2$] (**9a**) is markedly bent [C_α–N–C angle of 156(1)°] [17], although not so much as in the Re(I) complexes *trans*-[ReX(C-NMe)(dppe)$_2$] [139.4(10)°, X = Cl; 147.7(7)°, X = H] [7]. It is susceptible to alkylation and the dialkylaminocarbyne complexes *trans*- and *cis*-[M(CNRR′)(CNR)(dppe)$_2$]X (M = Mo or W; R = Me or ^{t}Bu; R′ = Me or Et; X = FSO_3, $MeSO_4$ or BF_4) were prepared by reaction of the corresponding diisocyanide (CNMe or CN^{t}Bu) complexes with $MeFSO_3$, Me_2SO_4 or [Et_3O][BF_4] [35,36]. The *trans*-to-*cis* isomerisation of these dialkylaminocarbyne complexes, as well as the susceptibility of the above aminocarbyne complexes *trans*-[M(CNHR)(CNR)(dppe)$_2$]$^+$ (**10**) to undergo proton-shift from the CNHR ligand to the metal (see the mechanistic study described in Section 3.3) giving the corresponding hydride products **12**, are, at least in part, a result of the destabilising effect of the strong π-electron acceptor isocyanide ligand which competes effectively with the aminocarbyne (in particular when they are in mutually *trans* positions) for the metal π-electron release.

The protonation studies were revisited by our group later on and, in the light of new evidence, confirmed by an X-ray analysis (see below), it was shown [37,38] that, when using HBF_4 as the proton source, the di(aminocarbyne) complexes *trans*-[M(C-NHMe)$_2$(dppe)$_2$][BF_4]$_2$ **11a** and **11b** formed via protonation of the corresponding monocarbynes **10a** and **10b** — undergo ready fluorination and carbyne–carbyne coupling to form the η^2-di(methylamino)acetylene [or η^2-ynedi(methylamine)] fluoro-complexes *trans*-[MF(η^2-MeHNC≡CNHMe)(dppe)$_2$][BF_4] (**14a**, M = Mo; **14b**, M = W) (Scheme 6). The latter compounds were previously formulated as their parent dicarbyne species and then provided [17], although unknowingly, the first example of protic coupling of isocyanide ligands. The use of other acids with conjugate bases with a weaker nucleophilicity than BF_4^- towards the metal centre, such as HCl or $HClO_4$, allowed the isolation of the corresponding di(aminocarbyne) intermediates *trans*-[M(C-NHMe)$_2$(dppe)$_2$]A$_2$ [**11a**, M = Mo; **11b**, M = W; A = HCl_2 or ClO_4] which were clearly shown to convert (Scheme 6) into the final η^2-diaminoacetylene (or ynediamine) products *trans*-[MX(η^2-MeHNC≡CNHMe)(dppe)$_2$]A (**14c**, M = Mo, X = Cl, A = HCl_2; **14d**, M = Mo, X = A = ClO_4; **14e**, M = W, X = A = ClO_4) [38].

The parent diisocyanide complexes *trans*-[M(CNMe)$_2$(dppe)$_2$] (**9a** or **9b**) can by fully regenerated from the η^2-diaminoacetylene products by base-induced cleavage of the acetylenic CC bond to C_1 fragments with concomitant deprotonation of the amino groups and defluorination of the metal. In fact, treatment of *trans*-[MF(η^2-MeHNC≡CNHMe)(dppe)$_2$][BF_4] (**14a** or **14b**) with LiMe or Li^{n}Bu leads to the formation of the starting diisocyanide complexes (Scheme 6) [37,38].



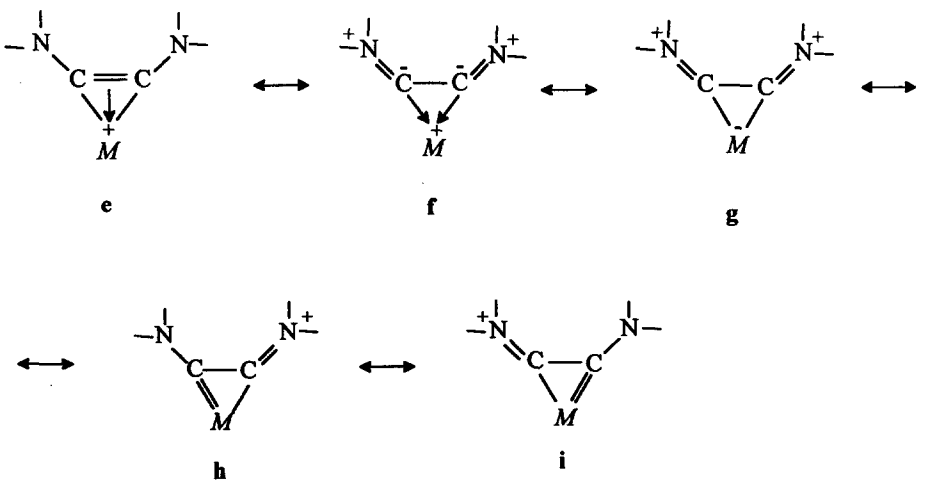
Scheme 6. Protonation of di(methylisocyanide) phosphinic complexes of Mo(0) or W(0) to give aminocarbyne complexes and derived diaminoacetylene products [17,32–34,37,38].

In the mono(aminocarbyne) complexes *trans*-$[M(CNHMe)(CNMe)(dppe)_2]^+$ (**10a** and **10b**), and as discussed above for the rhenium complexes, the aminocarbyne ligand [ν(C=N) 1515–1533 cm^{-1}] exhibits a marked carbene character, $\overset{+}{M}=C=\overset{+}{N}HMe$ which is even more pronounced in the di(aminocarbyne) complexes *trans*-$[M(CNHMe)_2(dppe)_2]^{2+}$ (**11a** and **11b**) which are better considered [32,38] as dicarbene or di(iminomethylenium) species [form **d**, $M = M(dppe)_2$] on account of the maximum number of available d electrons for the Group 6 metal and also as shown by spectroscopic data, e.g. ν(C=N) at frequencies ca. 100 cm^{-1} higher than those of the mono(aminocarbyne) complexes, i.e. in the range 1655–1635 cm^{-1} comparable to that of iminium salts

$$\underset{\mathbf{d}}{MeH\overset{+}{N}=C=M=C=\overset{+}{N}HMe}$$

The involvement of the nitrogen electron lone pairs in the π-system (amino groups behaving as electron donors) which thus presents 10 π-electrons delocalised along the NCMCN framework is believed to result in a stabilising effect of the 'dicarbyne' complexes which otherwise would be electron-deficient systems (with six metal–ligand π-electrons) and expected to have a low stability [32,38–41]. The π-bonding of the di(aminocarbyne) complexes (**11a** and **11b**) can be represented by a simplified qualitative π-MO scheme in which the multiple bond characters of the M–C and adjacent C–N bonds, as well as the π-electron release from the metal centre to the π*-CN orbitals of the CNHMe ligands, are accounted for by filled valence MOs with metal–C_α bonding and C_α–N antibonding characters [38].

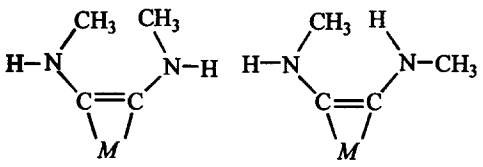
These complexes in solution (e.g. CH_2Cl_2), at room temperature, convert into (the conversion can be monitored by NMR) the corresponding η^2-diaminoacetylene compounds *trans*-$[MX(\eta^2\text{-}MeHNC{\equiv}CNHMe)(dppe)_2]^+$ (**14**) in which the diaminoacetylene ligand behaves as a formal four-electron donor, thus conferring the closed shell 18-electron configuration to the complexes. An extensive π-electron delocalisation occurs, as represented by forms **e**–**i** [$M = M(dppe)_2$, M = Mo or W] or related ones [38].



A partial carbene character of the ligand and a relevant contribution from the C=N bond [ν(C=N) ca. 1645–1630 cm^{-1}] in this description is evident. In agreement with the four-electron donor character of the diaminoacetylene ligand, the metal-bonded carbons exhibit, in the ^{13}C-NMR spectra, a low-field resonance at δ ca. 205 (M = Mo) or ca. 195 (M = W) [38] which, however, occurs at a significantly higher field than that of the metal-ligating carbon of the aminocarbyne CNHMe ligand in the mono- and di-aminocarbyne complexes, i.e. *trans*-[M(CNHMe)(CNMe)-(dppe)$_2$]$^+$ [δ ca. 249 (**10a**) or ca. 242 (**10b**)], *trans*-[M(CNHMe)$_2$(dppe)$_2$]$^{2+}$ [δ ca. 263 (**11a**) or ca. 255 (**11b**)] or *trans*-[ReCl(CNHR)(dppe)$_2$]$^+$ (R = H or Me, δ ca. 223).

The above description of the extensively π-electron delocalised coordination bond of the diaminoacetylene ligand is also corroborated by the X-ray diffraction analysis of *trans*-[MoF(η^2-MeHNC≡CNHMe)(dppe)$_2$][BF_4] (**14a**) [37,38].

Two independent (A and B) complex cations were found in the crystals, differing by the conformations of the diaminoacetylene ligand (forms **j** or **k**) [38].



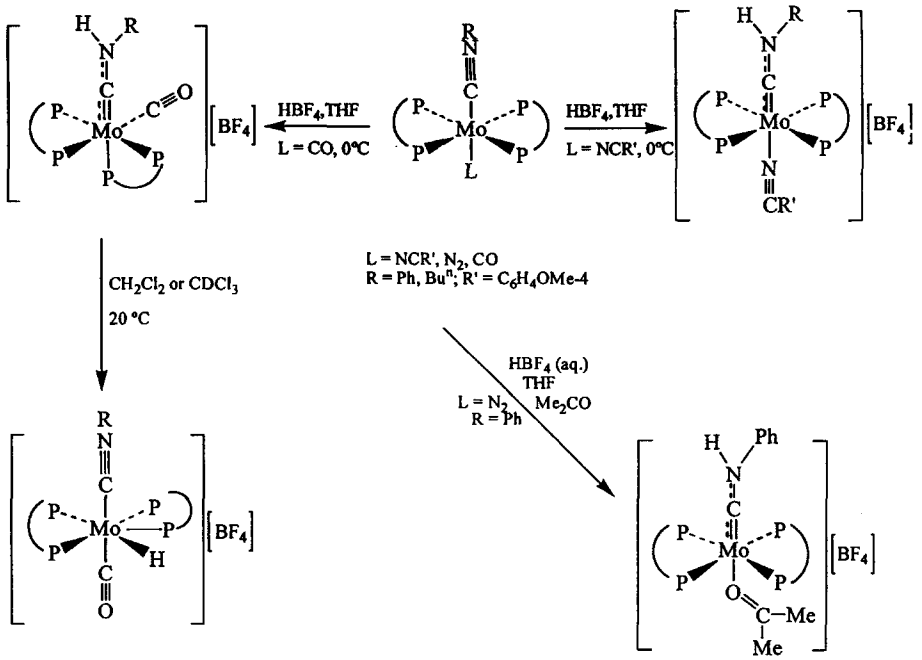
j **k**

The acetylenic C–C bond length, 1.37(1) Å (average), is consistent with a C(sp^2)=C(sp^2) bond and with a four-electron-donor alkyne ligand which also fits the Mo–C distance, 2.013(15) Å (average). The C(alkyne)–N distance, 1.37(2) Å, is somewhat shorter than that expected for a C(sp^2)–N(sp^3) bond and approaches the average value for a C(sp^2)–N(sp^2) bond length [38].

Protic coupling of isocyanide ligands to give diaminoacetylene species is a subject of significant interest to the development of strategies for carbon–carbon bond formation, in particular from small C_1-type species. It has been the object of great attention by other groups in different systems, as shown in the next section.

The protonation of the mono(isocyanide) complexes *trans*-[Mo(CNR)(L)(dppe)$_2$] [R = Ph or ^{n}Bu, L = NCR′ (R′ = C_6H_4OMe-4), N_2 or CO] has been reported recently by Hidai and co-workers (Scheme 7) [42]. These complexes are analogous to the abovementioned diisocyanide compounds *trans*-[Mo(CNR)$_2$(dppe)$_2$] (R = Me or ^{t}Bu), but present one of the isocyanide ligands replaced by an organonitrile, a dinitrogen or a carbonyl ligand (L). Proton attack was only detected at the isocyanide, among all these unsaturated ligands, and the former thus appears to be the more susceptible one to protic attack.

Hence, the aminocarbyne-nitrile complex *trans*-[Mo(CNHR)(NCR′)(dppe)$_2$][BF_4] (R = Ph or ^{n}Bu) was obtained on treatment of *trans*-[Mo(CNR)(NCR′)(dppe)$_2$], in THF at 0°C, with [Me_2OH][BF_4] whereas the aminocarbyne-acetone compound *trans*-[Mo(CNHPh)(Me_2CO)(dppe)$_2$][BF_4] was the isolated final product from the



Scheme 7. Protonation of mono(isocyanide) phosphinic complexes of Mo(0) to give aminocarbyne products [42].

reaction of *trans*-[Mo(CNPh)(N_2)(dppe)$_2$] with aqueous HBF_4 followed by recrystallisation of the crude product [42]. Protonation by [Me_2OH][BF_4] of the mixed isocyanide-carbonyl complexes *trans*-[Mo(CNR)(CO)(dppe)$_2$] (R = Ph or ^{n}Bu) in THF at 0°C affords the *cis*-isomers of the corresponding aminocarbyne-carbonyl products, *cis*-[Mo(CNHR)(CO)(dppe)$_2$][BF_4] (R = Ph or ^{n}Bu), which are unstable in solution at room temperature (20°C) and convert into the hydride-isocyanide complexes [MoH(CNR)(CO)(dppe)$_2$][BF_4] [42]. Methylation of *trans*-[Mo(CNR)(CO)(dppe)$_2$] by [Me_3O][BF_4] in CH_2Cl_2 gives the *cis*isomers of the corresponding aminocarbyne complexes, i.e. *cis*-[Mo(CNMeR)(CO)(dppe)$_2$][BF_4] [42].

The lower stability of the aminocarbyne complexes with a carbonyl co-ligand (in comparison with the related ones with a ligating organonitrile or acetone), in particular resulting into their *trans*-to-*cis* isomerisation and proton migration from the ligated CNHR to the metal, is in accord with the above behaviour of the aminocarbyne complexes bearing an isocyanide co-ligand, i.e. *trans*-[M(CNHR)(CNR)(dppe)$_2$]$^+$ (M = Mo or W, R = Me or ^{t}Bu) (**10**) [32–35] and *trans*-[M(CNRR')(CNR)(dppe)$_2$]$^+$ (R' = Me or Et) [35,36], and is also conceivably accounted for by the destabilising effect of the extensive π-electron acceptance of the ancillary ligand (CO or CNR, respectively).

The molecular structures of some of these aminocarbyne complexes of Mo, i.e. *trans*-[Mo(CNHPh)(Me_2CO)(dppe)$_2$][BF_4] and *cis*-[Mo(CNHPh)(CO)(dppe)$_2$][BF_4] and *cis*-[Mo(CNMe^{n}Bu)(CO)(dppe)$_2$][BF_4], have been determined by X-ray diffraction analyses [42] which corroborate the representation of the aminocarbyne ligand, as observed in the previous cases, as a hydrid of the carbene **a** and carbyne **b** structures (see above).

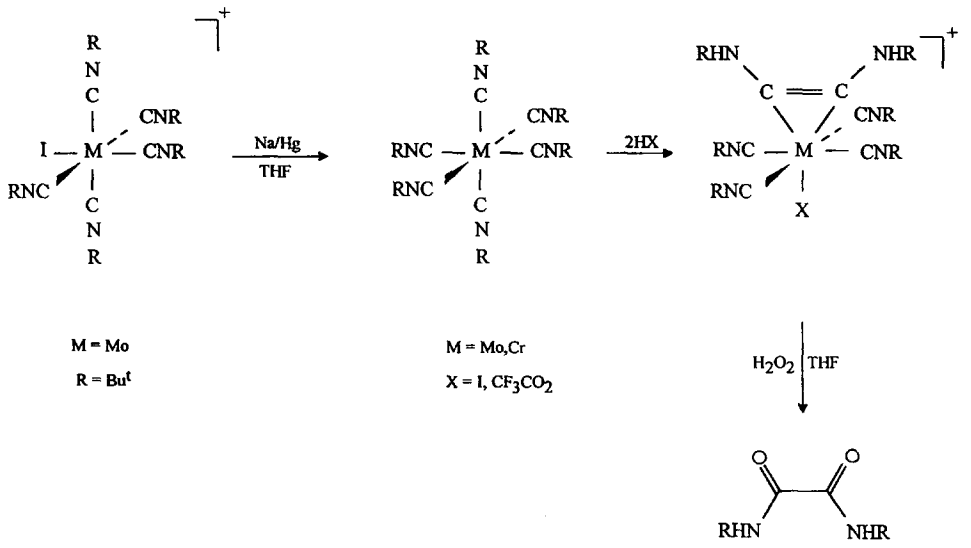
In the case of the protonation reaction of *trans*-[Mo(CN^{n}Bu)(N_2)(dppe)$_2$] by [Me_2OH][BF_4] (THF, 0°C), a different type of product was obtained. On the basis of multinuclear NMR data, it was formulated as the aminocarbene complex *trans*-[MoF(CHNH^{n}Bu)(dppe)$_2$][BF_4] with an agostic α-C–H bond [42]. Its formation corresponds to a double protonation at the CN^{n}Bu ligand, but the involvement of an aminocarbyne intermediate was not established. Moreover, no protic coupling of an isocyanide with another ligand was observed for any of the mono(isocyanide) complexes.

3.2. Other complexes

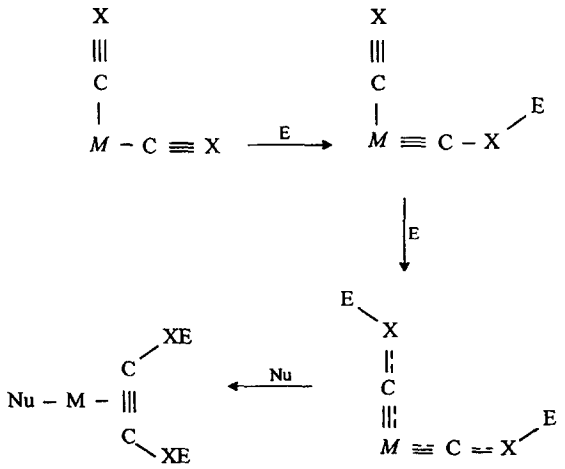
In the systems discussed above, the very high electron-richness of the {M^0(dppe)$_2$} (M = Mo or W) binding metal centres activates the ligating isocyanides to N-protonation to give the aminocarbyne species, without the need of any external electron source. However, when the binding metal site is not sufficiently electron-rich to activate the isocyanide towards protonation, the use of an external reducing agent can, in some cases, promote such a reductive coupling which was recognised for the first time by Lippard and co-workers [43] in 1977 in a system involving the hepta-coordinate Mo(II) complex [MoI(CN^{t}Bu)$_6$]I, a reducing agent (Zn) and a proton source, which, under refluxing conditions, gives the η^2-diaminoacetylene complex [MoI(η^2-^{t}BuHNC≡CNH^{t}Bu)(CN^{t}Bu)$_4$]I. This and related reactions have been reviewed [44] and shown to occur by first reduction (by Zn or Na/Hg) of the Mo(II) complex to the electron-rich Mo(0) homoleptic [Mo(CN^{t}Bu)$_6$] compound which, on reaction with acid (HX, e.g. $X^- = I^-$ or $CF_3CO_2^-$), forms the coupled product *trans*-[MoX(η^2-^{t}BuHNC≡CNH^{t}Bu)-(CN^{t}Bu)$_4$]X (Scheme 8). This study was later extended to the related Cr(0) complex [Cr(CN^{t}Bu)$_6$] which, on reaction with HI, affords the diaminoacetylene complex *trans*-[CrI(η^2-^{t}BuHNC≡CNH^{t}Bu)(CN^{t}Bu)$_4$]I [45]. The coupled ligand could be removed from this complex [45], as well as from its Mo analogue [46], in the form of *N,N'*-di-*tert*-butyloxamide, ^{t}BuHNC(=O)–C(=O)NH^{t}Bu, on oxidation by H_2O_2.

Related C–C coupling reactions were also investigated for carbon monoxide and evidence, although usually indirect, for the involvement of aminocarbyne or oxycarbyne intermediates (in the cases of CNR or CO couplings, respectively) was presented in these and related studies on Groups 6 and 5 transition metal complexes by the same group [19,45–47] as well as by Filippou's [39,48–52] and Mayr's [40,53,54] groups. They showed that electrophilic attack of a sufficiently activated alkyl isocyanide or CO ligand forms aminocarbyne M≡CNER (M = Mo or W centre, E = H or R, R = alkyl) or e.g. siloxycarbyne M≡COSiR_3 (M = V, Nb or Ta

centre) species which can lead to the formation of the corresponding diaminoacetylenes (RENC≡CNER) or acetylene diether ($R_3SiOC{\equiv}COSiR_3$) ligands. Cross-coupling reactions have also been accomplished and nucleophile-induced coupling at carbyne complexes was recognised in some cases. Such isocyanide or carbonyl coupling reactions to give an alkyne are believed to occur as shown in Scheme 9, the first two steps involving the sequential addition of an electrophile (E)



Scheme 8. Protic C–C coupling of isocyanides and peroxidative removal of the derived diaminoacetylene [43–45].



Scheme 9. Electrophilically induced C–C coupling of CNR or CO ligands (X = NR or O, respectively).

at the heteroatom of the CNR or CO ligands, to give a mono- and a di-carbyne intermediates, and the last step consisting of the coupling of the carbyne ligands in the latter complex promoted by the addition of a nucleophile (Nu) to the metal.

Hence, e.g. proton-induced coupling of carbyne and isocyanide ligands was observed namely by reaction of the carbyne complexes of the type $[MX(\equiv CR)(CO)_n(CN^tBu)_{4-n}]$ (M = Mo or W, X = Br or I, $n = 0$–2, R = Ph or NEt_2) or $[M(CNREt)(CNR)_5][BF_4]$ (R = Et or ^{t}Bu) with HX [Scheme 10(a and b)] to give the aminoalkyne (ynamine or ynediamine) complexes $[MX_2(\eta^2\text{-}RC{\equiv}CNH^tBu)(CO)_n(CN^tBu)_{3-n}]$ and $[MX(\eta^2\text{-}EtRNC{\equiv}CNHR)(CNR)_4][BF_4]$, respectively [48]. Conversely, the reverse reaction, i.e. the base-induced cleavage of the C≡C bond of the aminoacetylene ligand to give the carbyne and isocyanide ligands was also achieved [48d,e].

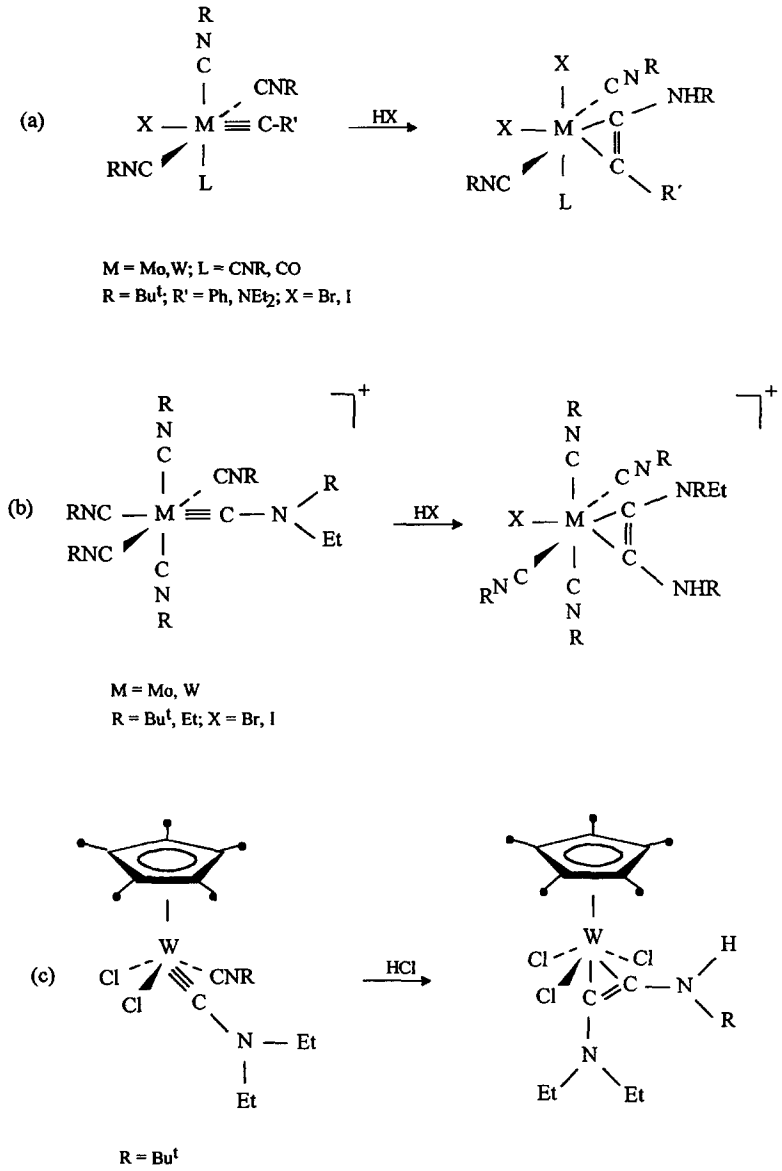
Similarly, reaction of *cis*-$[(Cp^*)WCl_2(CNEt_2)(CN^tBu)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (with the metal in a higher oxidation state) with HCl yields $[(Cp^*)WCl_3(\eta^2\text{-}^tBuHNC{\equiv}CNEt_2)]$ [Scheme 10(c)], whereas HCl adds across the metal–carbon triple bond in the related aminocarbyne complex without isocyanide ligand *cis*-$[(Cp^*)WCl_2(CNEt_2)\{P(OMe)_3\}]$ to give the carbene complex $[(Cp^*)WCl_3(=CHNEt_2)]$ which, on treatment with CN^tBu, forms $[(Cp^*)WCl_2(CNEt_2)(CN^tBu)_2]Cl$ without C–C coupling [49c]. This suggests that the carbene complex is not an intermediate in the above isocyanide–aminocarbyne coupling reaction which is believed (see Scheme 9) to occur via protonation of the isocyanide, i.e. a di(aminocarbyne) species.

However, the formation of the aminocarbyne intermediate in some of the above proton-induced carbyne–isocyanide coupling reactions in lower-valent complexes, e.g. $[WCl(CPh)(CO)(CN^tBu)(PMe_3)_2]$, appears to involve a first proton addition to the carbyne carbon to give a carbene ligand (=CHPh) followed by proton migration to the isocyanide-N atom (Scheme 11) [40,53b,54d,e]. No evidence for protonation at the metal centre was obtained.

The coupling of the two aminocarbyne ligands in $[(Cp^*)W(CNEt_2)_2(CNEt)][BF_4]$, generated by alkylation ($[Et_3O][BF_4]$) of the isocyanide–aminocarbyne precursor $[(Cp^*)W(CNEt_2)(CNEt)_2]$, was shown to be induced either by a nucleophilic reagent (CNEt) or an oxidizing agent (Br_2) to give, via a nucleophilic addition or an oxidative addition reaction (Scheme 12), the diaminoacetylene complexes $[(Cp^*)W(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)(CNEt)_2][BF_4]$ or $[(Cp^*)WBr_2(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)(CNEt)][BF_4]$, respectively [49a,b].

In these systems, the aminocarbyne and the derived diaminoacetylene ligands display structural features and coordination modes similar to those discussed above for our complexes with the $\{M(dppe)_2\}$ (M = Mo or W) metal sites. Moreover other electrophile- or nucleophile-induced coupling reactions of carbyne ligands (or with isocyanide or carbon monoxide) have also been described, mainly for some tungsten systems [40,53,54].

Isocyanide coupling in external oxidising conditions has recently been reported [55] for the reactions of the Group 5 metallate carbonyls $[M(CO)_6]^-$ (M = Nb or V) in THF with CN^tBu and I_2, in the presence of water, to give the corresponding diaminoacetylene complexes $[MI_2(\eta^2\text{-}^tBuHNC{\equiv}CNH^tBu)_4]I$. In the case of the Nb



Scheme 10. Protic coupling of carbyne and isocyanide ligands: (a) and (b) at lower [48]; and (c) higher valent [49c] molybdenum or tungsten complexes.

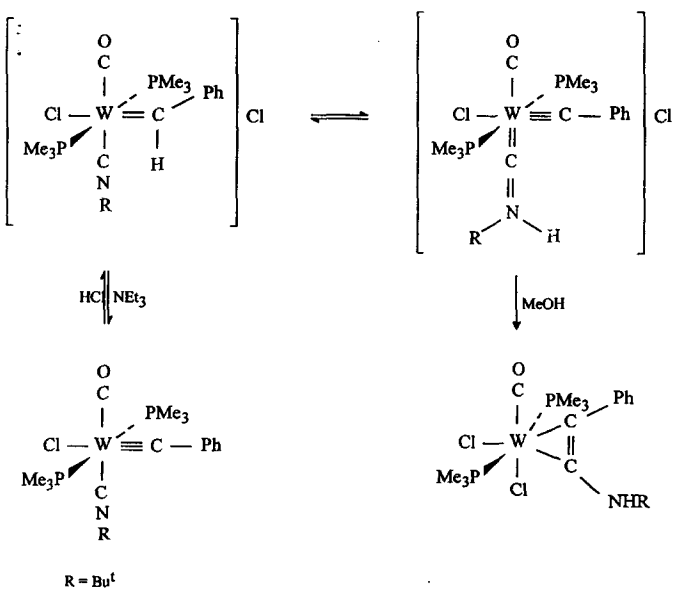
system, $[NbI(CO)_2(CN^tBu)_4]$, formed on oxidation of the starting Nb(−I) carbonyl by I_2 (in a controlled amount to avoid further oxidation to higher oxidation states metal species) is shown to convert into the final acetylene product by reaction with H_2O and is suggested [55b] to be a key intermediate in the coupling process. However, one should note that it exhibits IR ν(C≡N) at quite high wavenumbers

(2198 and 2155 cm^{-1}) and no evidence for the formation of any derived aminocarbyne intermediate by direct protonation at the isocyanide N-atom has been found.

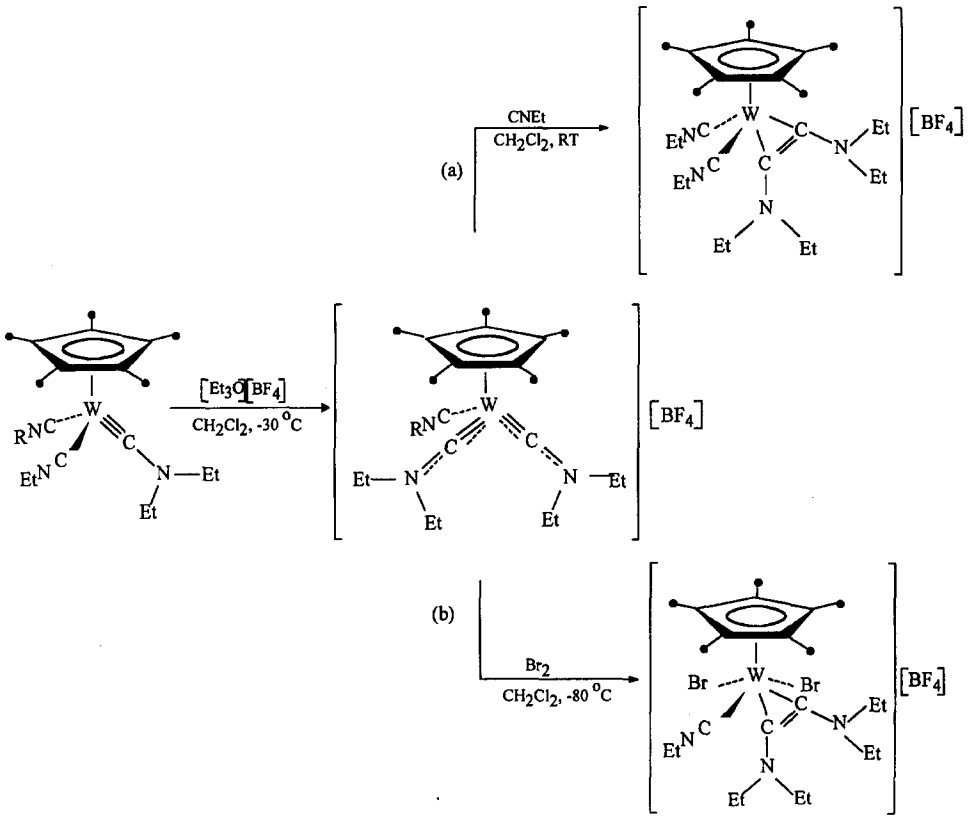
3.3. Mechanisms of protonation of isocyanides and of the protic C–C coupling in the diisocyanide complexes with the {M(dppe)$_2$} (M = Mo or W) centres

In spite of the rich investigation on C–C coupling reactions discussed above, in the great majority of cases the factors which drive the protic coupling step of isocyanides had not been fully elucidated. Moreover, no detailed mechanistic investigation had been reported, neither any kinetic study had identified the reactive species. Therefore, detailed mechanistic studies by stopped-flow spectrophotometry were performed on the above protonation reactions of coordinated isocyanides and ligand coupling in *trans*-[M(CNR)$_2$(dppe)$_2$] (R = Me or ^{t}Bu), allowing to estimate the rates of protonation of the metal and isocyanide sites, to demonstrate unambiguously the crucial role of the di(aminocarbyne) complexes as intermediates and to define factors of the acid-catalysed coupling reaction [56].

For the methylisocyanide complex *trans*-[Mo(CNMe)$_2$(dppe)$_2$] (**9a**) the mechanism of protonation (by HCl) was then showed (Scheme 13) to involve (first phase) the initial rapid ($k_1 \geq 1 \times 10^6$ $dm^3\,mol^{-1}\,s^{-1}$) proton addition to one of the isocyanide ligands (within the dead time of the stopped-flow spectrophotometer, 2 ms) to give the mono-aminocarbyne complex *trans*-[Mo(CNHMe)(CNMe)(dppe)$_2$]$^+$ (**10a**) which, for relatively low acid concentration, under-



Scheme 11. Proton-induced C–C coupling of isocyanide and carbyne ligands via initial protonation of the latter [40,53b,54d,e].

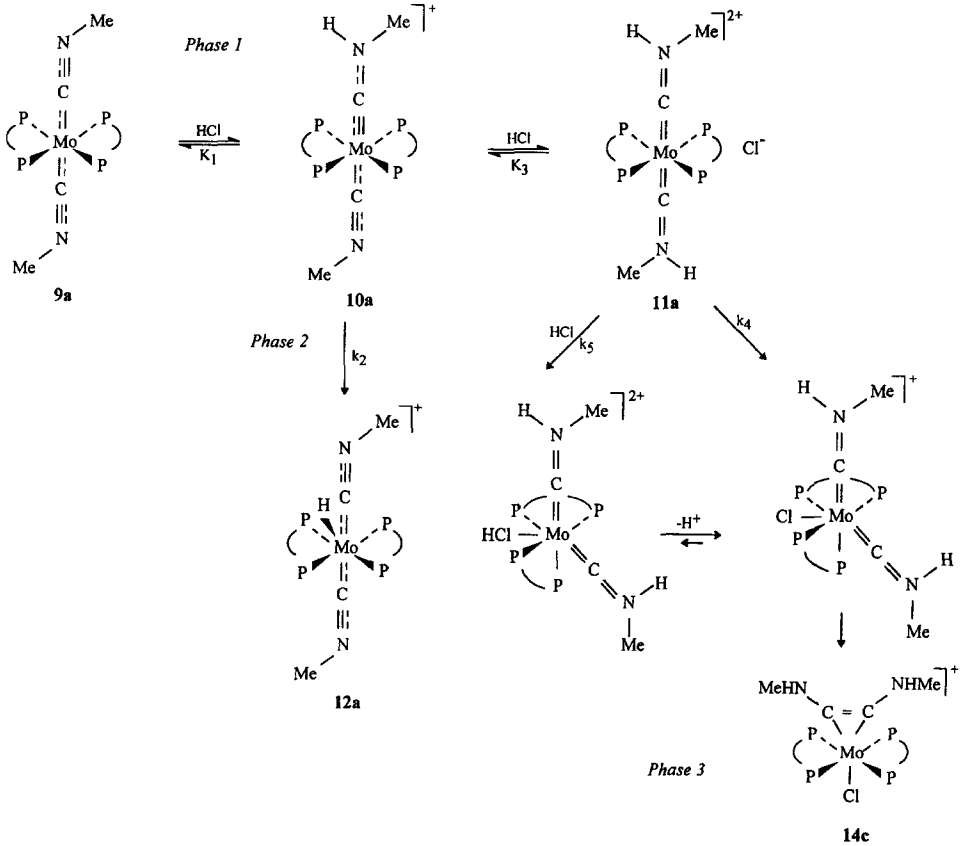


Scheme 12. Coupling of aminocarbyne ligands promoted by: (a) a nucleophilic addition or (b) an oxidative addition reaction [49a,b].

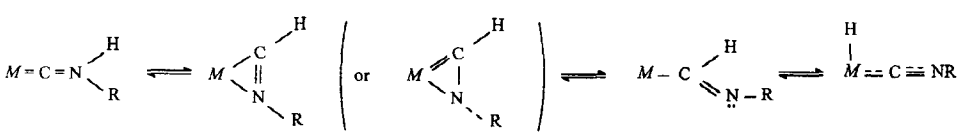
goes (second phase) rate-limiting ($k_2 = 8.2\ s^{-1}$) intramolecular migration of the hydrogen from the aminocarbyne to the metal yielding the hydride complex $[MoH(CNMe)_2(dppe)_2]^+$ (**12a**) which is then the dominant obtained product (e.g. ca. 94% for [HCl]/[Mo] = 2.0 when the initial concentration of the diisocyanide complex is 2.0 mmol dm^{-3}). The detailed pathway for this intramolecular H-migration process could not be established, but the involvement of a $\eta^1 \rightarrow \eta^2$ rearrangement of the aminocarbyne ligand was postulated (Scheme 14) [56].

However, for higher acid concentrations, further rapid protonation of the mono(aminocarbyne) complex occurs to give the then predominant di(aminocarbyne) *trans*-$[Mo(CNHMe)_2(dppe)_2]^{2+}$ (**11a**) in an equilibrium mixture (the first and second protonation steps correspond to rapidly established equilibria, K_1 and K_3). The hydride-forming pathway (phase 2) is then replaced by another one (phase 3) which involves the aminocarbyne coupling process at the di(aminocarbyne) intermediate to give *trans*-$[MoCl(\eta^2\text{-MeHNC}{\equiv}CNHMe)(dppe)_2]^+$ (**14c**). This transformation can occur either: (i) via an acid-independent pathway

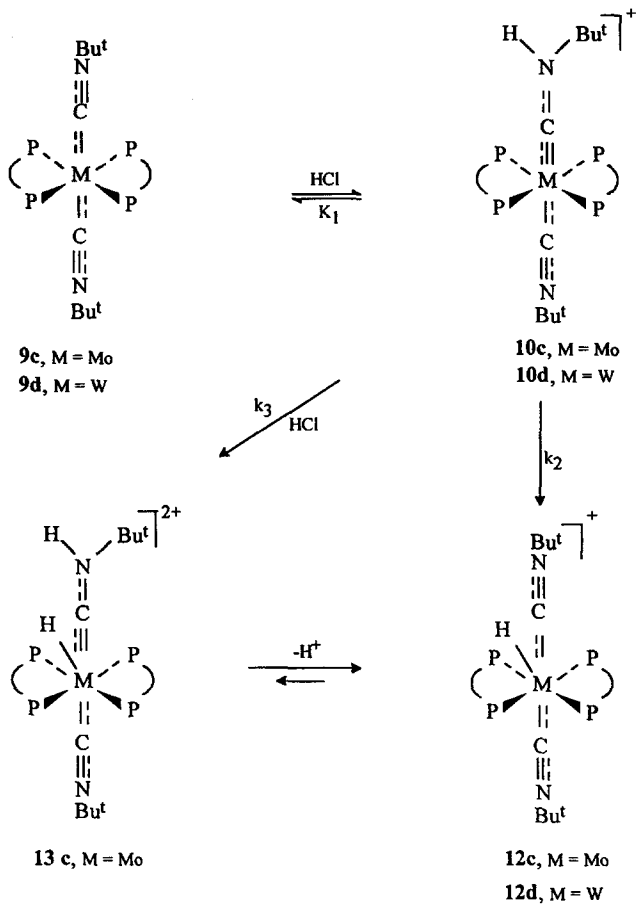
[$k_4 = (1.1 \pm 0.9) \times 10^{-2}$ s^{-1}] involving a *trans*-to-*cis* isomerisation (to bring the aminocarbyne ligands adjacent to one another to allow their coupling) and a nucleophilic chloride attack to the metal [from the ion-pair between this ion and the di(aminocarbyne) intermediate, in the low relative permittivity THF solvent, thus following a first-order process]; or (ii) via an acid-dependent route corresponding to the nucleophilic attack by the chlorine atom in HCl (a poorly dissociated acid in THF) [$k_5 = (32.3 \pm 0.9)$ dm^3 mol^{-1} s^{-1}] followed by rapid proton loss (increase of



Scheme 13. Mechanisms of protonation of the di(methylisocyanide) complex *trans*-[Mo(CNMe)$_2$(dppe)$_2$] (**9a**) to give aminocarbynes, hydride and (diamino)acetylene products [55].



Scheme 14. Proposed pathway for the intramolecular rearrangement of an aminocarbyne to a hydrido-isocyanide species [56].



Scheme 15. Mechanism of protonation of the di(*tert*-butylisocyanide) complexes *trans*-$[M(CN^tBu)_2(dppe)_2]$ (**9c**, M = Mo; **9d** W) to give aminocarbyne, hydride and hydride–aminocarbyne products [56].

the acidity of HCl on coordination), thus following an acid-catalysed process (involving also *trans* → *cis* isomerisation) [56].

The coupling of the two *cis*-aminocarbyne ligands finally occurs at the common and postulated seven-coordinate *cis*-$[MoCl(CNHMe)_2(dppe)_2]^+$ intermediate leading to the final η^2-diaminoacetylene complex **14c**.

The mechanism of the reaction of HCl with the ^{t}butylisocyanide complexes *trans*-$[M(CN^tBu)_2(dppe)_2]$ (M = Mo **9c** or W **9d**) to form the corresponding hydride complexes $[MH(CN^tBu)_2(dppe)_2]^+$ (**12c** or **12d**) was also investigated by stopped-flow spectrophotometry [56] and shown (Scheme 15) to involve also an initial rapid N-protonation ($k_1 \geq 1 \times 10^5$ dm^3 mol^{-1} s^{-1}) to give the aminocarbyne intermediates *trans*-$[M(CNH^tBu)(CN^tBu)(dppe)_2]^+$ (**10c** or **10d**) which then convert into the corresponding hydride complexes **12c** or **12d** by an intramolecular acid-independent

H-migration from CNH^{t}Bu to the metal [$k_2 = 0.48 \pm 0.01$ s^{-1} (M = Mo) or 1.25 ± 0.06 s^{-1} (M = W)] [56] as observed (see above) for the CNMe complexes. However, the conversion of the aminocarbyne–Mo to the hydride complex can follow an alternative acid-dependent route via further protonation of the former complex to give a dicationic hydride-aminocarbyne intermediate **13c** ($k_3 = 76.4 \pm 2.2$ dm^3 mol^{-1} s^{-1}) which, on proton loss from the aminocarbyne ligand, forms the final hydride product [56].

A notorious difference between the above *tert*-butylisocyanide and the methylisocyanide systems is that the aminocarbyne coupling reaction does not occur in the former, conceivably due to steric factors, involving the *tert*-butyl and phenyl groups of the two bulky dppe ligands that prevent the formation of the seven-coordinate *cis*-intermediate that would result from *trans* → *cis* isomerisation and nucleophilic addition to the metal.

3.4. Other aminocarbyne reactions

Apart from the C–C coupling reactions of ligated aminocarbynes to give aminoacetylenes, the CNHR ligands can also be considered [29] to represent intermediate stages in the enzymatic reduction of isocyanides to amines or ammonia and hydrocarbons [see also Section 2.2 and Scheme 4(b)]. In fact, such products have been obtained on treatment of the isocyanide complexes *trans*-[Mo(CNMe)$_2$(PMe$_2$Ph)$_4$] or *mer*-[W(CNMe)$_3$(PMe$_2$Ph)$_3$] (with labile phosphine co-ligands) with H_2SO_4 or HCl in methanol or ethanol, or in methanol alone, under W-filament irradiation, and an intermediate dinuclear μ-aminocarbyne species was isolated in the W system [15b]. No external reducing agent was employed and the maximum overall yield corresponded to the consumption of the six valence electrons of the binding Mo(0) or W(0) d^6 metal. These reactions paralleled the reduction of N_2 to NH_3 by similar acid or methanol treatment of *cis*-[M(N$_2$)$_2$(PMe$_2$Ph)$_4$] (M = Mo or W) [57,58] which are the parent complexes of the above isocyanide compounds, in reactions that are considered models of nitrogenase activity.

The dialkylaminocarbyne ligands CNR$_2$ (or CNRR′) can be obtained not only by alkylation of an activated isocyanide (CNR) ligand by an electron-rich metal centre, e.g. at *trans*-[M(CNR)$_2$(dppe)$_2$] (M = Mo or W; R = Me or ^{t}Bu) (**10a–10d**) [35,36] (see above) or at the metallates Na[(η^5-C$_5$R$''_5$)M(CO)$_n$(CNR)$_{3-n}$] (R$''$ = H or Me, R = Et or ^{t}Bu, $n = 2$ or 1) [50] but also from a ligated CO activated towards nucleophilic attack, in a polycarbonyl complex. The latter complex is known [59] since long in the synthesis of [MX(CNR$_2$)(CO)$_4$] (M = Mo or W, X = Cl, Br or I, R = Me or Et) from [M(CO)$_6$] (a similar process has been applied to chromium species [52c]), following a particular route of Fischer's general method to carbyne complexes, involving a complex sequence of a nucleophilic addition of an amide (e.g. LiNR$_2$) to the ligated C-atom followed by alkylation of the O-atom to give an alkoxy(dialkylamino)carbene intermediate, =C(OR)NR$_2$, which on reaction with a suitable Lewis acid [e.g. BX$_3$ or XC(O)C(O)X] generates the CNR$_2$ species. Another synthetic route involves the thermal rearrangement of the hydrido-thiocarbamoyl

complexes $[MoH\{\eta^2\text{-}C(S)NMe_2\}(LL)_2]$ [LL = dppe or depe ($Et_2PCH_2CH_2PEt_2$)] to the corresponding hydridosulfido-aminocarbynes *trans*-$[Mo(SH)(CNMe_2)(LL)_2]$, which is proposed to occur via hydride shift to the S atom of the thiocarbamoyl ligand followed by migration of the hydrosulfido group from the thus generated carbene ligand to the metal [60].

Features of general reactivity patterns of dialkylaminocarbyne complexes (without direct involvement of the aminocarbyne ligand) have been compared [48b,49c,51a,b] with those of typical Fischer-type and Schrock-type carbyne (≡CR, R = alkyl or aryl) complexes. Although this approach is out of the scope of this review on isocyanide-derived aminocarbyne complexes, it is noteworthy to mention some types of reactions that involve directly the CNR_2 ligands irrespective of their origin.

Hence, e.g. the CNR_2 ligands in the neutral low-valent half-sandwich complexes $[(Cp)W(CNEt_2)(CO)_2]$ (Cp = η^5-C_5H_5) [61], $[(Cp^*)W(CNEt_2)(CO)(L)]$ (L = CNEt, CN^{t}Bu or PMe_3) [52a], $[(Cp^*)WCl_2(CNEt_2)\{P(OMe)_3\}]$ [49c] and $[(Cp^*)Cr(CN^iPr_2)(CO)_2]$ [52b] are susceptible to protonation by HX (X = Cl or Br) which occurs at the ligated aminocarbyne-carbon [Scheme 16(a–c)] to give the corresponding aminocarbene (or aminomethylene) ($CHNR_2$) complexes $[(\eta^5\text{-}C_5H_5)WCl(CHNEt_2)(CO)_2]$, $[(Cp^*)W(Br)(CHNEt_2)(CO)(L)]$, $[(Cp^*)WCl_3(CHNEt_2)]$ and $[(Cp^*)CrX(CHN^iPr_2)(CO)_2]$, formed via overall HX addition across the metal–carbon triple bond of the initial aminocarbyne complexes.

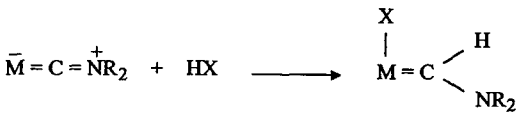
Similar reactions were reported [62] for the carbonyl complexes *trans*-$[MCl(CN^iPr_2)(CO)_3(PPh_3)]$ (M = Mo or W) which, on treatment with the dithiocarbamate salts $[NH_4][S_2CN(CH_2)_4]$, $[Et_2NH_2][S_2CNEt_2]$ or hydrated $Na[S_2CNMe_2]$, form the corresponding dithiocarbamate-aminocarbene complexes $[M(\eta^2\text{-}S_2CNR_2)_2(CNH^iPr_2)(CO)_2]$ [$R_2 = (CH_2)_4$, Et_2 or Me_2] [Scheme 16(d)].

The site of protonation is not the aminocarbyne-N atom in accord with the relevant contribution of the C=$\overset{+}{N}$R2 canonical form, and the reaction can be considered (if envisaged for CNHR instead of CNR_2) as a further step, beyond the aminocarbyne stage, in the protic conversion of an isocyanide to an amine or methane plus ammonia (see above).

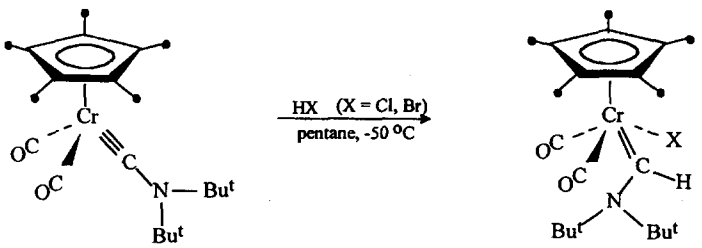
Other limited examples of reactions involving a CNR_2 ligand include the addition of CO_2 across the metal–carbon triple bond in the anionic diethylaminocarbyne complex $[(CO)_4Mo(\mu\text{-}PPh_2)_2W(CNEt_2)(CO)_2][NEt_4]$ to form the four-membered metallacycle $[(CO)_4Mo(\mu PPh_2)_2W\{=C(NEt_2)(C(=O)O\}(CO)_2][NEt_4]$ [63], and the [2 + 2]-cycloaddition (also across the W≡C bond) of $[(Cp^*)W(CNEt_2)(CO)_2]$ with the nitrilium salts $[RC{\equiv}NR'][BF_4]$ (R, R′ = alkyl) to give the η^3-iminocarbene complexes $[(Cp^*)W\{\eta^3\text{-}C(NEt_2)C(R)NR'\}(CO)_2][BF_4]$ [52c,d].

The ligation of one of the metal–C(carbyne) π-bonds of an aminocarbyne species, $M(CNRR')$, to a suitable transition metal fragment M' to form a bridging aminocarbyne ligand in a new heteronuclear complex has also been reported [64] and $[AuW\{\mu\text{-}CN(Et)Me\}(C_6F_5)(CO)_2(Cp)]$, $[\{CuW\{\mu\text{-}CN(Et)Me\}Cl(CO)_2(Cp)_2\}]$, $[M\{W\{\mu\text{-}CN(Et)Me\}(CO)_2(Cp)\}_2]^+$ (M = Cu, Ag or Au) or $[AuW\{\mu\text{-}CN(Et)Me\}(CO)_2(PPh_3)(Cp)]^+$, have been derived from the reactions of the

mononuclear aminocarbyne [W{CN(Et)Me}(CO)$_2$(Cp)] with the Group 11, d^{10}, metal species [Au(C$_6$F$_5$) (tetrahydrothiophene)], CuCl, [AuCl(PPh$_3$)], [CuI(PPh$_3$)] or [Ag(NO)$_3$(PPh$_3$)]. In these heteronuclear adducts the bonding of the bridging



(a)



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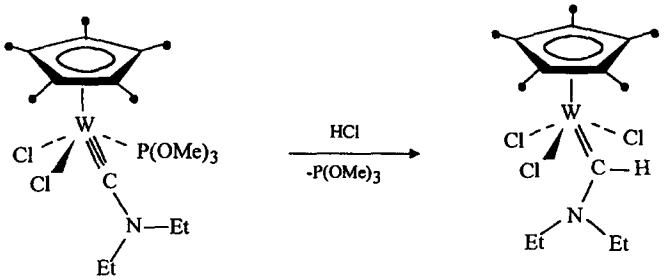
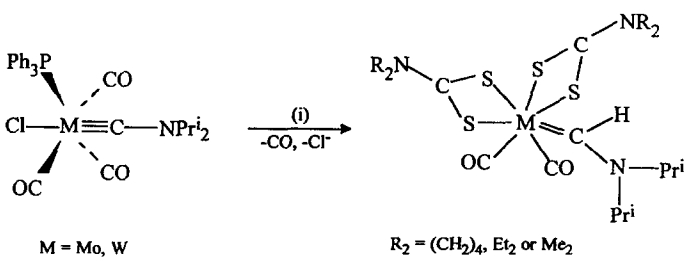


(c)



(d)

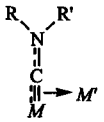
M = Mo, W

R_2 = $(CH_2)_4$, Et_2 or Me_2

(i) $[NH_4][S_2CN(CH_2)_4]$, $[Et_2NH_2][S_2CNEt_2]$ or $Na[S_2CNMe_2].2H_2O$

Scheme 16. α-protonation of aminocarbyne ligands (a: general reaction) in low-valent half-sandwich (b [52b] or c [49c]) or carbonyl (d [62]) complexes.

aminocarbyne ligand is described by form **I**, with a delocalised $M{\equiv}C{-}N$ π-bond [64] as in the starting mononuclear complex. These reactions extend to aminocarbyne ligands the well-established [65] addition reactions of mononuclear organocarbyne species, $M{\equiv}CR$, to a variety of transition-metal fragments to form dimetallacyclopropene complexes.



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We have already discussed above the coordination chemistry of alkylaminocarbyne species, CNHR, at Mo- or W-diphosphinic centres, which were derived from N-protonation at isocyanide (CNR) ligands. The simplest aminocarbyne CNH_2 was also generated at the same type of metal centres, in *trans*-$[MCl(CNH_2)(dppe)_2]$ (M = Mo [66] or W [67]), by double protonation of a cyanide ligand induced cathodically. The W compound undergoes a single-electron chemical or electrochemical oxidation to give the corresponding cationic species and the X-ray diffraction analyses of these two complexes indicate that the coordinated CNH_2 is best described by a dominant carbene (iminomethylenium, $=C{=}NH_2^+$) form. In particular, the C–N bond lengths of 1.200(12) or 1.156(24) Å [67], respectively, are shorter than that, 1.309(5) Å [8], of *trans*-$[ReCl(CNH_2)(dppe)_2][BF_4]$. The strong contribution of the canonical form $\bar{M}{=}C{=}\overset{+}{N}H_2$ (with localisation of electron density at the metal) is considered to account for the labilising effect of the ligating aminocarbyne on the Cl ligand *trans* to it, as observed in the ready ionisation of *trans*-$[MoCl(CNH_2)(dppe)]$ in the polar solvent NCMe to give *trans*-$[Mo(CNH_2)(NCMe)(dppe)_2]Cl$ [66].

Interestingly, *trans*-$[WCl(CNH_2)(dppe)_2]$ can behave as a 2H atom-transfer reagent to azobenzene (Ph–N=N–Ph) which is converted, in THF at 50°C, into hydrazobenzene (PhNHNHPh), as confirmed by deuterium experiments [67].

4. Outlook and prospects

The activation of isocyanides by low-valent electron-rich metal centres towards β-electrophilic addition provides a simple method to the synthesis of aminocarbyne (CNHR or CNR_2) complexes and therefore a convenient entry in this field of coordination and organometallic chemistry of multiple metal–carbon bonded species which still remains little explored in contrast with the extensively investigated chemistry of conventional Fischer-type and Schrock-type carbyne complexes.

The coordination bond and structure of the aminocarbyne ligands have already been well established, but their syntheses should be extended to a wider variety of transtion-metal centres and their reactivity, although promising, has only been investigated in a still limited number of situations. The most studied reaction is the proton-induced C–C coupling of isocyanides, to give aminoacetylenes, that has

been shown to involve aminocarbyne species as the key intermediates in the coupling process; various steps have been identified in a few cases and the detailed kinetics and mechanism have been established in one of them (detailed mechanistic studies are expected for other cases).

Protonation of CNR_2, deprotonation (by base or induced anodically) or dehydrogenation (cathodic or chemical, with CNH_2 behaving in a single case as 2H atom-transfer reagent to a particular substrate) of CNHR or CNH_2, and addition of unsaturated electrophiles across the metal–carbon triple bond (CNR_2 ligands) are still limited to rare cases but demonstrate the potential versatile chemistry of the aminocarbyne ligands and their use for syntheses.

Further developments on these and other reactions are foreseen, namely by extending the aminocarbyne C–C coupling reaction to cross-couplings between aminocarbynes and other unsaturated compounds, by performing the addition and cycloaddition reactions with a variety of unsaturated species, by developing the reactivity towards nucleophiles and electrophiles, by attempting to achieve the protic conversion of CNHR and CNH_2 into the products of nitrogenase reduction of isocyanides and aqueous cyanide, etc.

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