Aminocarbyne Ligands in Organometallic Chemistry

Lorenzo Biancalana, Fabio Marchetti *

University of Pisa, Department of Chemistry and Industrial Chemistry, Via Moruzzi 13, I-56124 Pisa.

Email address: fabio.marchetti1974@unipi.it

Webpage: https://people.unipi.it/fabio_marchetti1974/

ORCID ID:

Lorenzo Biancalana 0000-0002-9276-0095

Fabio Marchetti 0000-0002-3683-8708

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Abstract. Following the former synthetic work by the group of Ernst Otto Fischer on group 6 metal complexes, aminocarbyne (aminoalkylidyne) ligands have become popular across various transition metal groups. They are versatile ligands adapting to variable coordination modes (i.e. terminal, bridging and multibridging), metal oxidation states and co-ligands. They possess peculiar structural and reactivity features compared to nitrogen-lacking alkylidyne ligands, and especially when bridging coordinated to diiron bis-cyclopentadienyl frames exhibit a rich chemistry enabling the construction of unusual organometallic species. The bonding, electronic and steric effects, structural and spectroscopic features and reactivity trends of aminocarbyne ligands are reviewed with reference to the distinct cases (nuclearity of the complex and coordination mode, nature of the metal element, and type of substituent(s) on the aminocarbyne).

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1. Introduction

Carbyne (alkylidyne) ligands [1] constitute a milestone of organometallic chemistry, they have been reported for a wide variety of transition metal complexes and exhibit a versatile reactivity enabling important applications in organic synthesis [2]. On occasion of his Nobel lecture entitled "*On the road to carbene and carbyne complexes*", in 1973 Ernst Otto Fischer presented a very recent finding from his laboratory, i.e. the synthesis of the first metal-carbyne species (Equation 1) [3]. Everything originated from the attempt of the PhD student Gerhard Kreis to obtain the bromo-alkylidene $[Cr(CO)_5\{C(Br)Ph\}]$ via the reaction of $[Cr(CO)_5\{C(OMe)Ph\}]$ with BBr_3, which led instead to an air-sensitive yellow solid with a suspicious, low oxygen content according to elemental analysis [4].

$$[M(CO)_5\{C(OMe)R\}] + BX_3 \rightarrow [MX(CO)_4(CR)] + CO + BX_2(OMe) \quad (1)$$

M = Cr, Mo, W; R = Me, Ph; X = Cl, Br, I

Following such serendipitous and exciting discovery, Fischer and co-workers intensively worked to develop this piece of chemistry, and it was using the same strategy that soon after (1974) they reported the first aminocarbyne complex (Equation 2) [5].

$$[W(CO)_5\{C(NEt_2)(OEt)\}] + BX_3 \rightarrow [WX(CO)_4(CNEt_2)] + CO + BX_2(OEt) \quad (2)$$

X = Br, I (pentane solution)

One year later, Richards, Pombeiro and co-workers described the one-step synthesis of two aminocarbyne complexes from the protonation of isocyanides coordinated to an electron-rich metal center (Equation 3) [6].

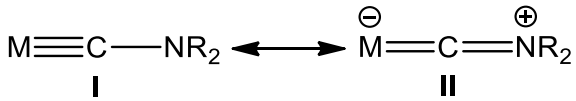
$$[M(CNMe)_2(dppe)_2] + 2HBF_4 \rightarrow [M(CNHMe)_2(dppe)_2][BF_4]_2 \quad (3)$$

M = Mo, W; dppe = $Ph_2P(CH_2)_2PPh_2$ (CH_2Cl_2 solution)

These pioneeristic findings led to the synthesis of numerous aminocarbyne complexes of group 6 metals. Then, many other metal aminocarbyne species with variable nuclearity have been prepared based on transition elements belonging to groups 5 to 11; their chemistry has been widely investigated and is still arousing a considerable attention, showing a plethora of reactivity profiles and outcomes. Most frequently, aminocarbynes are found coordinated in low valent metal complexes, and in such cases they are regarded as belonging to the class of Fischer alkylidynes. According to theoretical studies, the bond between a metal center (M) and a Fischer carbyne (CR) is formally described in terms of a positively charged two-electron donor fragment $\{CR^{+}\}$, contributing to the decrease of the oxidation state of the metal by one unit [7,8]. Frenking concluded that "although there is no direct connection between partial charges and formal-oxidation state, the charge distribution suggests that the Fischer carbyne complexes $[X(CO)_4W(CR)]$ (X = monoanionic ligand) should be considered as W^0 compounds" [8]. On the other hand, a Schrock alkylidyne is usually envisaged as a $\{CR^{3-}\}$ fragment and, however, ambiguities between the two types of alkylidynes are frequently encountered. With reference to the bonding scheme, in Fischer alkylidyne complexes the σ-donation from the lone pair on the sp orbital of $\{CR^{+}\}$ is counterbalanced by π backdonation directed from the metal to two empty p-orbitals (triple M≡C bond).

The introduction of the amino-substituent induces peculiar structural and reactivity properties. Thus, the competition of the nitrogen for the empty π-orbital(s) on the carbyne weakens the metal-carbon bond, suggesting a representation with a significant contribution from the 2-azavinylidene resonance (Scheme 1). When the aminocarbyne behaves as a μ_2-bridging ligand, the carbon-nitrogen bond usually maintains a significant double character, as it will be outlined in the appropriate sections of this review. Depending on the degree of substitution, aminocarbyne ligands are distinguished in tertiary (CNRR'), secondary (CNHR) and primary (CNH_2) aminocarbynes. The main chemical

implication of the presence of the amino group is a sluggish reactivity, compared to classical alkylidyne compounds.



Scheme 1. Aminocarbyne (**I**) and 2-azavinylidene (**II**) canonical forms in mononuclear complexes.

In general, carbyne ligands are strong π-acceptors. Based on the parametrization of redox potential values related to mononuclear rhenium adducts, Pombeiro built a scale of *net π-electron acceptor minus σ-donor character*, with the simplest aminocarbyne, i.e. [≡CNH_2], falling in the middle between a range of alkyl-substituted carbynes (upper in the scale) and carbon monoxide [9].

Few reviews have been published on specific aspects of the chemistry of aminocarbyne complexes [10,11,12], notwithstanding a comprehensive review embracing all the structural, spectroscopic and reactivity patterns in the various metal frameworks is unprecedented. Here, the relevance to possible applications in the fields of medicinal chemistry and catalysis will be also highlighted. Conventional colors for the graphic representation of X-ray crystal structures will be adopted.

2. Aminocarbyne ligands in mononuclear complexes

2.1. Group 6 metal complexes

2.1.1. From carbonyl ligands

Group 6 metal hexacarbonyl complexes are convenient starting materials to access a variety of mononuclear aminocarbyne derivatives. A viable strategy is the classical Fischer approach, consisting in the three-step transformation of a carbonyl ligand. First, nucleophilic attack of lithium dialkylamide to carbon monoxide in $M(CO)_6$ generates an iminoacyl function (Scheme 2, path *i*), which can be readily alkylated by triethyloxonium tetrafluoroborate to afford the stable alkoxido-aminoalkylidene product in moderate to good yields (path *ii*) [13]. The choice of the solvent is crucial for step *i*), and the use of diethyl ether in the place of THF avoids in some cases the formation of the undesired bis-addition product [14]. The subsequent reaction with an excess of BF_3 (path *iii*) at low temperature generates the thermally unstable ionic aminocarbyne compounds **1** [15,16,17]. When stored under inert atmosphere at -30 °C, the tungsten complexes decompose over few hours via CO release, presumably affording tetrafluoroborate adducts; otherwise, the chromium species $[Cr(CNMe_2)(CO)_5]BF_4$ (**1a**) resists for months under the same conditions [17]. The increased stability of the cationic adduct on going up from W to Cr within the sixth group may be ascribable to the lower electronegativity of the latter, enabling sufficient electron backbonding to strengthen the metal-carbonyl binding. However, the replacement of the $[BF_4]^-$ anion with $[SbX_6]^-$ (X = F, Cl; path *iv*) provides a stabilizing effect, reasonably due to the decreased coordinating ability of the latter anion, and $[W(CNEt_2)(CO)_5]SbCl_6$ (**2a**) could be characterized by single-crystal X-ray diffraction [18].

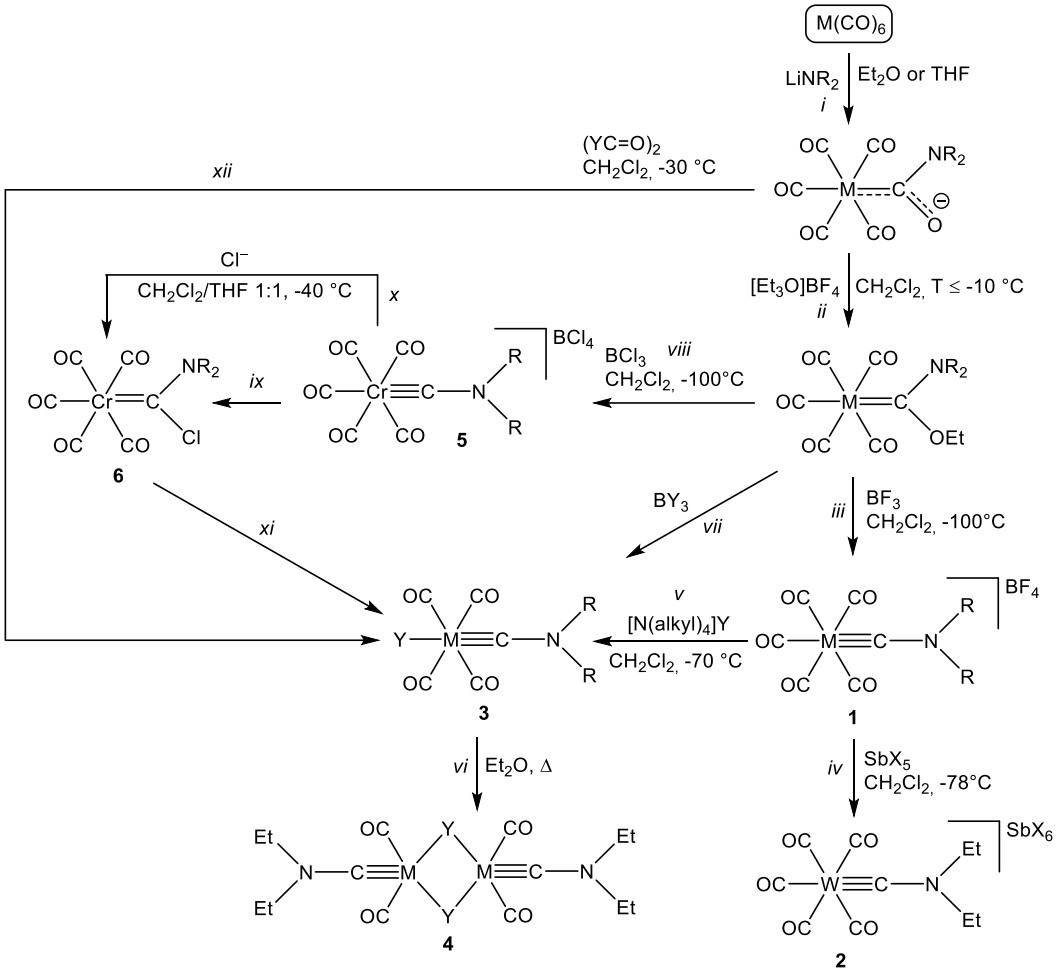
The highly reactive compounds **1** based on molybdenum add halides and pseudohalides as tetraalkylammonium salts at low temperature, converting into **3** [16], which contain the anionic ligand in trans position with respect to the aminocarbyne moiety. The addition of anions such as cyanate, 4-(trifluoromethyl)phenylselenolate or azide leads to the direct formation of binuclear bis-carbyne

structures comprising two bridging anionic ligands (**4**) [16]; the latter compounds are also obtained upon warming **3** in solution.

The formation of **3** can be directly achieved by treating the alkoxy-aminoalkylidene precursors [M{CNR_2(OEt)}$(CO)_5$] with BY_3 (Y = Cl, Br, I) instead of BF_3 (path *vii*, see also Equation 2) [5,18,19]. For the chromium compounds, the reaction proceeds through the formation of the ionic intermediates **5**, analogous to **1** (path *viii*) [17]. These decompose in dichloromethane solution at 0 °C giving the chloro-alkylidene **6**, as a result of nucleophilic attack of the chloride (from the counteranion) to the carbyne carbon of **5** (path *ix*). The addition of even a small amount of THF to the solution accelerates the reaction, probably due to the competition of the oxygen donor with the chloride ion for boron binding. Nucleophilic addition of chloride to chromium can also be realized by reacting **5** with a chloride salt in dichloromethane/THF mixture at low temperature (path *x*). Compounds **6** rearrange via CO extrusion and chloride migration to finally afford the aminocarbyne derivatives of type **3** (path *xi*) [17]. The minimum temperature required for such a rearrangement essentially depends on the nature of the N-substituents (R), a higher steric demand favoring the elimination of the chloride from the alkylidene group. It was demonstrated that the rearrangement of **6** to the corresponding final products **3** follows a first-order rate kinetic law [20]. A similar path was reported for the addition of lithium aryl-selenides (LiSeAr, Ar = Ph, 4-$C_6H_4CF_3$, 4-C_6H_4Br, 4-C_6H_4F, 4-C_6H_4Me, 4-C_6H_4OMe, 1-naphthyl) to [$Cr(CNEt_2)(CO)_5$]BF_4 (**1b**), which is initially directed to the carbyne carbon [21], then at higher temperatures the selenide anion migrates with CO elimination to give selenide analogues of **3** [22].

A general route to halide-aminocarbyne complexes of type **3** consists in the oxygen abstraction with oxalyl halide (path *xii*) on the iminoacyl intermediate formed upon amide addition to $M(CO)_6$ (M = Cr [23], W [14]). By this way, the products are finally isolated in 50-75% yields.

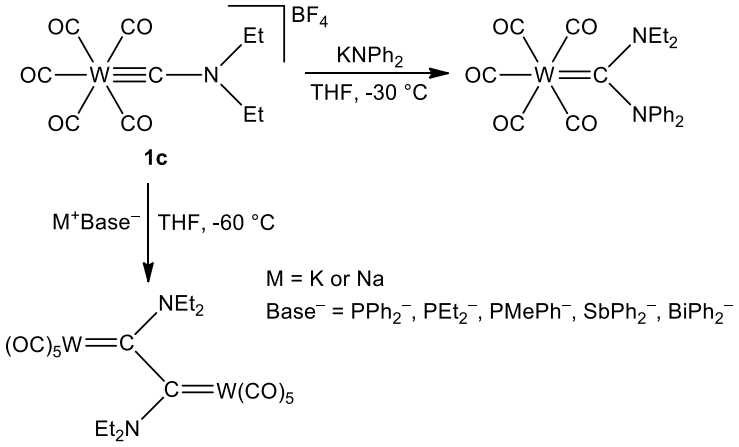
Interestingly, Lewis acids of boron and aluminum revealed unsuitable to remove the alkoxide function from the bis-alkylidene complexes *cis*-[M{CNR_2(OEt)}$_2(CO)_4$] (R = ^{i}Pr, Cy), and thus failed to produce any carbyne derivative [24].



Scheme 2. Synthesis and reactivity of mononuclear aminocarbyne complexes of group 6 metals via stepwise modification of a carbonyl ligand according to classical Fischer approach. *i*), *ii*): M = Cr, Mo, W; R = Me, Et, ^{i}Pr. *iii*): M = Mo, W; R = Et. *iv*): M = Cr, Mo, W; R = Me, Et; X = F, Cl. *v*) M = Mo; R = Et; alkyl = ^{n}Bu, Et; Y = Br, I, SCN. *vi*) M = Mo; R = Et. *vii*): M = Cr, R = Et (solvent: CH_2Cl_2); M = W, R = Me or Et (solvent: pentane); Y = Cl, Br, I. *viii*): M = Cr, R = Me, Et, piperidine. *ix*): R = Me, Et, pyrrolidine; CH_2Cl_2, 0 °C. *x*): R = Me, Et, pyrrolidine, Ph; Cl^- from $[NEt_4]Cl$ or $[N(PPh_3)_2]Cl$. *xi*): R = Me, Et, pyrrolidine, Ph. *xii*): M = Cr, W; R = ^{i}Pr; Y = Cl, Br.

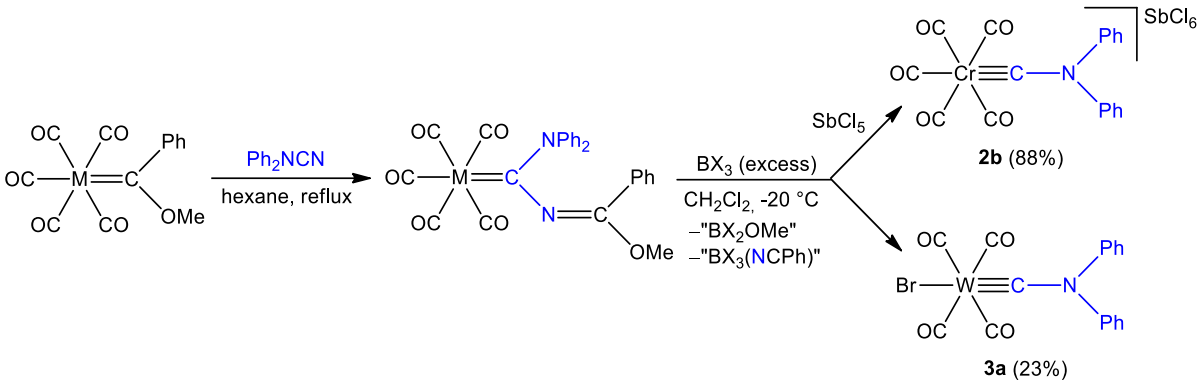
The electron-poor aminocarbyne carbon in cationic complexes **1** is susceptible to nucleophilic addition, and for instance the reaction of $[W(CNEt_2)(CO)_5]BF_4$ (**1c**) with $KNPh_2$ results in the formation of the diaminocarbene derivative, albeit in a low yield (Scheme 3). Instead, adding other

sodium or potassium salts of anions which are also good bases promotes the reductive dimerization of the carbyne moiety, affording a di-aminocarbene dimetallic structure in as high as 25% yield [25]. In particular, the reaction with K[PMe(Ph)] is non-selective, and a mixture of products, resulting from both reduction and nucleophilic attack, has been obtained in this case.



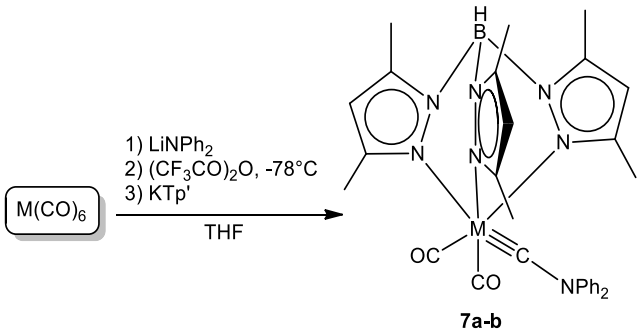
Scheme 3. Aminocarbyne to aminocarbene conversion by nucleophilic addition or reductive dimerization.

The synthetic sequence reported in Scheme 2, starting from the metal hexacarbonyls and proceeding via nucleophilic addition of an amide, is effective to obtain dialkyl-aminocarbyne compounds, but no aryl-aminocarbyne species was reported by this method. An alternative strategy is more appropriate to tether aryl substituents to the nitrogen atom within structures of types **1** and **3**. First, alkoxyalkylidene precursors undergo thermally-induced insertion of diphenylcyanamide into the metal-carbene bond; [26] then, the reactions with an excess of boron trihalides generates the *N*,*N*-diphenyl aminocarbyne function, incorporated either in cationic **2b** [27] or neutral **3a** [26a] complexes (Scheme 4).



Scheme 4. Synthesis of *N*,*N*-diphenylaminocarbyne complexes. M = Cr, X = Cl; M = W, X = Br. Published yields of isolated products in parentheses.

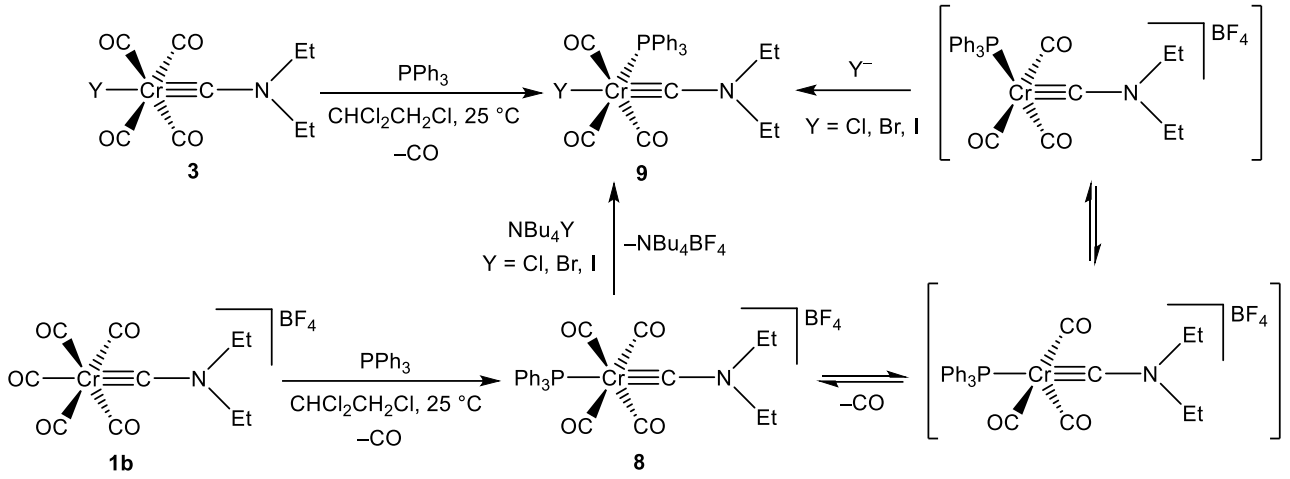
To the best of our knowledge, the only example of well-defined group 6 metal diphenyl-aminocarbyne complexes (**7a**) from the classical Fischer approach was recently prepared by Hill and co-workers according to a one pot procedure incorporating also a 3,5-dimethyltrispyrazol-1-yl-borato ligand (Tp'), Scheme 5 (see also Scheme 7, complex **7c**) [28].



Scheme 5. Synthesis of *N*,*N*-diphenylaminocarbyne tris(pyrazolyl)borate complexes (M = Mo, **7a**; M = W, **7b**).

The thermal stability of the ionic compounds **1** can be enhanced by halide substitution of one CO ligand. Moreover, the first-order reaction of $[Cr(CNEt_2)(CO)_5]BF_4$ (**1b**) with PPh_3 results in the formation of *trans*-$[Cr(CNEt_2)(CO)_4(PPh_3)]BF_4$ (**8**), which decomposes over 120 °C (Scheme 6) [29]. Compound **8** reacts with NBu_4Y (Y = Cl, Br, I) to give *mer*-$[CrY(CNEt_2)(CO)_3(PPh_3)]$, **9** [29]. The latter is also accessible from the corresponding structures of type **3** via halide addition. The

unexpected formation of **9** from **8** was explained to take place via a dissociative mechanism, starting with CO elimination to give a penta-coordinated species ($\Delta H^{\#}$ = 104-113 kJ mol^{-1}, $\Delta S^{\#}$ = 64-71 J mol^{-1} K^{-1}, experimental values) [30]. The resulting intermediate would rearrange to a square-pyramidal geometry with the carbyne ligand occupying the vertex position, and subsequent halide attack regenerates the octahedral geometry to give **9**.



Scheme 6. CO/PPh_3 substitution in Cr^0 aminocarbyne complexes, and proposed pathway for CO/halide exchange.

Various compounds belonging to the type **3** have been modified by substitution of CO ligands with a range of anionic and neutral Lewis bases. Thus, the reactions of *trans*-[$WY(CNR_2)(CO)_4$] with a chloride or bromide source, in dichloromethane at room temperature, yields the anionic bis-halide complexes *mer*-[$WY_2(CNR_2)(CO)_3]^-$, **10**, Equation 4 [31]. The latter undergo easy halide replacement by triphenylphosphine to give the tungsten analogues of **9** (Scheme 6).

trans-[$WY(CNR_2)(CO)_4$] (**3**) + EX → [E][$WY(X)(CNR_2)(CO)_3$]-*mer* ([E]**10**) + CO (4)

Y = Cl, Br; R = ^{i}Pr, Cy; E = NEt_4, PPN; X = Cl, Br

Complexes [$MX(CNR_2)(CO)_4$] react at room temperature with 4-methylpyridine (picoline; slight excess with respect to 1:2 molar ratio) and bidentate nitrogen donors (1:1 molar ratio) affording the

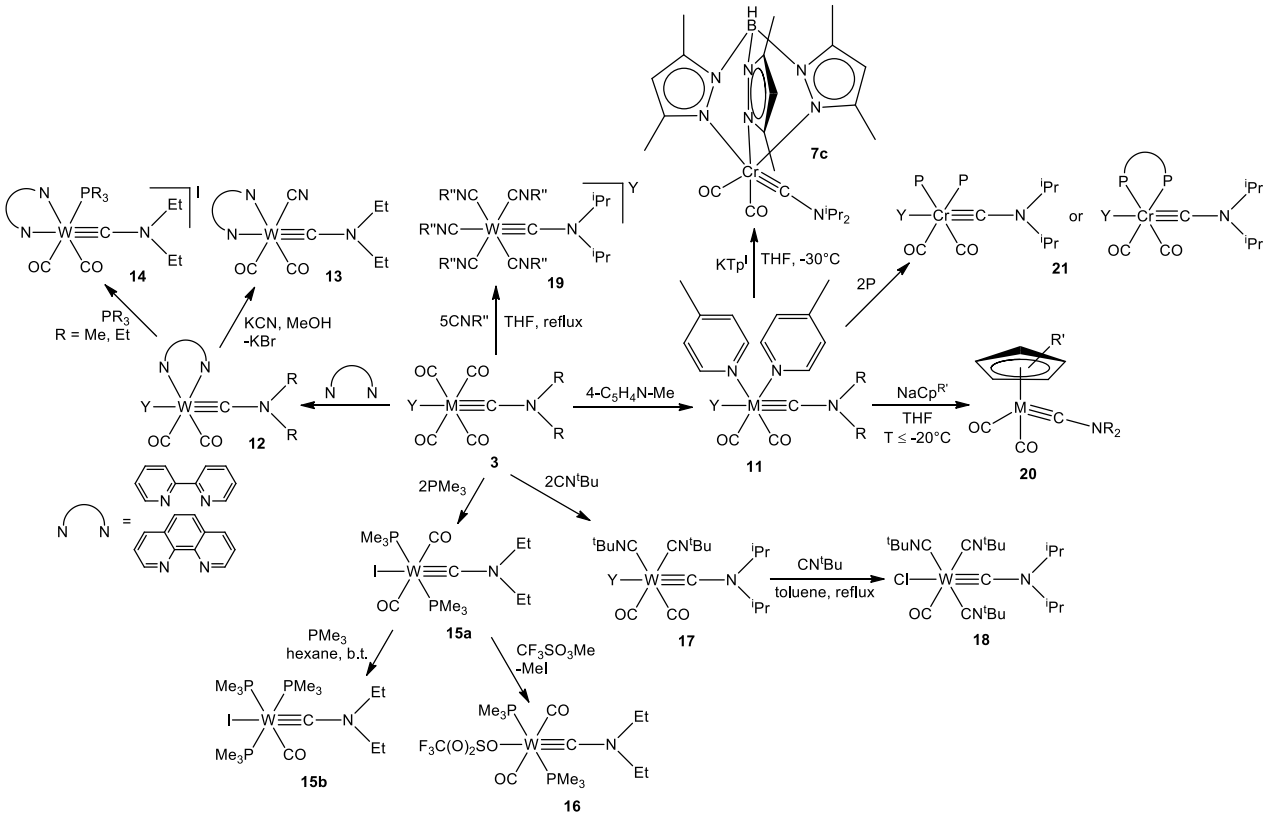
respective substitution products **11** and **12** in excellent yields, Scheme 7 [14,23]. Further modification can be achieved on **12** by bromide/cyanide replacement to give **13** (ca. 70% yields) [32] or iodide/phosphine substitution to give **14** [33]; these reactions are accompanied by a rearrangement placing the newly introduced ligand in *cis* with respect to the carbyne. The bromide ligand in a **12**-type structure has been also replaced by carbonylato anions of formula $[M(EPh_2)(CO)_5]^-$ (M = Cr, Mo, W; E = P, As, Sb) [34].

Compound $[WI(CNEt_2)(CO)_4]$ (**3a**) undergoes stepwise substitution of three carbonyl ligands by the same number of triethylphosphine molecules, the third substitution requiring heating in boiling hexane; the final product **15b** is obtained in a nearly quantitative yield and exhibits a *mer* structure [35]. The intermediate **15a** undergoes electrophilic iodide abstraction by methyl triflate, leading to the high-yield formation of **16**, containing a labile triflate ligand [36]. A similar outcome has been reported for the homologue of **15a** containing two CN^tBu ligands in the place of the phosphines.

The reactions of **3** with *tert*-butyl isocyanide afforded a bis-substituted product, **17**, in the case of M = W, and the third substitution to give **18** is viable by thermal treatment (80% yield). Conversely, up to five alkyl isocyanide ligands can be introduced in the chromium species (**19**) [23,37,38]; in general, polar solvents favor the removal of CO and halide ligands and the consequent formation of ionic products, while a lower degree of substitution and the formation of neutral complexes can be accomplished in less polar solvents.

The presence of two donating picolines increases the electron density on the metal center, and thus inhibits undesired reductive reactions which may be promoted by anionic nucleophiles. Therefore, the picoline derivatives represent a convenient entry to half-sandwich compounds, allowing the introduction of cyclic anionic ligands such as cyclopentadienyl (Cp), pentamethyl-cyclopentadienyl (Cp^*) and 3,5-dimethyltrispyrazolyl-borate (Tp'); the products (**20**, **7c**) were isolated in 49-75% yields. An example of tungsten complex analogous to **7c**, bearing a trisulfur methimazolyl ligand in place of Tp', has also been reported [39]. Similarly, the tetra-tert-butylisocyanide chromium complex has been exploited to obtain a series of half-sandwich isocyanide-adducts, although these reactions

are scarcely selective and the products may be unstable at room temperature and in chlorinated solvents [23]. The two picoline ligands may be straightforwardly replaced by a variety of phosphines and diphosphines, yielding the thermally stable compounds **21** [37].

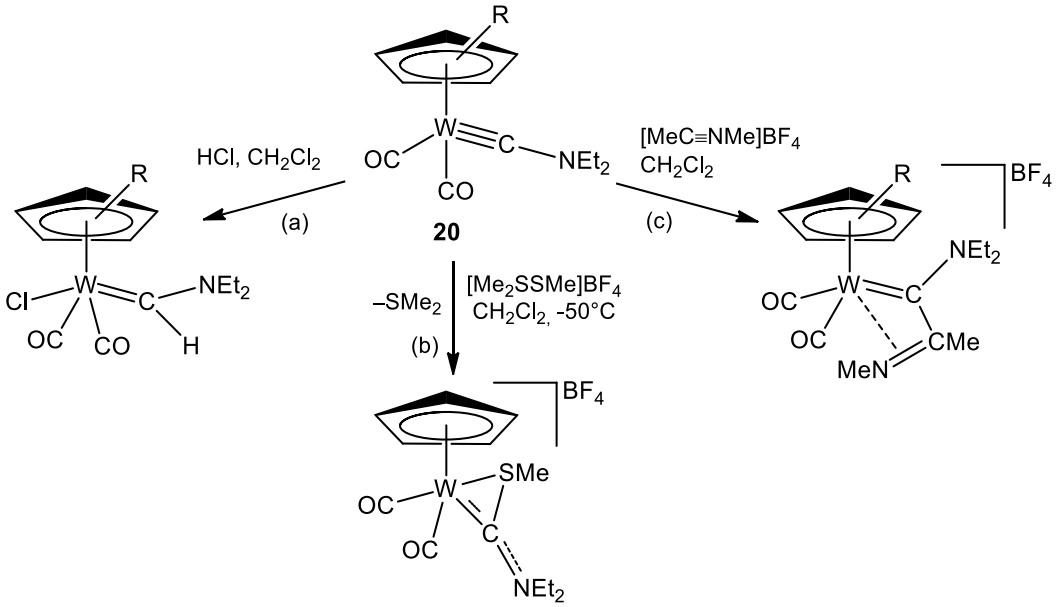


Scheme 7. Synthesis of aminocarbyne derivatives of **3** via substitution of carbonyls and other co-ligands. M = Cr, W; L = Cl, Br; R = ^{i}Pr, Cy; $Cp^{R'}$ = C_5H_5 (Cp), C_5Me_5 (Cp^*); R" = ^{t}Bu, ^{i}Pr; 2P = $2PMe_3$, $2PMe_2Ph$, $2P(OMe)_3$, $Ph_2PCH_2CH_2PPh_2$ (dppe); Y = Cl, Br, I. Reaction conditions: CH_2Cl_2 solution and T = 20-40 °C, unless otherwise specified.

The strongly donor $Cp^{R'}$ ligand in complexes of type **20** renders the aminocarbyne relatively electron-rich and, therefore, susceptible to the typical reactivity of Schrock carbynes. In other words, the substantial electrophilic nature of the aminocarbyne in **1** might be reversed with the introduction of a cyclopentadienyl co-ligand. Therefore, the reaction of $[W(Cp^R)(CNEt_2)(CO)_2]$ (**20**) with HCl affords the amino-alkylidene $[W(Cp^R)(Cl)\{CN(H)Et_2\}(CO)_2]$ in nearly 90% yields, as the result of protonation of the carbyne (Scheme 8a) [40]. Accordingly to the nucleophilic nature of the

aminocarbyne center, $[W(Cp)(CNEt_2)(CO)_2]$ (**20a**) reacts with dimethyl(methylthio)sulfonium tetrafluoroborate leading to a cationic product with a chelating methylthio-alkylidene ligand, in 69% yield (Scheme 8b) [41].

Furthermore, $[W(Cp^*)(CNEt_2)(CO)_2]$ (**20b**) undergoes [2+2] cycloaddition of a nitrilium cation, determining a clean aminocarbyne to aminocarbene conversion (72% yield), Scheme 8c [42].



Scheme 8. Electrophilic additions to aminocarbyne tungsten complexes with an ancillary cyclopentadienyl ligand. (a) Cp^R = Cp, T = - 20 °C; R = Cp*, T = -78 °C to room temperature. (b) Cp^R = Cp. (c) R = Cp^*, T = -78 °C to room temperature.

A terminal $\{W{\equiv}CNEt_2\}$ moiety within a dinuclear tungsten-molybdenum poly-carbonyl complex is attacked by CO_2 in dichloromethane under mild conditions, affording a κ^2*C,O*-coordinated cyclic aminoalkylidene ligand, $\{\overline{W{=}C(NEt_2)C(=O)O}\}$ [43].

The tungsten analogue of **21** with two trimethylphosphite [44] ligands (**21a**) has been prepared from the bis-pyridine precursor $[WI(CNEt_2)(CO)_2(pyridine)_2]$ (**11a**), Equation 5.

$$[WI(CNEt_2)(CO)_2(pyridine)_2] + 2\ P(OMe)_3 \rightarrow [WI(CNEt_2)(CO)_2\{P(OMe)\}_2] + 2\ pyridine \qquad (5)$$

11a **21a**

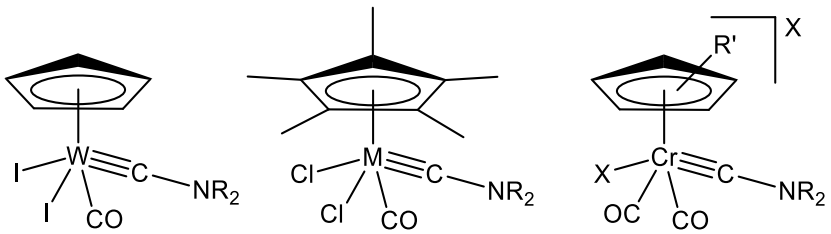
Treatment of **21a** with iodine, in dichloromethane at low temperature, proceeds with oxidative decarbonylation (from W^0 to W^{+II}) to quantitatively yield $[W(I)_3(CNEt_2)(CO)\{P(OMe)\}_2]$, **22**, Equation 6. A parallel chemistry has been developed with nitrile and bidentate nitrogen adducts (instead of trimethylphosphite) [45,46].

$$[WI(CNEt_2)(CO)_2\{P(OMe)\}_2] + I_2 \rightarrow [W(I)_3(CNEt_2)(CO)\{P(OMe)\}_2] + CO \qquad (6)$$

21a **22**

The decarbonylative oxidation is a quite general strategy to access halide-aminocarbyne complexes of group 6. It has been employed to produce the piano-stool $[W(Cp)(I)_2(CNEt_2)(CO)]$, **23** (91% yield) [47] and $[M(Cp^*)(Cl)_2(CNEt_2)(CO)]$, **24** (80-100%; M = Mo, W) [48] from the respective precursors **19** upon treatment with I_2 or $PhICl_2$. Complexes **24** can be further decorated by substitution of the two chlorides with 1,2-dithiolates, the products manifesting the same reactivity (carbyne protonation by HCl) as that described above for **20**.

On the other hand, the oxidation of $[Cr(Cp^{R'})(CNEt_2)(CO)_2]$ ($Cp^{R'}$ = Cp, Cp^*) by Br_2 or $PhICl_2$ proceeds with no carbonyl dissociation to give $[Cr(Cp^{R'})(X)(CNEt_2)(CO)]^{0/+}$ (**25**) [49]. The latter are unstable compounds losing CO at room temperature, and can be stabilized by replacement of the carbonyls with *tert*-butyl isocyanide ligands. The generic structures of **23**-**25** are supplied in Scheme 9.



23 **24** **25**

M = Mo, W

$Cp^{R'}$ = Cp, Cp*

X = Cl, Br

Scheme 9. Structures of piano-stool halide aminocarbyne complexes.

The X-ray crystal structures of representative compounds discussed in the present paragraph are shown in Figure 1.

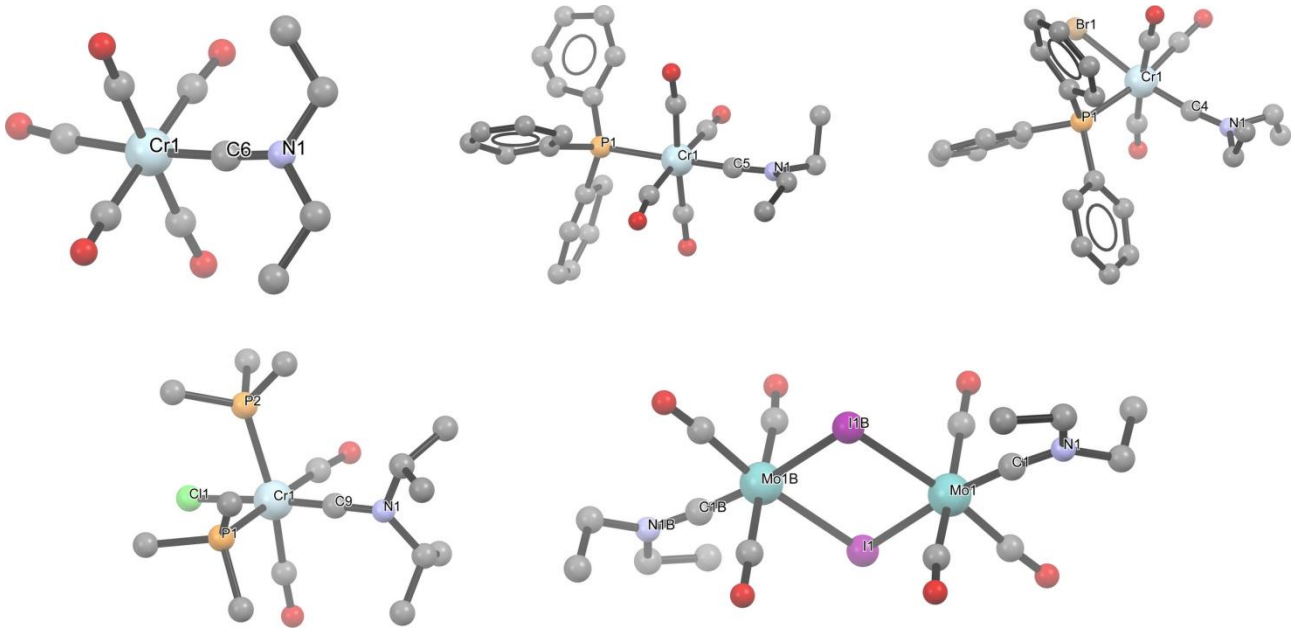


Figure 1. Views of the X-ray structures of: the cation of $[Cr(CNEt_2)(CO)_5]BF_4$ (**1b**) [73], the cation of $[Cr(CNEt_2)(CO)_4(PPh_3)]BF_4$ (**8a**) [29], $[Cr(Br)(CNEt_2)(CO)_3(PPh_3)]$ (**9a**) [29] (top); $[Cr(Cl)(CN^iPr_2)(CO)_2(PMe_3)_2]$ (**21b**) [37], $[Mo(CNEt_2)(CO)_3]_2(\mu\text{-}I)_2$ (**4a**) [16] (bottom). Hydrogen atoms omitted for clarity.

2.1.2. From isocyanide ligands

Isocyanides are classical platforms for the synthesis of aminocarbyne ligands [50], and the first example in this regard was reported at the dawn of the history of carbyne complexes (see Introduction) [6]. This piece of chemistry was previously reviewed until 2001 by Pombeiro and co-workers, and here is resumed [10, 11]. A range of homoleptic compounds with electron-rich isocyanides react with

a variety of suitable electrophiles in a 1:1 molar ratio, and the corresponding mono-aminocarbyne derivatives **26** are obtained in excellent yields, Equation 7 [51,52].

$M(CNR)_6 + EX \rightarrow [M(\equiv CNRE)(CNR)_5]X$ (**26**) (7)

M = Mo, W; R = Et, ^{t}Bu; EX = $[Me_3Si]CF_3SO_3$, $[Me_2Si(^tBu)]CF_3SO_3$, $[Et_3O]BF_4$

The use of $SiMe_3Cl$ instead of trimethylsilyl triflate gives rise to an equilibrium reaction [51], while alkylation of $M(CNEt)_6$ by two equivalents of $[Et_3O]BF_4$ leads to the bis-aminocarbyne species $[M(CNEt_2)_2(CNEt)_4][BF_4]_2$ (**27**), however its isolation was prevented by the concomitant formation of ionic by-products [53]. On treatment with $[NEt_4]Br$, **27** undergo carbyne-carbyne coupling to give the alkyne derivatives $[MBr\{\eta^2\text{-}Et_2NC\equiv CNEt_2\}(CNR)_4]Br$ in moderate yields [53,54]. Intramolecular coupling reactions between two aminocarbyne units have been also observed on tungsten cyclopentadienyl complexes, and a theoretical investigation confirmed that the process is favored by π-donor substituents on the carbyne function [55].

Ethyl isocyanide alkylation by $[Et_3O]BF_4$ was used to access the piano-stool aminocarbyne compounds $[MCp^R(CNEt_2)(CO)_2]$ (**20**, M = Mo or W; Cp^R = Cp, Cp^*), which in turn exhibit a versatile chemistry [56]. Note that, instead, the alkylation of the bulkier tert-butyl isocyanide may be non-selective, the alkylation of the metal center becoming competitive [57].

The isocyanide methylation strategy in electron rich systems was exploited to straightforwardly obtain the 3,5-dimethyltrispyrazol-1-yl-borato complexes [Mo(Tp')(CNRR')(CO)$_2$], **28** (R = R' = Me; R = Ph, R' = Me) [58] and *cis*-$[Mo(CNMeR)(CO)(dppe)_2]BF_4$ (**29**, R = Me or Ph; dppe = 1,2-diphenylphosphinoethane) [59].

Beside alkylation and silylation reactions, in some cases also the protonation of coordinated isocyanides is effective to access aminocarbyne ligands [59, 60]. The first example dates back to 1975 (Equation 3), and another one is shown in Equation 8 (**29b**, 65% yield) [59]. In the latter case, the

newly generated secondary aminocarbyne may be unstable, for instance towards isomerization to isocyanide-hydride, resulting in a net protonation at the metal center [59].

trans-[Mo(CNPh)(N_2)(dppe)$_2$] + HBF_4 + Me_2CO → *trans*-[Mo(CNHPh)($OCMe_2$)(dppe)$_2$]BF_4 + N_2 (8)

29b

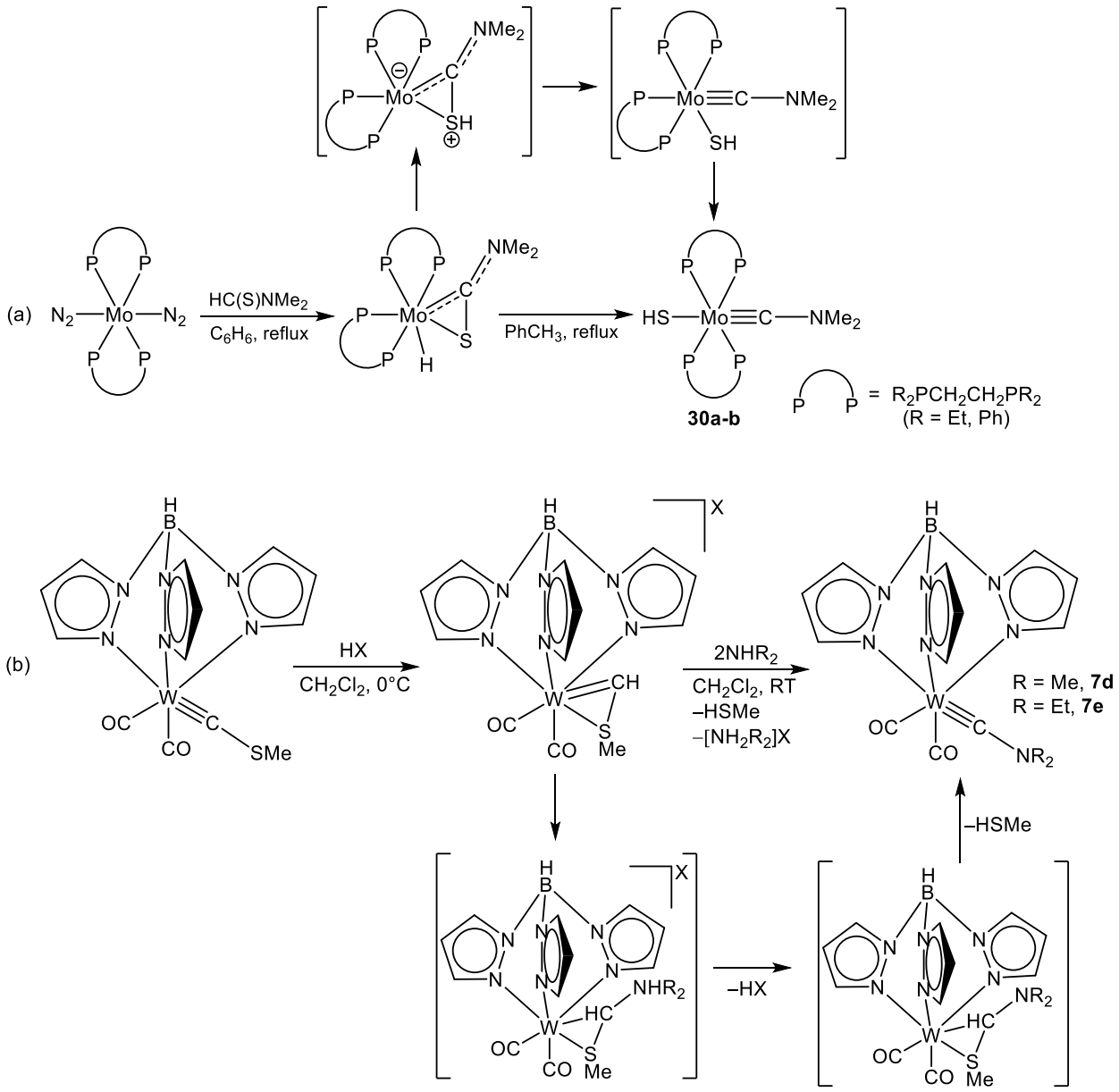
Compounds of type **26** undergo C-C bond forming carbyne-isocyanide coupling promoted by hydrogen iodide in THF, affording alkyne derivatives, Equation 9 [51]. Analogous carbyne-isocyanide coupling was observed from [W(Cp^*)Cl_2($CNEt_2$)(CN^tBu)], following the addition of HCl in diethyl ether at -78 °C [61]. These facts are in alignment with the hypothesis that aminocarbyne species act as intermediates along the alkyne forming coupling reaction of isocyanides on group 6 metal centers [62].

[M(CNRE)$(CNR)_5$]$^+$ + HI → [MI{η^2-N(ER)C≡CNHR}$(CNR)_4$]$^+$ (9)

26 (M = Mo, W; R = Et, ^{t}Bu)

2.1.3. Other synthetic methods

Tertiary aminocarbyne ligands have been installed in some group 6 metal complexes via fragmentation of thio-alkylidenes or modification of halo-carbynes. Thus, *trans*-[Mo$(N_2)_2$(*PP*)$_2$] (*PP* = {R_2PCH_2}$_2$, R= Ph, Et) undergo oxidative addition by *N*,*N*-dimethylthioformamide upon removal of the labile dinitrogen ligands in refluxing benzene, affording the seven-coordinated hydrido-thiocarbamoyl [MoH(κ*C*,κ*N*-C(S)NMe_2)(*PP*)$_2$] in 85-90% yields (Scheme 10a). The latter quantitatively rearranges to the hydrosulfido-aminocarbyne *trans*-[Mo(SH)($CNMe_2$)(*PP*)$_2$] (**30a-b**), by means of heating in toluene [63]. The proposed mechanism for the formation of the aminocarbyne ligand in **30a-b** involves the initial migration of the hydride to the sulfur atom, to generate a 16-electron alkylidene intermediate, [Mo{C(NMe_2)(SH)}(*PP*)$_2$].

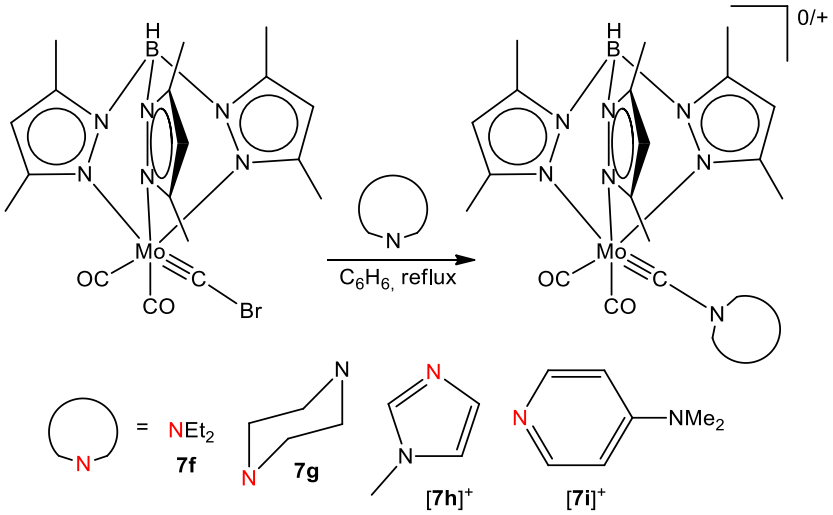


Scheme 10. Synthesis of aminocarbyne ligands via stepwise modification of (a) *N*,*N*-dimethylthioformamide and (b) thiocarbyne ligand (X = CH_3SO_3, CH_3CO_2, BF_4).

Similarly, the thiocarbyne complex [W(Tp)(CSMe)$(CO)_2$] is protonated by strong acids (CH_3SO_3H, CH_3CO_2H, HBF_4) to produce a κ^2*C*,*S*-coordinated thio-alkylidene ligand (Scheme 10b) [64]. The subsequent reaction with secondary amines generates the air-stable aminocarbyne **7d-e** in ca. 30% yields [65]. By analogy with the synthesis of **30a-b**, it is presumable that the reaction proceeds with initial amine attack to the carbene, followed by deprotonation of the amino substituent promoted by a second equivalent of amine, and final loss of HSMe. Compound **7e** reacts with *trans*-

$[Pt(H)(PEt_3)_2(acetone)]BF_4$ to afford in 44% yield the heterodinuclear complex $[W(Tp)(CO)Pt(PEt_3)_2\{\mu\text{-}\kappa^1C,\kappa^2C,N\text{-}CH(NEt_2)\}(\mu\text{-}CO)]BF_4$ (**31**), containing a bridging amino-alkylidene ligand, as a result of regioselective addition of the Pt-H bond across the W≡C bond [66].

Beside the chromium and tungsten complexes **7a-e** (see Schemes 5, 7 and 10) [67], Hill and co-workers described the straightforward synthesis of analogous 3,5-dimethyltrispyrazolyl-borate molybdenum compounds where the aminocarbyne moiety is generated through the modification of a bromocarbyne precursor, which is easily available from $Mo(CO)_6$. Simple substitution of the bromide by a range of nitrogen nucleophiles affords **7f-g** and [**7h-i**]Br in 64-93% yields (Scheme 11 and Figure 2). Notably, this strategy is effective not only with simple dialkylamines, but also with piperazine, imidazoles and 4-dimethylaminopyridine, giving raise to aminocarbynes not accessible using the routes discussed above [68]. The bromocarbyne compound is unreactive towards diphenylamine or lithium diphenylamide, thus the diphenylaminocarbyne derivative must be prepared using the classical Fischer procedure (see Scheme 5).



Scheme 11. Aminocarbyne formation via bromide/amine nucleophilic substitution on a bromocarbyne ligand. The reactions leading to **7f-g** produce HBr as side product.

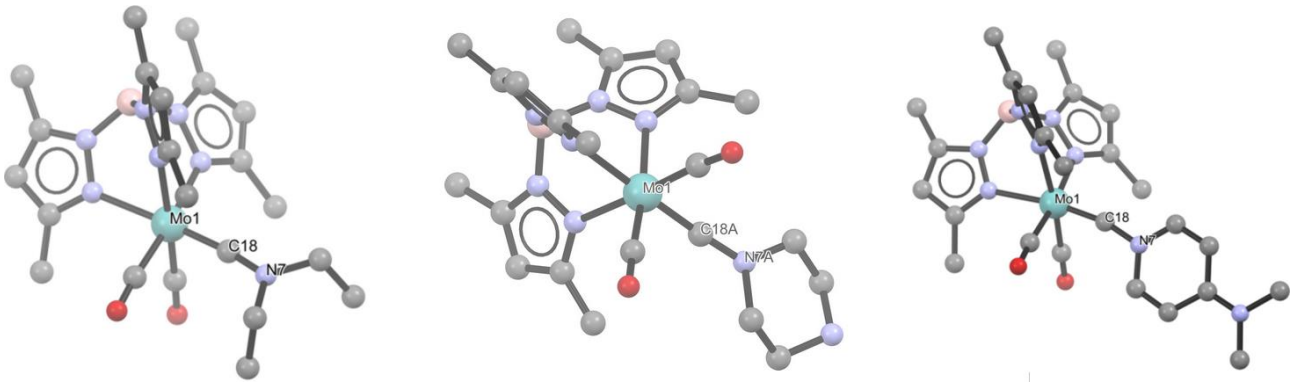


Figure 2. View of the X-ray structures of **7f**, **7g** and [**7i**]$^{+}$ (bromide as counteranion) [68]; H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): **7f**, Mo-carbyne 1.853(3), carbyne-N 1.316(4), Mo-carbyne-N 172.2(3); **7g**, Mo-carbyne 1.853(3), carbyne-N 1.324(4), Mo-carbyne-N 175(2); [**7i**]$^{+}$, Mo-carbyne 1.807(4), carbyne-N 1.394(5), Mo-carbyne-N 166.9(3).

Interestingly, Chisholm and co-workers reported the reaction of a W^{+III} alkoxide with dimethylcyanamide in hexane at room temperature, readily affording a precipitate of a nitrido polymer and the soluble aminocarbyne dimer **32**, Equation 10 [69].

$$W_2(O^tBu)_6 + Me_2NC{\equiv}N \rightarrow [W(\equiv N)(O^tBu)_3]_x + [W(CNMe_2)(O^tBu)_3]_2 \qquad (10)$$

32

The X-ray structure of **32** shows a trigonal-bipyramidal coordination at each tungsten atom (Figure 3). The synthesis reaction may be viewed as a [C≡N] oxidative cleavage, and the product provides unambiguous evidence for the adaptation of the aminocarbyne moiety to a high valent metal center (W^{+VI} in **32**, regarding the CNR_2 ligand as a Schrock carbyne as in complexes **24** and derivatives, see Section 2.1).

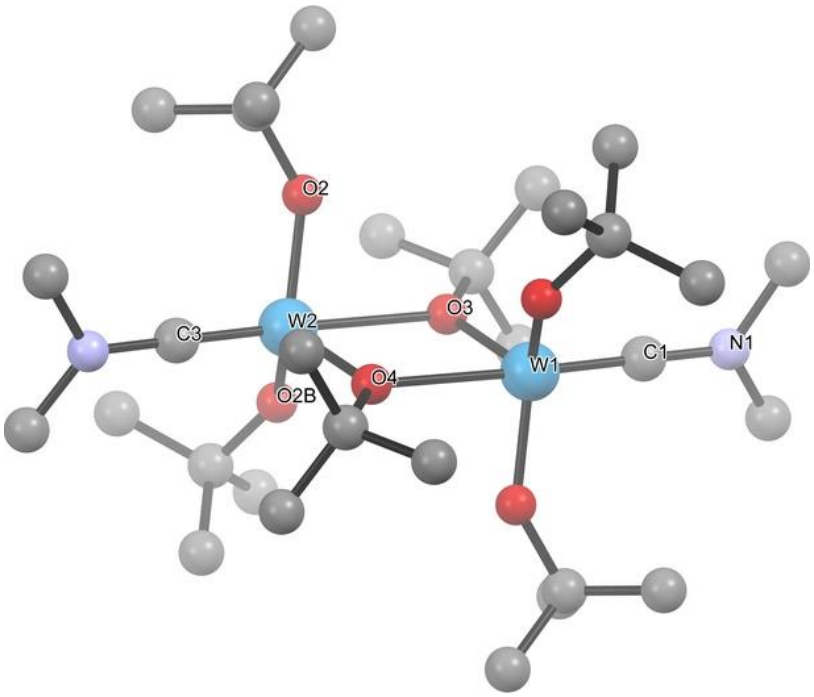
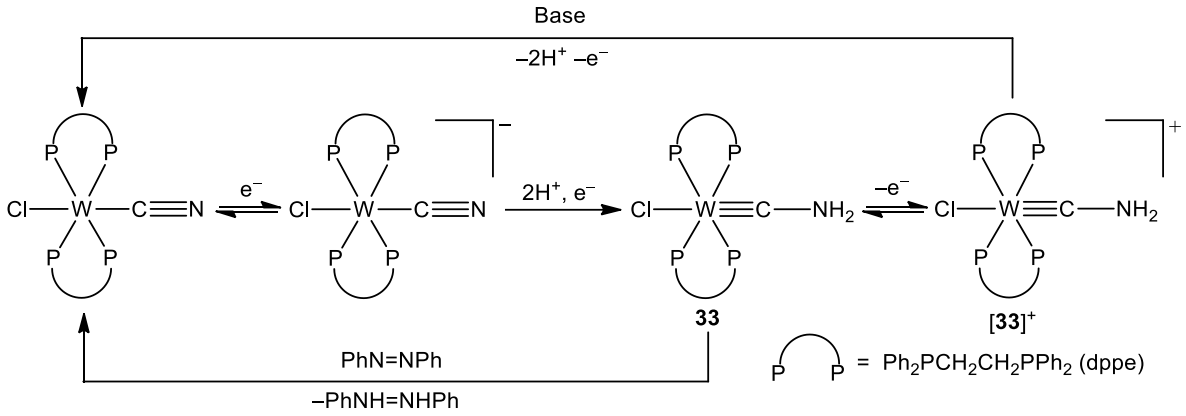


Figure 3. View of the X-ray structure of **32** [69]. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): W1-C1 1.77(2), C1-N1 1.34(2), W-μ-O 2.43(1) and 1.94(1), W-t-O 1.89(1), W1-C1-N1 179(2).

Besides isocyanides (vide infra), the cyanide ligand is another possible source for the formation of primary and secondary aminocarbyne ligands (see also Section 5). The electrochemical one-electron reduction of *trans*-[W(CN)Cl(dppe)$_2$] in CH_2Cl_2/[NBu$_4$]BF$_4$ is a reversible process, which in the presence of phenol (acting as H^+ donor) becomes an irreversible two-electron process affording the aminocarbyne *trans*-[W(CNH$_2$)Cl(dppe)$_2$] (**33**, Scheme 12) [70]. The latter complex can be reversibly oxidized by one electron, either chemically or electrochemically. Both **33** and [**33**]$^+$ (as tetrafluoroborate salt) have been isolated and characterized by single crystal X-ray diffraction analyses, with the latter exhibiting an exceptionally short carbyne-N distance (Figure 4). In the presence of a base, [**33**]$^+$ is readily converted into the parent cyanide complex. Likewise, **33** reacts with azobenzene behaving as a double hydrogen transfer agent, regenerating the cyanide species.



Scheme 12. Electrochemical generation of the simplest aminocarbyne ligand via cyanide double protonation.

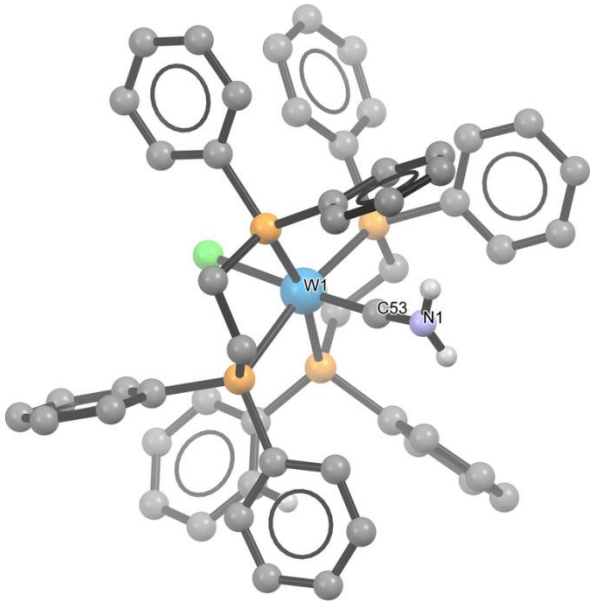


Figure 4. View of the X-ray structure of [**33**]$^{+}$ [70]. H atoms (except NH_2) omitted for clarity. Bond lengths (Å): W1-C53 1.872(8), C53-N1 1.200(12).

2.1.4. Structural and spectroscopic features

Structural and spectroscopic data related to aminocarbyne ligands in selected group 6 mononuclear complexes are compiled in Table 1. A comparison of the structures of *trans*-[Cr(Cl)($CN^{i}Pr_2$)$(CO)_4$] (**3b**) [16] with those of the homologous classical alkylidyne complexes *trans*-[Cr(Cl)(CMe)$(CO)_4$]

[71] and *trans*-[Cr(Cl)(CPh)(CO)$_4$] [72] outlines that the Cr-carbyne distances in the latter [1.710 Å and 1.725(4) Å respectively] are shorter than in the former [1.747(5) Å]. These data outline that the aminocarbyne moiety possesses a less pronounced electron-acceptor character compared to non hetero-substituted alkylidynes, resulting in a decrease of the metal-carbyne bond order, as predicted by Pombeiro (see Introduction) [73]. The electronic effect of the amino-substituent is more evident from IR data. For instance, in the phenyl-carbyne complex [W(Cl)(≡CPh)(CO)$_2$(bipy)] the highest CO stretching vibration occurs at 1986 cm^{-1}, versus 1946 cm^{-1} in the related aminocarbyne species [W(Cl)(CN^{i}Pr$_2$)(CO)$_2$(bipy)] (**12a**) [74]. Another interesting comparison can be traced including the tungsten cationic complexes [W(CNEt$_2$)(CO)$_5$]SbCl$_6$ (**2a**), [W(CO)$_5$(NO)][Al(OR^F)$_4$] [75], [W(CO)$_5$(L)]BPh$_4$ (L = bis(1,3,4,5-tetramethylimidazol-2-ylidene)phosphanide) [76], [W(CO)$_5$(PPh$_3$)] and [W(CO)$_5$(PCy$_3$)] [76]: the highest infrared carbonyl wavenumber respectively falls at 2142 (CH_2Cl_2 solution), 2183 (ATR), 2061 (ATR), 2071 (cyclohexane) and 2071 cm^{-1} ($CHCl_3$), suggesting that the π-acceptor ability of the aminocarbyne fragment is almost intermediate between those of nitrosyl and phosphines.

On the other hand, the carbyne-nitrogen length appreciably decreases along the series [Cr(Br)(CN^{i}Pr$_2$)(CO)$_2$(PMe$_2$Ph)$_2$] [**21c**, 1.312(5) Å] > [Cr(Br)(CNEt$_2$)(CO)$_4$] [**3c**, 1.294(12) Å] > [Cr(CNEt$_2$)(CO)$_4$(PPh$_3$)]BF$_4$ [**8a**, 1.252(16) Å] ≈ [Cr(CNEt$_2$)(CO)$_5$]BF$_4$ [**1b**, 1.256(12) Å], indicating a progressive enhancement of π-overlap with nitrogen, favored by the improved π-acceptor capability of the co-ligands and the net positive charge, which in turn weakens the metal to carbyne back-donation (see Scheme 1). Consistently, the IR stretching vibration of the carbyne-N bond is 1506 cm^{-1} in **21c** and rises up to 1575 cm^{-1} in **8a**.

On comparing the infrared absorptions related to [M(Cp)(CN^{i}Pr$_2$)(CO)$_2$] (**20**, M = Cr, W), it appears that the higher electronegativity of tungsten decreases the metal to carbyne backbonding mode, thus enforcing the azavinylidene character [ῡ(CN) = 1561 cm^{-1} for M = W and 1552 cm^{-1} for M = Cr]. On the other hand, in the W^0 complex [W(Cp*)(≡CN^{i}Pr$_2$)(CO)$_2$] (**20c**) the greater electron donor ability of the pentamethylcyclopentadienyl ring increases the competition of the metal center for the orbitals

of the carbyne carbon, and thus the carbyne-nitrogen bond order reduces [$\tilde{\upsilon}$(CN) = 1549 cm^{-1}]. A comparable situation is found in the W^{+VI} complex $[W(CNMe_2)(^tBuO)_3]_2$ (**32**), where the carbyne-N bond appears significantly elongated [1.34(2) Å], reflecting the effective π-donation to the metal from the alkoxide ligands. Ongoing from **20c** to $[W(Cp^*)(Cl)_2(CN^iPr_2)(CO)]$ (**24a**), the increase by two units of the oxidation state of the metal affects the backbonding, and as a consequence the carbyne-N bond order increases [$\tilde{\upsilon}$(CN) = 1582 cm^{-1}].

The effect of the nitrogen substituents on the donor capability of the amino group is evident in that the highest infrared carbonyl stretching wavenumber is 2143 cm^{-1} in $[Cr(CNPh_2)(CO)_5]SbCl_6$ (**2b**) and 2134 cm^{-1} in $[Cr(CN^iPr_2)(CO)_5]SbCl_6$ (**2c**), and 2113 cm^{-1} in $[WBr(CNPh_2)(CO)_4]$ (**3a**) and 2103 cm^{-1} in $[WBr(CNEt_2)(CO)_4]$ (**3d**): the higher the basicity of the amino-group, the higher the charge available on the metal for backbonding to the carbonyl ligands, resulting in a decrease of the C-O bond order.

The ^{13}C NMR chemical shift of the carbyne carbon is another diagnostic parameter, and the values reported in Table 1 range in between 225-310 ppm. In general, the ^{13}C resonance of aminocarbyne centers is downfield shifted with respect to that of classical carbyne ligands in related metal complexes. For instance, it falls around 235-240 in **12a** and **3d** [74] to be compared with 265.8 ppm ($CDCl_3$ solution) in $[W(Cl)(CPh)(CO)_2(bipy)]$ and 297.2 ppm (CD_2Cl_2, 0 °C) in *trans*-$[W(Br)(CCy^*)(CO)_4]$ (Cy^* = 2-^{i}Pr-5-Me-cyclohexyl) [77], respectively.

It appears that the metal center significantly affects the ^{13}C NMR chemical shift, decreasing along the series Cr > Mo > W: for instance, the values for $[Cr(Cl)(CN^iPr_2)(CO)_2(pic)_2]$ (**11b**) and $[W(Cl)(CN^iPr_2)(CO)_2(pic)_2]$ (**11c**) are respectively 257.1 and 239.5 ppm (CD_2Cl_2 solutions), while the values for $[Mo(Tp')(CNPh_2)(CO)_2]$ (**7a**) and $[W(Tp')(CNPh_2)(CO)_2]$ (**7b**) are respectively 239.0 and 235.5 ppm ($CDCl_3$ solutions). The same trend, i.e. the upfield shift of the ^{13}C NMR resonance in homologous complexes with a different metal center on going down a transition metal group, is common with the carbonyl ligand [78].

Table 1. Spectroscopic and X-ray data related to aminocarbyne ligands in selected group 6 mononuclear complexes.

Compound	IR [a]	^{13}C NMR [b]	X-Ray		Ref.
	ũ(CN) / cm^{-1}	δ(CN) / ppm	d(M-C) / Å	d(C-N) / Å	
[Cr(CNEt$_2$)(CO)$_5$]BF$_4$ (**1b**)			1.797(9)	1.256(12)	[73]
[Mo(CNEt$_2$)(CO)$_5$]BF$_4$ (**1c**)		269.0			[15]
[W(CNEt$_2$)(CO)$_5$]SbCl$_6$ (**2a**)					[17]
[Cr(CNPh$_2$)(CO)$_5$]SbCl$_6$ (**2b**)		273.7			[27]
[Cr(CN^{i}Pr$_2$)(CO)$_5$]SbCl$_6$ (**2c**)		285.1			[27]
[WI(CNEt$_2$)(CO)$_4$] (**3a**)		234.6			[18b]
[Cr(Cl)(CN^{i}Pr$_2$)(CO)$_4$] (**3b**)	1566	266.3	1.747(5)	1.297(6)	[17]
[Cr(Br)(CNEt$_2$)(CO)$_4$] (**3c**)			1.720(10)	1.294(12)	[73]
[WBr(CNEt$_2$)(CO)$_4$] (**3d**)		235.6			[18b]
[Cr(SePh)(CNEt$_2$)(CO)$_4$] (**3e**)	1575		1.750(12)	1.278(15)	[21]
[WCl(CN^{i}Pr$_2$)(CO)$_4$] (**3f**)	1570	235.9			[14]
[W(Br)(CNPh$_2$)(CO)$_4$] (**3g**)		225.0			[26a]
[W(CN)(CNEt$_2$)(CO)$_4$] (**3h**)		245.9			[17]
[Mo(CNEt$_2$)(CO)$_3$]$_2$(□-I)$_2$ (**4**)			1.795(18)	1.335(23)	[15]
[Mo(Tp')(CNPh$_2$)(CO)$_2$] (**7a**)		239.0	1.827(2)	1.346(2)	[28]
[W(Tp')(CNPh$_2$)(CO)$_2$] (**7b**)		235.5	1.837(3)	1.356(4)	[28]
[Cr(Tp')(CN^{i}Pr$_2$)(CO)$_2$] (**7c**)	1504	256.4			[52]
[W(Tp)(CNEt$_2$)(CO)$_2$] (**7e**)		254.6			[65]
[Mo(Tp')(CNEt$_2$)(CO)$_2$] (**7f**)	1526	251.9	1.853(3)	1.316(4)	[68]
[Mo(Tp')$\{$CN(C$_4$H$_8$NH)$\}$(CO)$_2$] (**7g**)	1528	247.7	1.853(3)	1.324(4)	[68]
[Mo(Tp')$\{$CN(4-NC$_5$H$_4$NMe$_2$)$\}$(CO)$_2$]Br [**7i**]Br	1574	214.1	1.807(4)	1.394(5)	[68]
[Cr(CNEt$_2$)(CO)$_4$(PPh$_3$)]BF$_4$ (**8a**)	1575	282.2	1.757(11)	1.252(16)	[29], [30],[73]
[Cr(Br)(CNEt$_2$)(CO)$_3$(PPh$_3$)] (**9a**)	1570	264.1	1.752(12)	1.235(16)	[29], [30], [73]
[Cr(Cl)(CNMe$_2$)(CO)$_3$(PPh$_3$)] (**9b**)		236.2			[18a]
[Cr(Cl)(CNEt$_2$)(CO)$_3$(PPh$_3$)] (**9c**)		263.9			[18a]
[Cr(Br)(CNMe$_2$)(CO)$_3$(PPh$_3$)] (**9d**)		235.5			[18a]
[Cr(I)(CNMe$_2$)(CO)$_3$(PPh$_3$)] (**9e**)		234.5			[18a]
[Cr(I)(CNEt$_2$)(CO)$_3$(PPh$_3$)] (**9f**)	1570	268.4			[18a], [30]
[W(Cl)(CNCy$_2$)(CO)$_3$(PPh$_3$)] (**9g**)		239.6			[31]
[W(I)(CNEt$_2$)(CO)$_3$(PMe$_3$)] (**9h**)	1537	236.1			[35]
[Cr(Cl)(CN^{i}Pr$_2$)(CO)$_2$(pic)$_2$] (**11b**)	1502	257.1			[52]
[W(Cl)(CN^{i}Pr$_2$)(CO)$_2$(pic)$_2$] (**11c**)	1521	239.5			[14]
[W(Cl)(CN^{i}Pr$_2$)(CO)$_2$(bipy)] (**12a**)		240.4			[14]
[W(Br)(CNEt$_2$)(CO)$_2$(bipy)] (**12b**)		240.0			[32]
[W(CN)(CNEt$_2$)(CO)$_2$(bipy)] (**12c**)		257.9			[32]
[W(Cl)(CN^{i}Pr$_2$)(CO)$_2$(CN^{t}Bu)$_2$] (**17a**)	1538	235.2			[14]
[W(I)(CNEt$_2$)(CO)$_2$(CN^{t}Bu)$_2$] (**17b**)	1563	236.0			[45]
[W(I)(CNEt$_2$)(CO)(CN^{t}Bu)$_3$] (**18**)	1533				[44]
[W(Cp*)(CN^{i}Pr$_2$)(CO)$_2$] (**20c**)	1549	265.3			[14]
[Cr(Cp)(CN^{i}Et$_2$)(CO)$_2$] (**20d**)	1562	282.1			[79]
[Cr(Cp)(CN^{i}Pr$_2$)(CO)$_2$] (**20e**)	1552	281.7			[52]
[W(Cp)(CN^{i}Pr$_2$)(CO)$_2$] (**20f**)	1561	263.4			[14]
[Cr(Cp)(CN^{i}Pr$_2$)(CO)(CN^{t}Bu)]	1519	276.6			[52]
[Cr(Tp')(CN^{i}Pr$_2$)(CO)(CN^{t}Bu)]	1545	254.6			[52]
[Cr(Cl)(CN^{i}Pr$_2$)(CO)$_2$(PMe$_3$)$_2$] (**21b**)	1508	256.0	1.740(2)	1.312(3)	[37]
[Cr(Br)(CN^{i}Pr$_2$)(CO)$_2$(PMe$_2$Ph)$_2$] (**21c**)	1506	258.2	1.733(4)	1.312(5)	[37]
[W(I)$_3$(CNEt$_2$)(CO)$_2$(bipy)]	1580				[43]

[W(Cp*)(Cl)$_2$(CN^{i}Pr$_2$)(CO)] (**24a**)	1582	306.2			[14]
[W(Cp)(Cl)$_2$(CN^{i}Pr$_2$)(CO)] (**24b**)	1601	310.0			[14]
[Mo{CN(^{t}Bu)(SiMe$_2$^{t}Bu)}(CN^{t}Bu)$_5$] CF$_3$SO$_3$ (**26a**)	1473	259.8	1.866(9)	1.32(1)	[62a]
[W(CNEt$_2$)(CNEt)$_5$]BF$_4$ (**26b**[BF$_4$])	1540	243.8			[62a]
[Cr(CN^{i}Pr$_2$)(CO)(CN^{i}Pr)$_4$]Cl (**27a**)	1549	271.0			[37]
[W(CNMe$_2$)(^{t}BuO)$_3$]$_2$ (**32**)			1.77(2)	1.34(2)	[69]
trans-[W(CNH$_2$)Cl(dppe)$_2$] (**33**)		217.2	1.868(17)	1.156(24)	[70]
trans-[W(CNH$_2$)Cl(dppe)$_2$]BF$_4$ [**33**]BF$_4$			1.872(8)	1.200(12)	[70]

[a]Solid state (KBr disk) or CH_2Cl_2 solution; [b]$CDCl_3$, D_2Cl_2 or other common deuterated solvent. Abbreviation list: Cp* = C_5Me_5, bipy = 2,2′-bipyridine, Tp = trispyrazolylborate, Tp' = 3,5-dimethyltrispyrazol-1-yl-borate, pic = 4-methylpyridine, dppe = $Ph_2PCH_2CH_2PPh_2$.

2.2. Mononuclear complexes based on other transition metals

Only few mononuclear aminocarbyne complexes of metals not belonging to group 6 have been described. The first case of a monoiron aminocarbyne complex was reported by Fischer in 1984, prepared according to the classical procedure in dichloromethane at low temperature, Equation 11 [80]. Subsequently, Anderson and Hill obtained the same cation, [**34a**]$^+$, from carbamoyl and carbamoylato precursors [81]. The iodide salt [**34a**]I resulted stable in the solid state for years. According to the authors, the aminocarbyne ligand in [**34a**]$^+$ is a monocationic fragment isolobal with [NO]$^+$, while the alternative trianionic formulation (Schrock alkylidyne) would make the complex "*a somewhat implausible tricarbonyl derivative of tetravalent iron*".

$$[Fe\{=C(OEt)(N^iPr_2)\}(CO)_3(PPh_3)] + 2BCl_3 \rightarrow \underset{[\mathbf{34a}]^+}{[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)]BCl_4} + BCl_2OEt \qquad (11)$$

The second case of a monoiron aminocarbyne complex is the neutral one [Fe(≡CN^{i}Pr$_2$)(O$_2$CCF$_3$)(CO)$_2$(PPh$_3$)] (**34b**), which was synthesized in a high yield by the three-step reaction of Fe(CO)$_5$ with LiN^{i}Pr$_2$, (CF$_3$CO)$_2$O and PPh$_3$ [82].

The carbyne centers in [**34a**]I and **34b** resonate at typical low fields in the respective ^{13}C NMR spectra, resembling what found for group 6 metal aminocarbyne carbonyl complexes (see above).

However, a considerable shift is seen on going from [**34a**]$^{+}$ (266.5 ppm) to **34b** (217.4 ppm), as a consequence of the different net electronic charges of the complexes.

In the X-ray structure of [**34a**]$^{+}$, the carbyne-N distance is rather short, 1.266(7) Å, and the Fe-carbyne distance consequently elongated, 1.734(6) Å, suggesting a significant azavinylidene contribution (Scheme 1). Compounds [**34a**]X and **34b** remain rare examples of isolated monoiron aminocarbyne carbonyl species, while much more chemistry has been developed on di- and polynuclear carbonyl systems (vide infra). Some monoiron-aminocarbyne complexes have recently appeared in the literature, being relevant to the N_2 fixation process and the reductive conversion of cyanide to ammonia and methane. In these cases, the aminocarbyne moiety is essentially generated by protonation of cyanide or isocyanide units [83,84]. The more robust dialkylaminocarbyne complex [Fe(CNMe$_2$)(SiP)], **35** (SiP = κ*Si*,κ^3*P*-(2-^{i}Pr$_2$PC$_6$H$_4$)$_3$Si), was synthesized in 82% yield by the sequential addition of Na(Hg) and methyl triflate to a DME solution of the parent cyanide compound [84]. A view of the X-ray structure of **35** is shown in Figure 5, displaying a short Fe-C distance and a long C-N distance, thus supporting the prevailing aminocarbyne nature (rather than azavinylidene) of the carbon ligand. A downfield ^{13}C NMR resonance (279.6 ppm) was assigned to the carbyne, while the infrared absorption attributed to the CN bond occurs at 1520 cm^{-1} (KBr plate). Interestingly, the aminocarbyne moiety of **35** is disrupted upon reaction with proton and electron equivalents, affording a mixture of methane, dimethylamine and a small amount of trimethylamine.

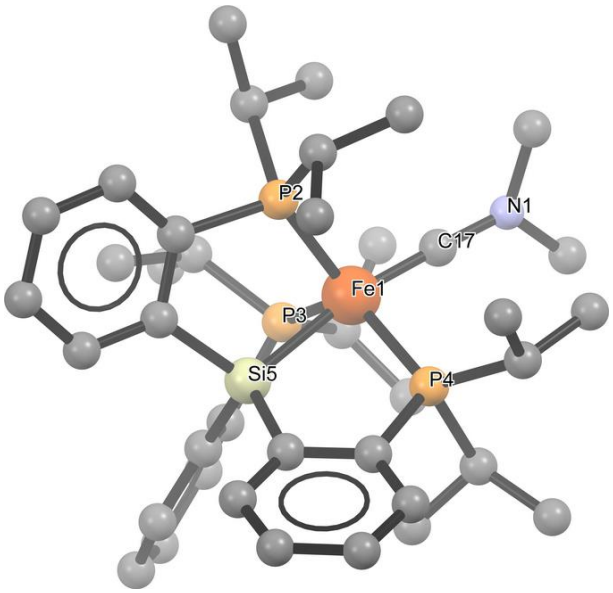
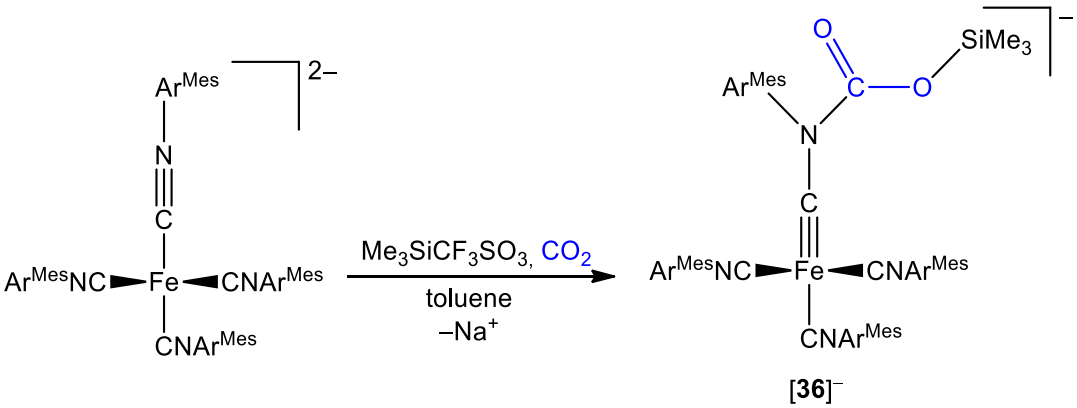


Figure 5. View of the X-ray structure of **35** [84]. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Fe1-C17 1.710(1), C17-N1 1.328(1), Fe1-C17-N1 177.83(10).

The carbamato-substituted aminocarbyne compound [**36**]$^{-}$ was obtained by silylative trapping of one molecule of CO_2 by a Fe^{-II} tetraisocyanide anion, and isolated as a crystalline material in 39% yield, Scheme 13 [85]. In the X-ray structure of Na[**36**], salient bond distances are Fe-carbyne 1.658(10) and the exceptionally long carbyne-N 1.448(12) Å, revealing a substantially pure carbyne nature (structure **I** in Scheme 1). The related ^{13}C NMR resonance falls at 225.9 ppm.



Scheme 13. Building of aryl-carbamato aminocarbyne on a low-valent iron isocyanide complex (sodium salts). Ar^{Mes} = 2,6-(2,4,6- $C_6H_2Me_3)_2C_6H_3$.

The unique example of terminal cobalt-(amino)carbyne complex, **37**, was claimed to be prepared by Figueroa and co-workers, by the reduction of a precursor containing a bulky isocyanide ligand with an excess of KC_8 in benzene, Equation 12 [86].

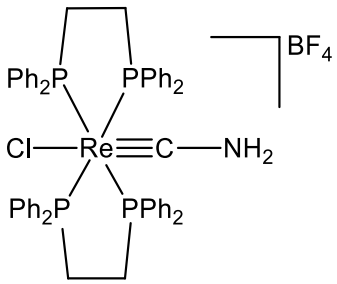
$$[CoI_2(Cp^*)(CNAr)] + KC_8 \rightarrow [K_2(Et_2O)_2][Co(Cp^*)(CNAr)] \quad (12)$$

Ar = 2,6-(C_6H_3)(2,4,6-$C_6H_2{}^iPr_3$)$_2$ **37**

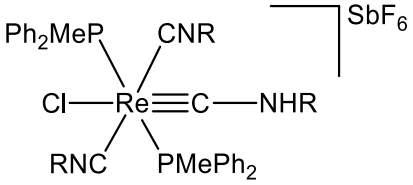
In the X-ray structure of **37**, the Co-CN distance is 1.670(3) Å, i.e. significantly contracted with respect to a range of Co-carbene species, providing the best evidence for the carbyne nature of the ligand. Consistently, the infrared band due to the C-N bond falls at 1509 cm^{-1}. On the other hand, the supposed carbyne center resonates at 181.0 ppm in the ^{13}C NMR spectrum, i.e. significantly shielded compared to what usually observed in iron-carbyne moieties.

Primary and secondary rhenium aminocarbyne complexes were obtained by protonation of isocyanide ligands, and their structures are shown in Scheme 14 (compounds **38a-c**) [87,88,89]. The aminocarbyne function in **38a** is easily deprotonated, either to the related isocyanide via electrochemical oxidation [90] or to cyanide in the presence of a variety of suitable reactants [91].

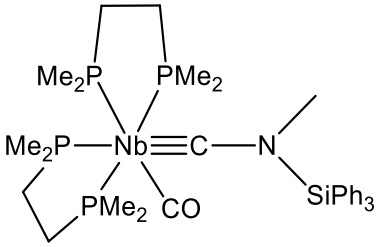
Finally, aminocarbyne compounds of low valent group 5 metals are likely intermediates along the reductive coupling of carbonyl and isocyanide ligands on niobium and tantalum centers. One of the aminocarbyne species was stabilized by silylation of a reaction mixture (compound **39** in Scheme 14), and then fully characterized [92].



38a



R = Me, **38b**
R = ^{t}Bu, **38c**



39

Scheme 14. Rhenium and niobium aminocarbyne complexes in the literature [89, 92]. Selected bond lengths (Å) and angles (°) from crystallographic characterizations: **38a**, Re-carbyne 1.802(4), carbyne-N 1.309(5), Re-C-N 171.9(3); **38b** (R = ^{t}Bu), Re-carbyne 1.82(1), carbyne-N 1.30(1), Re-C-N 175.7(9); **39**, Nb-carbyne 1.923(8), carbyne-N 1.38(1), Nb-C-N 172.2(6). IR (ϑCN/cm^{-1}): **38a**, 1595; **38b** (R = Me), 1594; **38c** (R = ^{t}Bu), 1588; **39**, 1419. ^{13}C NMR (δ/ppm): **38a**, 222.4; **38b** (R = Me), 228.5; **38c** (R = ^{t}Bu), 227.5.

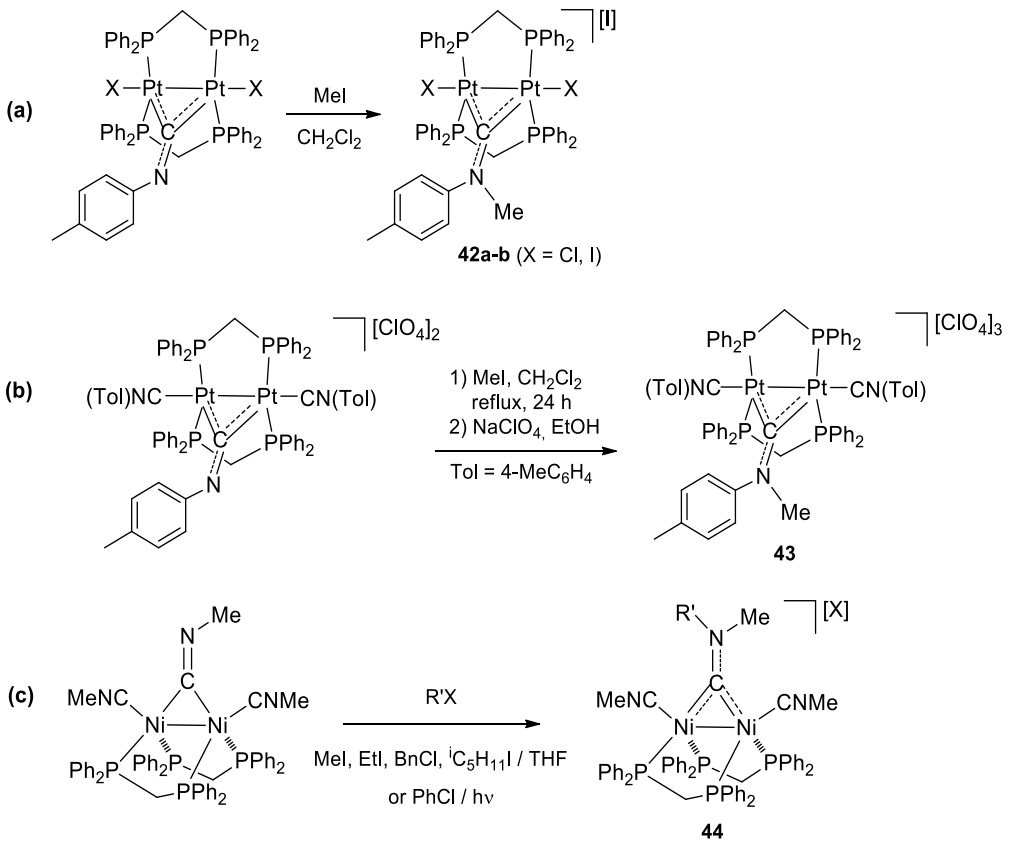
3. Bridging tertiary aminocarbyne ligands in homo-dinuclear complexes

Several homo-dimetallic complexes containing a bridging aminocarbyne ligand of the type {μ_2-CNRR'} (tertiary aminocarbyne) are known, and in particular monocationic diiron and diruthenium bis-cyclopentadienyl complexes constitute the entry to diverse organometallics. In general, no examples have been reported of di- and polymetallic systems containing any type of terminal aminocarbyne ligand (vide infra), highlighting a net preference for bridging coordination which is indicative of a marked π-acceptor behavior (vide infra).

3.1. Synthetic routes

3.1.1. From isocyanide alkylation

Being common to the preparation of terminal aminocarbyne species (Section 2.1.2), the alkylation of an isocyanide ligand represents the most feasible strategy to obtain {μ_2-CNRR'} ligands in dimetallic systems. The Lewis basicity of the nitrogen atom is regulated by the degree of backbonding from the metal center(s) to the isocyanide, which in turn depends on the net charge of the complex and the presence of competing π-acceptor co-ligands. Therefore, the bridging 4-tolyl isocyanide ligand in the neutral Pt^{I} halide complexes $[Pt_2X_2(\mu\text{-CNTol})(\mu\text{-dppm})_2]$ is readily alkylated by an excess of methyl iodide in dichloromethane to give the aminocarbyne **42** in nearly quantitative yields (Scheme 15a). Instead, the analogous methylation is considerably slower for the dicationic complex $[Pt_2(CNTol)_2(\mu\text{-CNTol})(\mu\text{-dppm})_2]^{2+}$, finally affording **43** in 83% yield (Scheme 15b) [93]. The electron-rich Ni^0 complex $[Ni_2(CNMe)_3(dppe)_2]$ reacts with one equivalent of alkyl- and aryl-halides to generate **44** in high yields [94,95]; interestingly, phenyl addition to the isocyanide was realized via photolytic treatment in solution of chlorobenzene [96].



Scheme 15. Synthesis of diplatinum and dinickel complexes with bridging tertiary aminocarbyne ligands.

Alkylation reactions of isocyanide ligands in bis-cyclopentadienyl carbonyl diiron complexes have been thoroughly investigated over the years, thus enabling a detailed analysis of the factors governing this chemistry. The mono-isocyanide adducts $[Fe_2Cp_2(CO)_3(CNR)]$ are prepared via CO substitution from the reaction of a variety of alkyl and aryl isocyanides with a slight molar excess (1.1 to 1.6 eq.) of the commercial dimer $[Fe_2Cp_2(CO)_4]$ in acetonitrile, thus preventing the occurrence of bis-substitution (Equation 13) [97].

$$[Fe_2Cp_2(CO)_4]\ (excess) + CNR \xrightarrow[\substack{RT/reflux\\ -CO}]{MeCN} [Fe_2Cp_2(CO)_3(CNR)] \qquad (13)$$

Complexes $[Fe_2Cp_2(CO)_3(CNR)]$ exist in solution as mixtures of interconverting isomers: an equilibrium between cis-trans isomers (with reference to the Cp ligands) and terminal-bridging

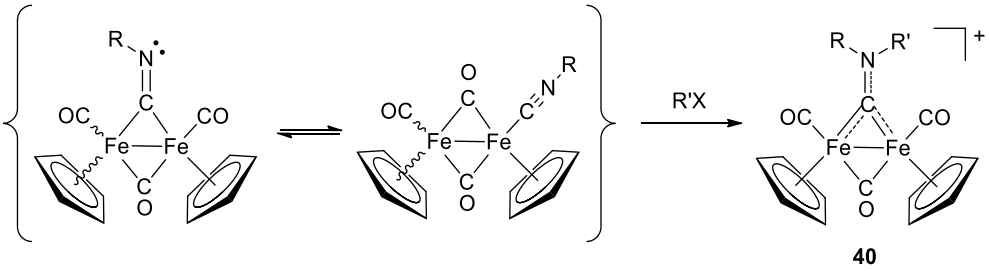
isomers (with reference to the CNR ligand) can be established according to the Adams-Cotton mechanism [98]. However, only terminal isocyanide species may be observed with bulky R groups (e.g. cyclohexyl, 2,6-dimethylphenyl = Xyl, tert-butyl), the isocyanide migration to the bridging site being hampered due to steric reasons [97,99]. The mono-isocyanide adducts react with an excess of alkyl halides (R'X) to afford **40** in high yields [100,101], and this reaction has been extended to some Cp-substituted diiron species. In the products, the Cp rings preferentially adopt the mutual cis geometry, and the aminocarbyne moiety is always found as bridging between the two metal atoms (Scheme 16). In principle, the occupation of the bridging site by the isocyanide in $[Fe_2Cp_2(CO)_3(CNR)]$ favors the electrophilic attack, since the enhanced backbonding from the two metals increases the localization (basicity) of the nitrogen lone pair. Indeed, according to our experience, the treatment of $[Fe_2Cp_2(CO)(\mu\text{-}CO)_2(CNXyl)]$ with ethyl or allyl iodide fails to produce the related aminocarbyne [102].

The alkylating strength of R'X parallels the reactivity typically observed in the nucleophilic substitutions by organic reagents, concerning both R' (allyl, benzyl, Me > Et > ^{i}Pr > ^{t}Bu >> Ph) and the leaving group (X = I >> Br > Cl). Instead, the effect exerted by the isocyanide substituent (R) is mostly steric in nature, *i.e.* a higher reactivity is associated to decreased bulkiness (R = Me > Et > Ph > Bn >> ^{i}Pr > ^{t}Bu) [100,101].

The use of powerful alkylating agents, such as trialkyloxonium tetrafluoroborates, dialkyl sulfates and dialkyl fluorosulfonates, is sometimes accompanied by side-reactions [100,103]. Actually trifluoromethanesulfonates, CF_3SO_3R' (R' = Me, Et), turned out to be the best reagents from a preparative standpoint, allowing the high-yield synthesis of a number of aminocarbyne derivatives (Scheme 16) [101,104]. For instance, CF_3SO_3Me is well performing also to methylate $[Fe_2Cp_2(CO)(\mu\text{-}CO)_2(CNXyl)]$ (see above).

The use of acetonitrile as solvent in the place of low polarity solvents (*i.e*. benzene, diethyl ether, CS_2) is useful to minimize the formation of the *trans*-Cp isomers [104]. Recently, a straightforward procedure was reported to access **40** directly from $[Fe_2Cp_2(CO)_4]$ in a multigram scale [105,106]: the

preliminary reaction of the isocyanide with $[Fe_2Cp_2(CO)_4]$ (Equation 13) is followed by treatment with the alkylating agent in the appropriate solvent/temperature conditions, without the need of isolating the neutral intermediate $[Fe_2Cp_2(CO)_3(CNR)]$. The salt of **40** is easily separated from unreacted $[Fe_2Cp_2(CO)_4]$ and other by-products by means of alumina chromatography and finally isolated in generally high yield.



40

Scheme 16. Alkylation of the isocyanide (usually undergoing exchange between bridging and terminal sites) in diiron bis-cyclopentadienyl complexes, affording a bridging tertiary aminocarbyne ligand. R'X = alkyl halides (see text), $[OR'_3]BF_4$, R'_2SO_4, R'_2SO_3F, $R'CF_3SO_3$. Experimental conditions: solvent CH_2Cl_2, MeCN or others, room temperature or above.

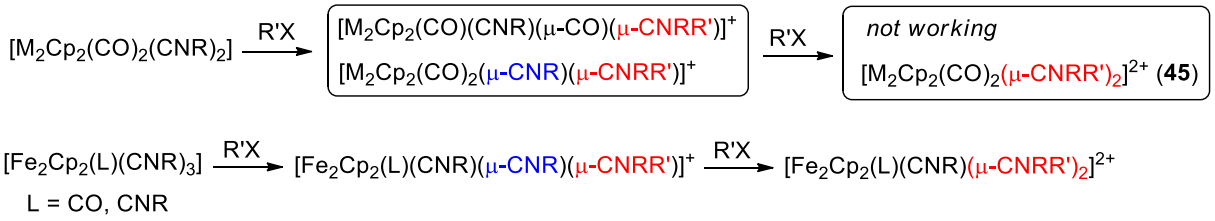
A series of diruthenium analogues of **40**, i.e. **41**, has also been obtained via the reaction of $[Ru_2Cp_2(CO)_4]$ with an excess of isocyanides at high temperature, followed by methylation in dichloromethane solution (Scheme 17) [107,108] The CO/CNR substitution was achieved either in xylene or in THF in the presence of trimethylamine-N-oxide.

$$[Ru_2Cp_2(CO)_4] + CNR\ (excess) \xrightarrow[\text{reflux}\ -CO]{\text{xylene or THF/Me}_3\text{NO}} [Ru_2Cp_2(CO)_3(CNR)] \xrightarrow[CH_2Cl_2,\ RT]{CF_3SO_3Me} [Ru_2Cp_2(CO)_3\{\mu\text{-CNR(Me)}\}]^+$$

41

Scheme 17. Two-step synthesis of diruthenium complexes with a bridging aminocarbyne ligand. R = Me, CH_2Ph.

Diiron and diruthenium compounds containing two (or more) isocyanide ligands may undergo both mono- and bis-alkylation, the first alkylation being usually selective under stoichiometric conditions. Thus, complexes $[Fe_2Cp_2(CO)_{4-x}(CNR)_x]$ (x = 2-4), and related Cp-substituted species, and $[Ru_2Cp_2(CO)_2(CNBn)_2]$ react with one equivalent of alkyl halides [100,109] or trifluoromethanesulfonates [104,107b] to quantitatively afford the mono-aminocarbyne products (Scheme 18). Then, only those cations still containing a reactive, *bridging* isocyanide are susceptible of a second alkylation (from an excess of $MeSO_3F$ or MeI/EtI), which leads to bis-cationic complexes (**45**) containing two bridging aminocarbynes [109,110]. On the other hand, the absence of a bridging isocyanide in the mono-cationic derivative and the lack of an accessible pathway for terminal to bridging migration prevents the second electrophilic attack even under forcing conditions [104,110,111].



Scheme 18. Bis-alkylation patterns of diiron/diruthenium bis-cyclopentadienyl poly-isocyanide complexes. The family of complexes **45** includes Cp' species (Cp' = η^5-C_5H_4Me).

A comparative view of the X-ray structures of cationic aminocarbyne complexes based on the $\{Fe_2Cp_2(CO)_x\}$ scaffold (x = 2 or 3) is provided in Figure 6.

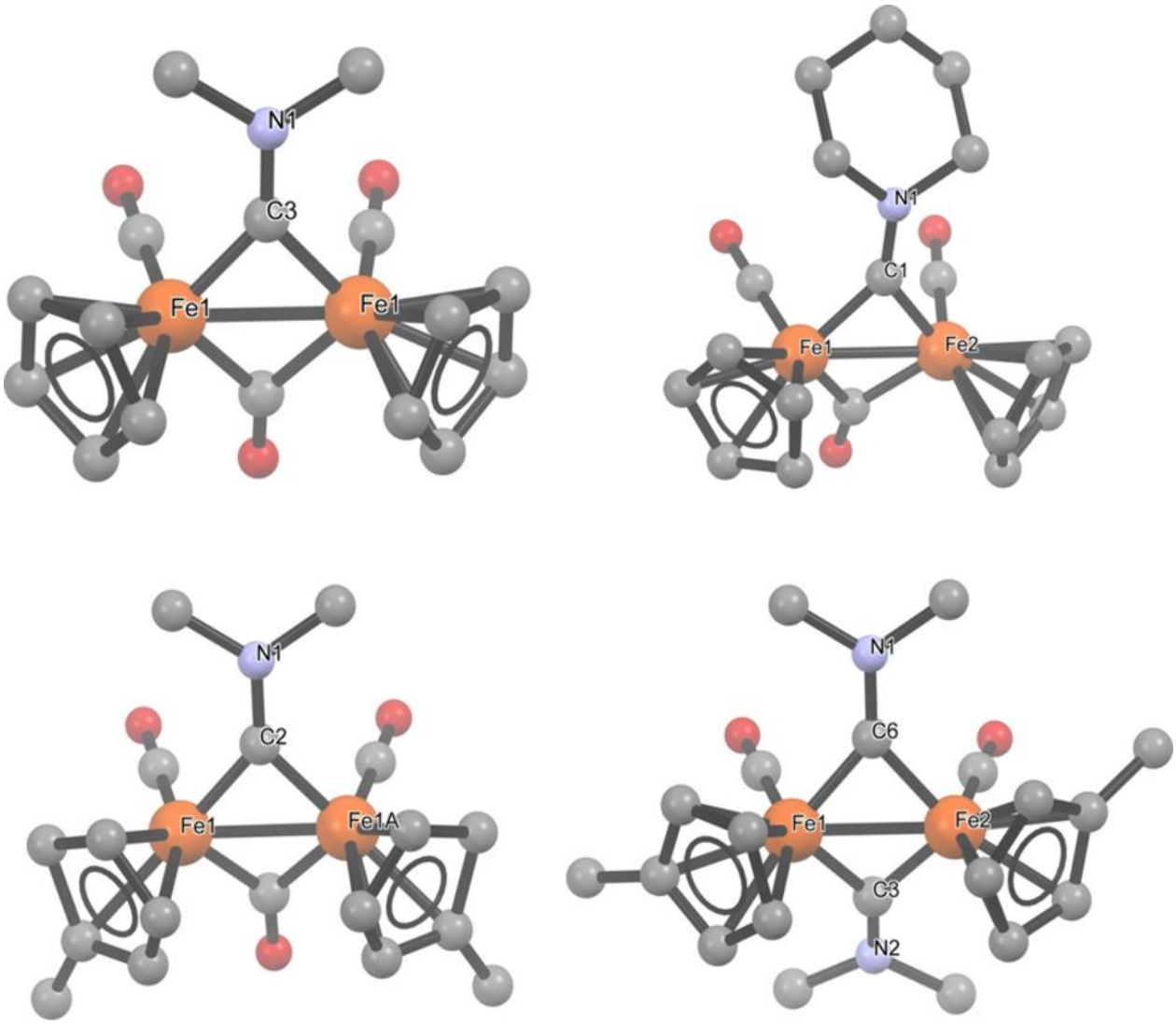


Figure 6. Comparative view of the X-ray structures of the cations $[Fe_2Cp_2(CO)_3(\mu\text{-}CNMe_2)]^+$ (**40a**, $CF_3SO_3^-$ salt) [105], $[Fe_2Cp_2(CO)_3\{\mu\text{-}C(NC_5H_{10})\}]^+$ (**40b**, $[W_2(CO)_{10}(\mu\text{-}CN)]^-$ salt) [116], $[Fe_2Cp'_2(CO)_3(\mu\text{-}CNMe_2)]^+$ (**40c**, I^- salt) [100] and $[Fe_2Cp'_2(CO)_2(\mu\text{-}CNMe)_2]^{2+}$ (**45a**, $CF_3SO_3^-$ salt) [104]. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Fe-Fe 2.5218(7) (**40a**), 2.519(1) (**40b**), 2.508 (**40c**), 2.500(1) (**45a**); Fe-carbyne 1.875(2) (**40a**), 1.876(8) (**40b**, average value), 1.850 (**40c**), 1.884(10) (**45a**, average value); carbyne-N 1.297(4) (**40a**), 1.280(8) (**40b**), 1.300 (**40c**), 1.295(9) (**45a**, average value); Fe-carbyne-Fe 84.53(13) (**40a**), 84.4 (**40b**), 85.35 (**40c**), 83.2(3) (**45a**).

A special case is represented by bidentate diisocyanide ligands, which generate a tetranuclear scaffold by bridging two $\{Fe_2Cp_2(CO)_3\}$ units [112,113]. The 1,2-diisocyanoethane ligand undergoes a double alkylation with excess $[Me_3O]BF_4$ to afford the bis-aminocarbyne $[Fe_2Cp_2(CO)_3\{\mu\text{-}CN(Me)CH_2\}]_2$ (**40d**). However, the rigid 1,2-diisocyanobenzene can be alkylated only once under identical conditions, due to steric reasons. Similarly, a homoleptic diiron(0) isocyanide adduct was reported to be quickly bis-alkylated in THF solution (Equation 14, yields 56-60%) [114].

$$[Fe_2(CNEt)_6(\mu\text{-}CNEt)_3] + 2RI(\text{excess}) \rightarrow [Fe_2(CNEt)_6(\mu\text{-}CNEt)\{\mu\text{-}CNEt(R)\}_2][I]_2 \qquad (14)$$

R = Me, I [**46**][I]$_2$

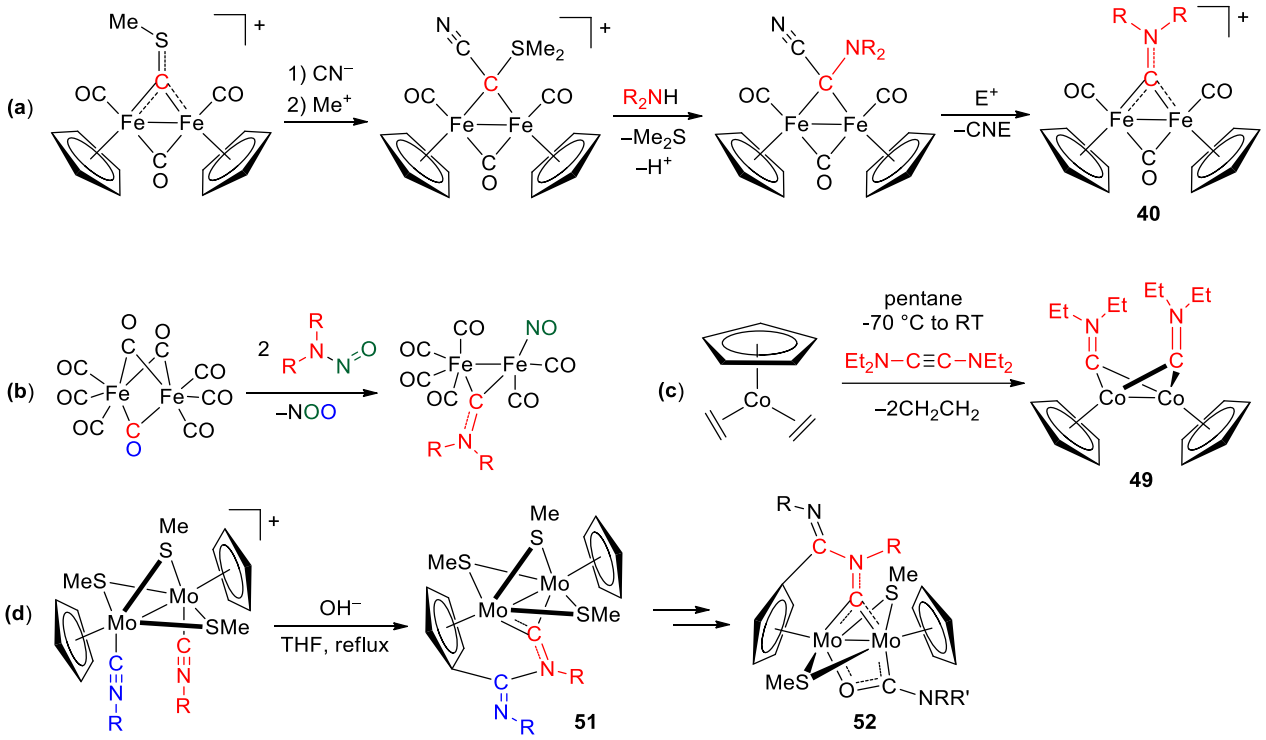
Complex $[Fe_2Cp_2(CO)(CNMe)_2(CS)]$ comprises two different Lewis basic heteroatoms: the addition of methyl iodide leads to selective S-methylation while the stronger methylating agent $MeSO_3F$ affords the mixed aminocarbyne-thiocarbyne species $[Fe_2Cp_2(CO)(CNMe)(\mu\text{-}CNMe_2)(\mu\text{-}CSMe)]^{2+}$ (**47**) in 56% yield [115].

3.1.2. Other methods

An alternative route to diiron/diruthenium aminocarbyne complexes based on the $\{M_2Cp_2(CO)_3\}$ scaffold exploits the reactivity of a thiocarbyne precursor (Scheme 19a). Sequential cyanide addition and methylation generate a sulfonium salt, and its aminolysis is followed by cyanide abstraction with a strong electrophile [116]. Remarkably, this method allows the preparation of a cyclic aminocarbyne group otherwise not accessible, when piperidine is employed in the aminolysis step. The structure of $[Fe_2Cp_2(CO)_3\{\mu\text{-}C(NC_5H_{10})\}]^+$ (**40b**) was crystallographically determined as $[W_2(CO)_{10}(\mu\text{-}CN)]^-$ salt (Figure 6) and evidences a relatively shorter carbyne-nitrogen distance compared to **40a** [1.280(8) vs. 1.297(4) Å], reflecting the higher electron donor capability of the C_5 ring compared to two methyl groups [116].

Bridging aminocarbyne ligands on a diiron frame have also been constructed from the reaction of $Fe_2(CO)_9$ with N-nitrosoamines (R_2NNO, R = Me, Et), affording $[Fe_2(CO)_6(NO)(\mu\text{-}CNR_2)]$ (**48**) as the main product (Scheme 19b) [117], wherein the carbyne center derives from the scission of one CO ligand. Aminoalkynes $Et_2NC{\equiv}CX$ (X = SPh, NEt_2, $SiMe_3$) may be exploited as another source for aminocarbyne, upon cleavage of the C-C triple bond. This reactivity has been observed uncleanly with iron carbonyls [118], while the straightforward reaction of (cyclopentadienyl)-bis(ethene)cobalt with bis(diethylamino)acetylene results in the 65% yield formation of the dicobalt bis-aminocarbyne product **49** (Scheme 19c and Figure 7) [119]. Another example of ligand cleavage is represented by the dithiocarbamato moiety within the mono-tungsten complex $[W(CO)_2\{Sn(CHSiMe_3)_2\}(S_2CNEt_2)_2]$, which was converted into aminocarbyne upon heating in benzene solution; thus the dinuclear complex $[\{W(\kappa^2\text{-}S_2CNEt_2)\}_2(\mu\text{-}CNEt_2)(\mu\text{-}S)(\mu\text{-}S_2CNEt_2)\{\mu\text{-}S_2Sn(CHSiMe_3)_2\}]$ (**50**) was isolated in 35% yield [120].

Pétillon, Schollhammer and co-workers deeply investigated the chemistry of dimolybdenum tris-thiolato isocyanide complexes. The Cp deprotonation of $[Mo_2Cp_2(\mu\text{-}SMe)_3(CNR)_2]BF_4$ by means of sodium hydroxide (or tetramethylammonium hydroxide) triggers a peculiar intramolecular condensation process involving the two isocyanides, resulting in the formation of a ring-tethered aminocarbyne ligand (**51**, see Scheme 19d and the X-ray structure of **51a** in Figure 7) [121]. The reaction is nearly quantitative in the case of R = Xyl, while the formation of by-products occurs with R = ^{t}Bu. A similar outcome was observed using sodium acetylide in the place of the hydroxide (thiolate/acetylide replacement, see **51b** in Table 2). Under prolonged heating and in the presence of an excess of isocyanide, **51** undergoes further hydroxide-isocyanide coupling and converts into **52** upon elimination of one thiolate unit [121b].



Scheme 19. Alternative routes for the installation of μ_2-tertiary aminocarbyne ligands (red) in dinuclear complexes: (a) anion abstraction from aminocarbene (R_2 = Me_2 or C_5H_{10}; E = HCF_3SO_3, $MeCF_3SO_3$, $[W(CO)_5(THF)]$); (b) cleavage of carbonyl ligand and N-nitrosoamine (R = Me or Et); (c) cleavage of bis(amino)alkyne; (d) base-promoted isocyanide-isocyanide C-N coupling (R = Xyl = 2,6-$C_6H_3Me_2$ or ^{t}Bu; R' = H, Et, ^{n}Bu).

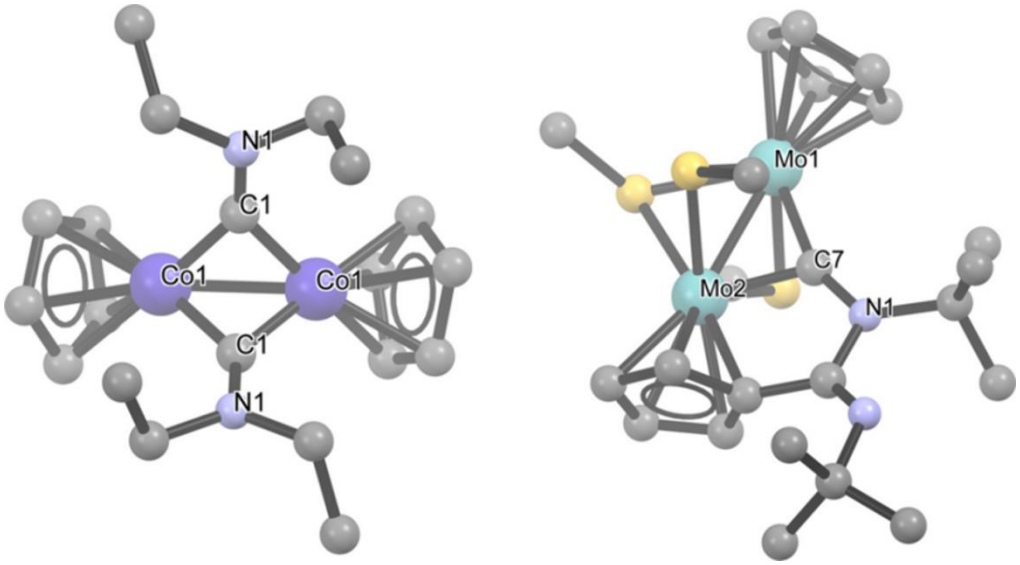


Figure 7. Views of the X-ray structures of $[Co_2Cp_6(\mu\text{-}CNEt_2)_2]$ (**49**) [119] and $[Mo_2Cp(\mu\text{-}SMe)_3\{\mu\text{-}(\eta^5\text{-}C_5H_4)C(N^tBu)NC(^tBu)\}]$ (**51a**, R = ^{t}Bu) [121a]; H atoms omitted for clarity. Selected bond lengths (Å): **49**, Co-Co 2.3662(11), Co-carbyne 1.821(3), carbyne-N 1.312(3); **51a**, Mo-Mo 2.584(1), Mo-carbyne 2.117(2), carbyne-N 1.361(2).

3.2. Reactivity

Studies on the reactivity of tertiary aminocarbyne ligands bridging coordinated in homo-dimetallic complexes have been essentially circumscribed to the rich chemistry of bis-cyclopentadienyl carbonyl iron and ruthenium species. Remarkably, the reactions of such category of compounds can be finely controlled by the experimental conditions, and generally proceed with regio- and stereo-selectivity, thus offering straightforward pathways to access a vast variety of hydrocarbyl ligands. The aminocarbyne unit can be directly involved or act as a spectator ligand, but in the latter case still playing a crucial role in promoting and directing the reactivity.

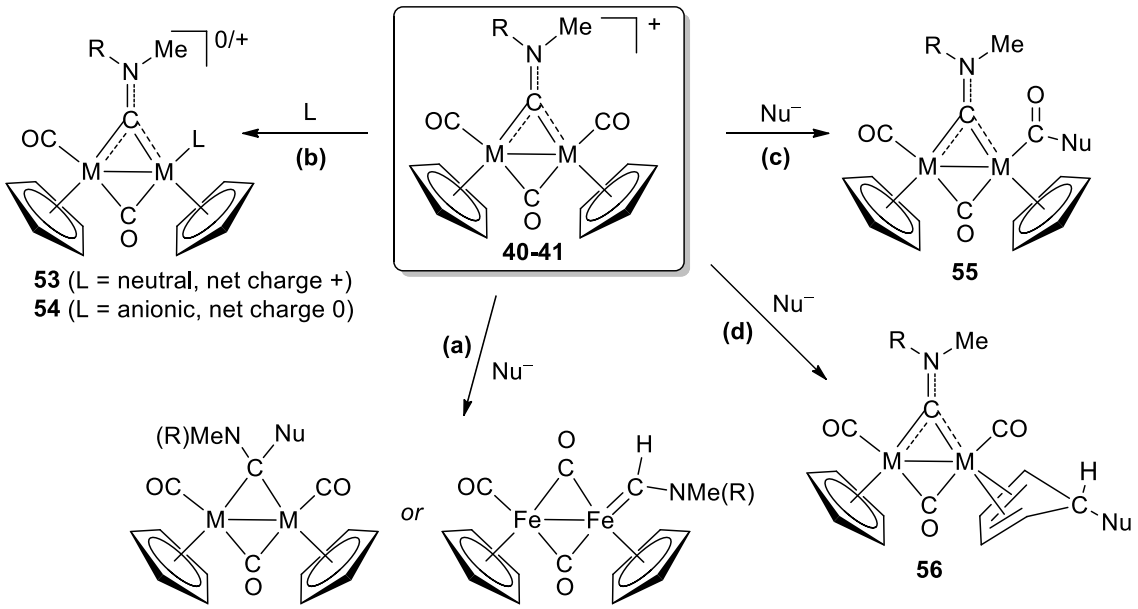
3.2.1. Nucleophilic addition and CO substitution reactions

The aminocarbyne ligand in **40**-**41** is substantially inert: as a matter of fact, nucleophilic additions to these complexes are favored by their net cationic charge, but additions to the carbyne are limited to the cases of hydride (from $NaBH_4$) and cyanide (from NBu_4CN). Instead, a range of other anionic nucleophiles gives rise to attack to either the terminal CO or the Cp ring. In general, all of these reactions are regioselective, i.e. the site of attack is dictated by the nature of the nucleophile and, in some cases, by steric effects exerted by the aminocarbyne N-substituents.

Thus, the reactions of **40**-**41** (M = Fe, R = Me, Et, Bn, 2-naphthyl; M = Ru, R = Bn) with $NaBH_4$, in THF at room temperature, lead to aminoalkylidene complexes (Scheme 20a) [105,107b,110,122]. Accordingly, DFT calculations carried out on the diiron system predict the carbyne atom to be the thermodynamically favored site of hydride addition. However, the reaction outcome seems affected by the electronic properties of R: when R is an alkyl (Me, Et or Bn), the newly generated carbene

moiety interchanges its position with a terminal CO, otherwise it remains bridging when R is 2-naphthyl. Furthermore, the presence of R = Xyl determines a steric protection towards the carbyne center, deviating the hydride addition to one cyclopentadienyl ligand [105]. Analogously, the reactions of **40-41** with $[NBu_4]CN$ in dichloromethane yield the amino(cyano)alkylidene derivatives $[M_2Cp_2(CO)_3\{\mu\text{-}C(CN)NMe(R)\}]$, Scheme 20a [107b,110,122]. Interestingly, the latter complexes may restore the aminocarbyne function by cyanide migration to one terminal iron site, replacing one CO ligand, in aqueous solution at room temperature or under thermal treatment [105]. The reaction of $[Fe_2Cp_2(CO)_3\{\mu\text{-}CNMe(Xyl)\}]$ (**40e**) with $[NBu_4]CN$ in CH_2Cl_2 directly proceeds with CO/CN^- substitution affording $[Fe_2Cp_2(CN)(CO)_2\{\mu\text{-}CNMe(Xyl)\}]$ (**54a**, Scheme 20b) [105].

The carbonyl ligand of **40-41** is selectively attacked by lithium acetylides [123], 2-thienyllithium [124] and organo-cuprates [108,125], resulting in the formation of the acyl derivatives **55** [126], and thus preserving the aminocarbyne group (Scheme 20c). Then, the acyl moiety can be sequentially converted into functionalized carbene and alkyl fragments [105]. On the other hand, the Cp ring is the preferential site for the addition of lithium alkyls and Grignard reagents, affording the η^4-cyclopentadiene complexes **56** (Scheme 20d) [108,125]. In the diruthenium system, a competition between CO and Cp as addition site was observed when $PhCH_2MgCl$ was investigated as nucleophile [108]. Dealkylation of the aminocarbyne group by nucleophilic abstraction is a rare process, which has been reported to occur in one case under drastic conditions [100].



Scheme 20. Overview of nucleophilic addition and CO substitution reactions on diiron and diruthenium bis-cyclopentadienyl complexes. (a) $Nu^- = H^-$ (from $NaBH_4$) or CN^- (from NBu_4CN). (b) via direct substitution: L = CN^-, R = Xyl, M = Fe; via CO displacement with Me_3NO: L = N≡CR', NH_2R', NHR'_2, pyridine, $Ph_2C{=}NH$, C≡NR', phosphines, H^- (bridging coordinated, from $NaBH_4$), CN^- (from NBu_4CN), halide, NCS^-, NCO^-, N_3^-, $S_2CNEt_2^-$, $CH(CN)_2^-$, Ph^- (from Li/Na salts). (c) $LiC{\equiv}CR'$, LiC_4H_3S, $Li_2Cu(CN)R'_2$. (d) LiR', R'MgCl.

The synergic electronic effects provided by the CO and Cp ligands confer a substantial robustness to the dinuclear frame of **40-41**, which is usually inert to substitution reactions. A general, effective strategy to replace one carbonyl ligand with a range of neutral and anionic fragments is the treatment with trimethylamine N-oxide, converting CO into CO_2. By this way, it is possible to introduce nitriles [127], amines [128], imines [128], isocyanides [129], hydride [130], halides and pseudohalides [131,132], dithiocarbamates, carbanions and phosphines (Scheme 20b) [132]. In most cases, the acetonitrile adducts (**53-NCMe**) are first generated, and then NCMe is replaced with the desired L; else, the CO/L substitution is performed in one pot. In general, the L ligand in **53-54** type compounds occupies a terminal coordination site, apart from very few exceptions (e.g. hydride and CNMe in **53j**, see Table 2). Note that some unsaturated L groups can be then employed as starting materials for the

assembly of unusual organometallic architectures, via sequential nucleophilic/electrophilic additions [133].

In summary, the aminocarbyne ligand in complexes **40-41** is sluggish to C-C bond forming reactions; as a matter of fact, the η^5-cyclopentadienyl ring, being usually considered an ancillary ligand in organometallic chemistry, is significantly more reactive towards carbanionic nucleophiles. Such inertness deeply contrasts with the extreme electrophilicity exhibited by the carbyne ligand in the related $[Fe_2Cp_2(CO)_3(\mu\text{-}CR)]^+$ complexes (R = H, Me), which was highlighted by Casey in the 1980s [134]. For instance, a dichloromethane solution of $[Fe_2Cp_2(CO)_3(\mu\text{-}CH)]PF_6$ adds carbon monoxide at ambient temperature and pressure, affording the bridging alkylidene product $[Fe_2Cp_2(CO)_3\{\mu\text{-}CH(CO)\}]PF_6$ in 90% yield [135]. Such striking difference, i.e. the considerable lower electrophilic behavior of the carbyne ligand in $[Fe_2Cp_2(CO)_3\{\mu\text{-}CNMe(R)\}]^+$ compared to $[Fe_2Cp_2(CO)_3(\mu\text{-}CR)]^+$, is ascribable to the competition of the carbyne carbon for the nitrogen lone pair in the former, resulting in a significant iminium character (vide infra).

The diiron bis-aminocarbyne complexes $[Fe_2Cp_2(CO)_2\{CNR(R')\}_2]^{2+}$ (**45**, Scheme 18) undergo more facile CO substitution with respect to the related mono-aminocarbyne species **40** [136]. Note that CO/MeCN exchange was ascertained on an acetonitrile solution of $[Fe_2Cp_2(CO)_2(\mu\text{-}CNMe_2)_2]^+$ (**45b**) stored at –10 °C for months. Conversely, no products of nucleophilic addition to the aminocarbyne have been reported for **45**. This observation suggests that the electrophilic character of the carbyne atom is lower in **45** than in **40**, presumably due to the increased nitrogen to carbyne π-donation, balancing the weakening of iron to carbyne π-backdonation due to the double positive charge. Otherwise, the double charge and the increased inductive effect exerted by the $\{R_2N^+{=}C\}$ moiety enhance the electrophilic character of the N-substituents. Therefore, demethylation can occur as promoted by mildly Lewis-basic species like cyanide or aliphatic phosphines (Equation 15, bistriflate salt) [136].

$[Fe_2Cp_2(CO)_2\{CNMe_2\}_2]^{2+} + PR_3 \rightarrow [PR_3Me]^+ + [Fe_2Cp_2(CO)_2(CNMe)(CNMe_2)]^+$ (15)

45 **(**R = Me, Et)

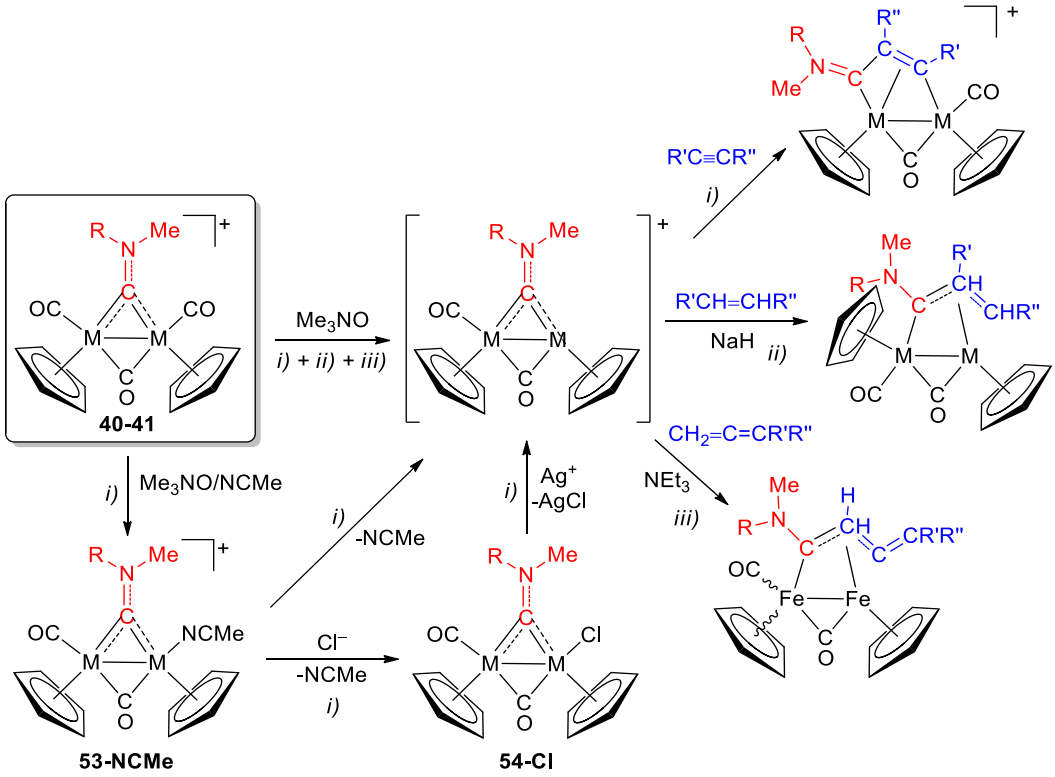
3.2.2. C-C and C-N coupling reactions

The generation of a coordination vacancy on the diiron/diruthenium **40-41,** via CO elimination, favors the direct C-C bond coupling of the carbyne center with unsaturated species under mild conditions. The cooperativity provided by the dimetallic framework drives these reactions and stabilizes the resulting hydrocarbyl ligands by multisite coordination. Basically, three different strategies can be adopted to obtain the hypothetical 34-electron Lewis acidic fragment $[M_2Cp_2(CO)_2\{\mu\text{-}CNMe(R)\}]^+$ (Scheme 21), which is formally the reactive species: 1) direct CO removal with Me_3NO, usually in THF (see also Scheme 20b); 2) CO/NCMe substitution in acetonitrile solution, affording the isolable intermediate $[M_2Cp_2(CO)_2(NCMe)\{\mu\text{-}CNMe(R)\}]^+$ (**53-NCMe**), which then releases the labile NCMe ligand in the presence of a suitable reactant (see above); 3) chloride abstraction from $[M_2Cp_2(Cl)(CO)_2\{\mu\text{-}CNMe(R)\}]$ (**54-Cl**), preliminarily prepared from **53-NCMe**, with a silver salt. Alkynes are expected to occupy the free site of $[M_2Cp_2(CO)_2\{\mu\text{-}CNMe(R)\}]^+$ via η^2-coordination, and fast alkyne insertion into the metal-carbyne bond follows [137], affording a bridging vinyliminium ligand in an uncommon $\mu\text{-}\eta^1\text{:}\eta^3$ coordination fashion (Scheme 21, routes *i*). Interestingly, the alkyne insertion may be reversed under suitable conditions, and the base-promoted formation of diiron aminocarbyne complexes of type $[Fe_2Cp_2(CO)_2(L)\{\mu\text{-}CNMe(R)\}]^{0/+}$ (**53-54**; R = Me, 4-C_6H_4OMe or Xyl; L = SMe, C≡CSiMe_3 or CN^{t}Bu) has been observed from vinyliminium precursors [138].

The alkyne/aminocarbyne coupling is highly regioselective, in that the less hindered substituent (H in the case of terminal alkynes) is finally found adjacent to the iminium group, and displays a huge substrate scope and functional group tolerance. To date, around 100 different diiron vinyliminium complexes have been prepared directly from alkyne insertion [139,140,141,142], and they exhibit a fertile chemistry as summarized in a recent review [12]. It should be mentioned here that the stepwise

modification of vinyliminium ligands may lead to rare tetrasubstituted selenophenes, which can be finally removed from coordination in mild conditions (treatment with water in air). This is a significant use of diiron aminocarbyne complexes as easily available and convenient organometallic reagents for the synthesis of functionalized organics otherwise not accessible [143].

The highly regio- and stereo-selective assembly of the aminocarbyne with EWD-substituted alkenyl (Scheme 21, route *ii*; EWD = electron-withdrawing) [144] and 1,1-disubstituted allenyl anions (Scheme 21, route *iii*) [145] is performed in one pot from **40-41**, affording respectively amino-allylidene and aminobutadienylidene derivatives, in 70-80% yields [146]. In both reactions, the preliminary {C=C} η^2-coordination enhances the Csp^2-H acidity of the organic reactant, then deprotonation triggers the intramolecular coupling.



Scheme 21. C-C coupling reactions between aminocarbyne (R = alkyl or aryl) in diiron/diruthenium complexes and alkynes (routes *i)*, R' = H, alkyl, aryl, CO_2Me, $SiMe_3$, 2-thiophenyl, pyridyl, other; R" = H, alkyl, Ph, CO_2Me); alkenes (route *ii)*, R' = H, CO_2Me; R" = CN, CO_2Me, Ph); allenes (route *iii*), R', R" = H, Me or CO_2Et). $CF_3SO_3^-$ as counteranion for cationic complexes.

Another class of reactions consists in the selective assembly of two ligands promoted by the addition of an anionic nucleophile to diiron cationic complexes belonging to the family **53** (Scheme 22). Hydride attack to $[Fe_2Cp_2(CO)_2(CNXyl)\{\mu\text{-}CNMe(Xyl)\}]^+$, **53a**, selectively occurs at the terminally coordinated isocyanide (intermediate formation of **57**), then the migration of the resulting formimidoyl group to the aminocarbyne is thermally induced and generates a $\mu\text{-}\eta^1{:}\eta^1$-aldimine-aminoalkylidene ligand (Scheme 22a) [129].

On the other hand, addition of lithium acetylides to **53a** [147] and to the bis-isocyanide complex $[Fe_2Cp_2(CNXyl)_2(\mu\text{-}CO)\{\mu\text{-}CNMe(Xyl)\}]^+$ (**58**) [148] promotes a C-N bond coupling between the two terminally coordinated ligands, i.e. CO and CNXyl in the case of **53a** and two CNXyl in the case of **58**. In these cascade reactions, the aminocarbyne ligand, despite being a spectator one, plays a pivotal role in terms of electronic effects.

Nitrile ligands in $[Fe_2Cp_2(CO)_2(N{\equiv}CZ)\{\mu\text{-}CNMe(R)\}]^+$ do not behave as leaving groups towards carbanionic reagents (except CN^-). In particular, the simplest nitrile, i.e. acetonitrile (Z = Me), is usually deprotonated by strong Brønsted bases (including lithium acetylides), converting into cyanomethyl (Equation 16) [149]: this rearrangement has been rarely observed in organometallic chemistry [150].

$$[Fe_2Cp_2(CO)_2(NCMe)\{\mu\text{-}CNMe(R)\}]CF_3SO_3 + NaH \rightarrow [Fe_2Cp_2(CH_2CN)(CO)_2\{\mu\text{-}CNMe(R)\}] + NaCF_3SO_3 + H_2 \quad (16)$$

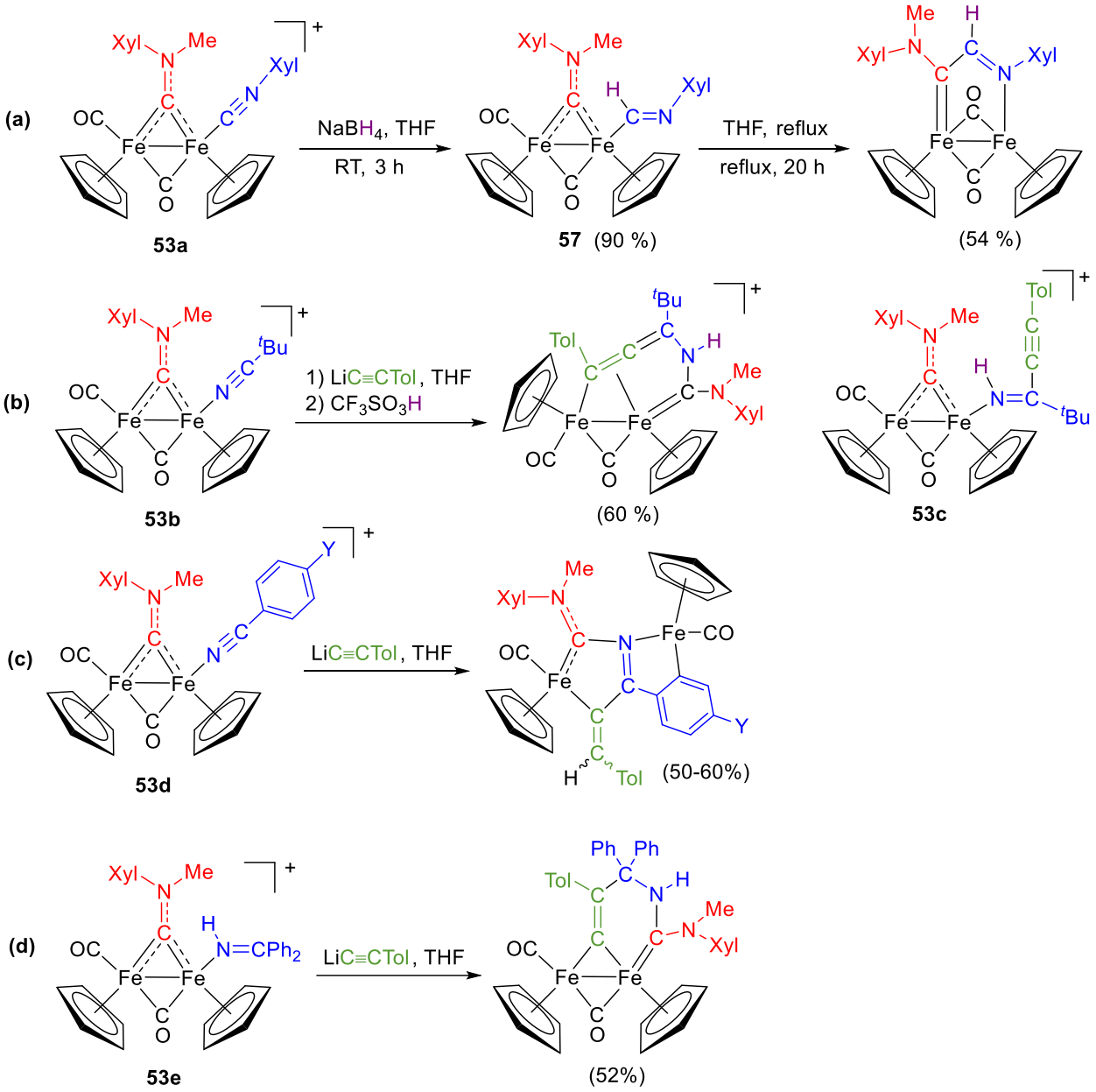
[**53-NCMe**]CF_3SO_3 (R = Me, Bn, Xyl) **59**

On the other hand, nitrile ligands lacking acidic hydrogens might undergo nucleophilic attack by lithium acetylides, to generate a reactive intermediate; in general, these reactions are clean when involving the {NMe(Xyl)} group and lithium 4-tolyl-acetylide (LTA), proceed with carbyne-N bond formation and their final outcome is strictly dependent on the nature of the nitrile substituent Z. More in detail, **53b** (Z = ^{t}Bu) reacts with LTA affording a seven-membered dimetallacycle ($\eta^1{:}\eta^2$-allene/η^1-diaminocarbene) in 60% yield, after addition of triflic acid to the mixture (Scheme 22b); when the H^+

addition is anticipated, the initial product of acetylide attack to the nitrile is blocked at an imine stage, and the aminocarbyne function is preserved (**53c**). Differently, the treatment of **53d** (Z = 4-substituted phenyl) with LTA gives rise to a more complex transformation, including Fe-Fe bond cleavage and ortho-metalation of the aryl nitrile substituent (Scheme 22c) [151]; this reaction has been reported for a series of aryl-nitriles and two additional examples descend from the {NMe_2} starting compound **40a**.

The reaction of the benzophenone imine adduct **53e** with LTA somehow resembles those involving nitrile ligands, and a π-vinylidene diaminoalkylidene product was obtained as a result of aminocarbyne/imine/acetylide assembly (Scheme 22d) [128].

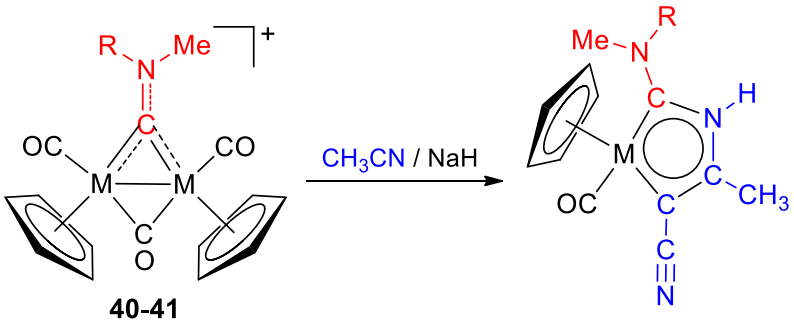
In summary, the coupling processes depicted in Scheme 22 show a considerable diversity and are almost unique according to the substituents in the diiron scaffold and the acetylide reactant.



Scheme 22. Intramolecular C-C and C-N coupling reactions between the aminocarbyne ligand (red) and fragments obtained by addition of, respectively, hydride (violet) and lithium 4-tolyl-acetylide (green) to terminal unsaturated ligands (blue). $CF_3SO_3^-$ as counteranion for cationic complexes. (c) Y = H, Br, OMe, CO_2Me, CF_3. Published yields of isolated products in parentheses.

The reaction of **40-41** with potassium hydride in acetonitrile solution provides a rare intermolecular carbyne-N coupling, which is accompanied by the disruption of the dimetallic frame and leads to the formation of a metalla-pyrrole in moderate yields (Scheme 23), being $[M_2Cp_2(CO)_4]$ (M = Fe, Ru)

the likely co-product [152]. It is presumable that this transformation proceeds with the condensation of two nitrile molecules promoted by the strong base NaH, giving the anion $[Me(NH)C=C(CN)H]^-$ which is able to attack the carbyne.



Scheme 23. Intermolecular coupling between the aminocarbyne ligand in diiron/diruthenium complexes (red; $CF_3SO_3^-$ as counteranion) and the anion derived from the condensation of two acetonitrile molecules (blue). M = Fe, Ru; R = Me, CH_2Ph.

3.3. Bonding description, structural and spectroscopic features

Bridging aminocarbyne ligands are usually associated to low-valent middle/late transition metals and can be conveniently envisaged as two-donor monocationic fragments (Fischer alkylidyne) [93,124,153], see Scheme 1. A possible exception is represented by the ditungsten compound $[\{W(\kappa^2\text{-}S_2CNEt_2)\}_2(\mu\text{-}CNEt_2)(\mu\text{-}S)(\mu\text{-}S_2CNEt_2)\{\mu\text{-}S_2Sn(CHSiMe_3)_2\}]$ (**50**), where the aminocarbyne should be best described as a trianionic fragment (Schrock alkylidyne) bonded to a W^V–W^V core[120].

According to the molecular orbital scheme proposed by Kubiak and co-workers [95], two metal-carbon bonds are formed with *sp*$_2$-type orbitals on the aminocarbyne carbon and *d*-type orbitals on the M-M frame. The remaining empty p orbital on the carbyne is available to receive electron density both from the metals and from the nitrogen lone pair, the latter interaction being favored by electron donor N-substituents (Scheme 24a). This π bonding competition determines the degree of "*carbyne*" or "*iminium*" character of the ligand, resembling the carbyne/azavinylidene dualism described for

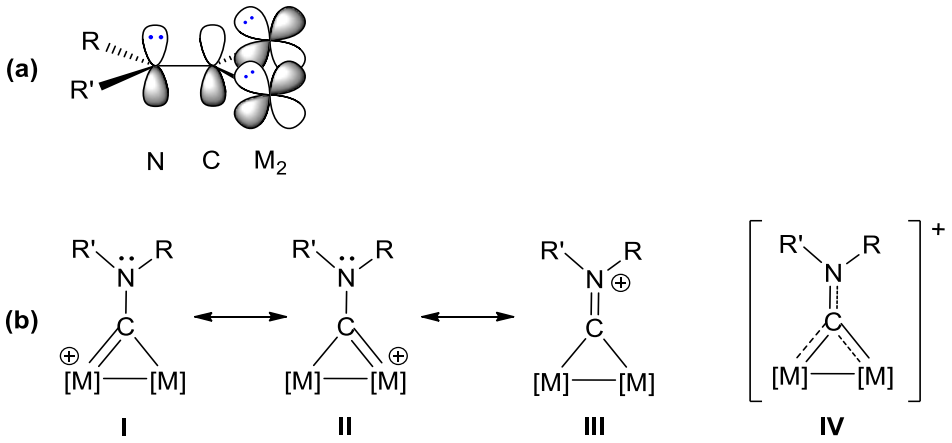
terminal aminocarbyne ligands (see Scheme 1). Thus, three canonical structures may be drawn for bridging aminocarbyne ligands in dimetallic complexes (Scheme 24b).

Reminiscent of this situation, the dimolybdenum μ-alkoxy-carbyne complex $[Mo_2Cp_2(CO)_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)]$ was DFT investigated by Ruiz and co-workers [154], concluding that the π-contribution to the Mo_2-carbyne bonding is decreased by the competitive heteroatom-carbyne π overlapping, which is reflected in a partial double bond nature of the carbyne-O bond.

Despite the variability of metal elements and co-ligands, the majority of μ_2-aminocarbyne ligands share similar structural and spectroscopic features and reactivity patterns, evidencing a hybrid situation where both the carbyne and the iminium character are relevant. Therefore, an overall delocalization of the π interactions and the positive charge should be considered as the best bonding description (Scheme 24b, structure **IV**) [116]. A DFT study conducted on a couple of complexes $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CNMe(R)\}]^+$ afforded Mayer bond order values of 1.58 (R = Cy, **40f**) and 1.54 (R = 1H-indol-6-yl, **40g**) for the (μ-C)–N bond, revealing an almost perfect aminocarbyne-iminium hybridism; only a slight decrease is found on going from **40f** to the CO/Cl^- substitution product $[Fe_2Cp_2(Cl)(CO)(\mu\text{-}CO)\{\mu\text{-}CNMe(Cy)\}]$ (**54b**), for which the Mayer bond order is 1.52 [106]. It is remarkable that aminocarbyne ligands in neutral diiron complexes **54** exhibit structural and spectroscopic features close to those of the parent cationic species **40** (Figure 8), with an almost unaltered carbyne-nitrogen partial double bond [108,130].

Analogous bonding pattern and considerations are valid for μ_2-CNRR' ligands in trimetallic systems and for μ_2-CNHR/μ_2-CNH_2 ligands, which will be discussed in Sections 4-5.

The substantial contribution of the iminium form to the nature of the bridging aminocarbyne ligand in dimetallic complexes reflects the relative inertness of such carbyne center towards the addition of nucleophiles (see Section 3.2.1).



Scheme 24. (a) π-orbital system related to the coordination of a generic aminocarbyne ligand bridging two metal centers. (b) Canonical structures representing the aminocarbyne (**I**, **II**) and iminium (**III**) character, and combined representation with delocalized charge (**IV**).

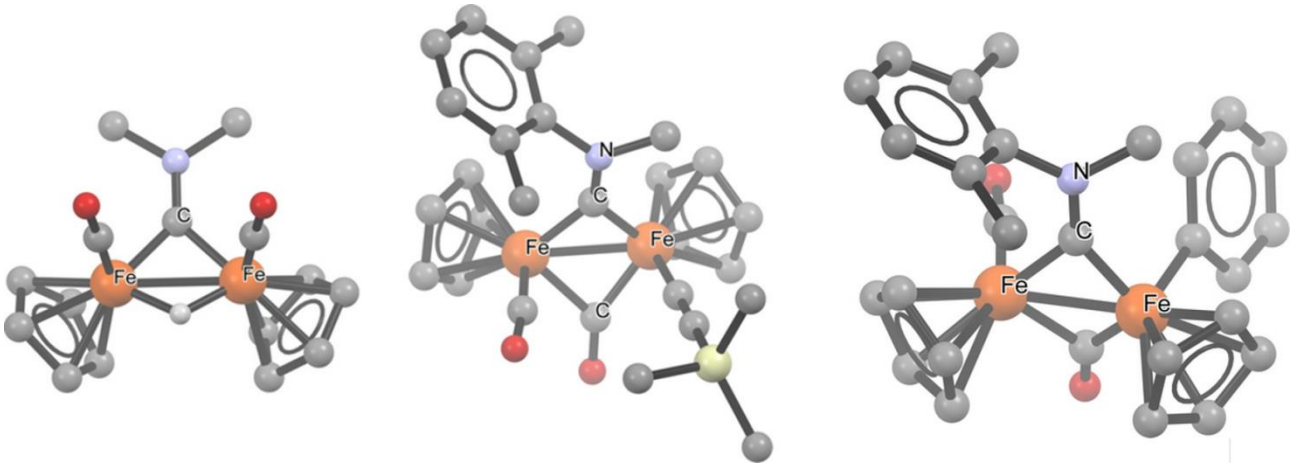
A selection of crystallographic and spectroscopic data is collected in Table 2. The carbyne-N bond length spans in the 1.26 – 1.34 Å range, matching the interval defined by the two extremes of typical $C(sp_2)$-$N(sp_2)$ single bond (ca. 1.36 Å) and $C(sp_2)$=N double bond (1.27 Å) [155]. The generally observed planarity of the {μ-CNRR'} fragment as well as the sp_2 hybridization of the nitrogen atom (*ca*. 120°) confirm a significant carbyne-N π interaction [93,94,117]. On the other hand, M-carbyne distances are relatively short, suggesting a multiple bond order.

A wide number of data is available for diiron bis-cyclopentadienyl carbonyl compounds, which thus constitute an ideal platform for comparative analysis. The Fe-carbyne bond distances in the symmetric complexes $[Fe_2Cp_2(CO)_3(\mu\text{-}CNMe_2)]^+$ (**40a**, Figure 6) [105] and $[Fe_2Cp_2(CO)_2(\mu\text{-}H)(\mu\text{-}CNMe_2)]$ (**54c**, Figure 8) [130] measure respectively 1.875(2) and 1.862(4) Å, in alignment with the increased backbonding in the neutral hydride bis-carbonyl **54c** with respect to the cationic tris-carbonyl **40a**; subsequently, the carbyne-N distance elongates on going from **40a** [1.297(4) Å] to **54c** [1.312(3) Å].

An interesting comparison is traced between **40a** [Fe-μ-C = 1.875(2) Å] and the homologous alkylidyne complex $[Fe_2Cp_2(CO)_3(\mu\text{-}CMe)]^+$ [**60**, Fe-μ-C = 1.84 Å, see Figure 8], the latter

evidencing a slightly better backbonding from the iron atoms to the purely carbyne carbon, in the absence of any competition for this π-interaction from the carbyne substituent [156].

A marked bonding asymmetry within the {Fe_2C_2} rectangle is evident in neutral complexes when one of the two irons hosts a mono-anionic terminal ligand (X), this iron being more tightly linked with the two bridging ligands. Such binding is reinforced via the backbonding mode, as nicely observed along the series of X-ray characterized complexes [$Fe_2Cp_2(CO)_2(X)\{CNMe(Xyl)\}$] (X = N_3, **54d** [131]; X = C≡CSiMe_3, **54e** [138c]; X = Ph, **54f** [132]): the electron donor capability of X progressively increases along the series, as indicated by the trend of the carbonyl wavenumbers, and this results in a shortening of the related Fe-carbyne distance and increase of the asymmetry ($\Delta_{Fe\text{-}C}$), see Figure 8 and Table 2. The asymmetry is even more pronounced concerning the bridging carbonyl. However, the μ-CO ligand generally experiences longer Fe-C distances than μ-CNRR'. For instance, the values for $[Fe_2Cp_2(CO)_3\{\mu\text{-}CNMe(Xyl^{Cl})\}]^+$ (**40h**) are: Fe-μ-CN 1.871(4) and 1.875(4), Fe-μ-CO 1.933(5) and 1.939(4) Å [138c]. Combined, this data is in alignment with a better π-acceptor capability of the μ-aminocarbyne ligand compared to μ-CO (see Introduction).



	40a	**54c**	**54d**	**54e**	**54f**	**60**
X		μ-H	N_3	$CCSiMe_3$	Ph	
$\Delta_{Fe\text{-}carbyne}$		=	0.028(6)	0.051(10)	0.080(10)	=
$\Delta_{Fe\text{-}\mu\text{-}CO}$		=	0.086(6)	0.178(13)	0.188(13)	=
ũ(CO)/cm^{-1} (CH_2Cl_2 solution)	2022, 1990, 1835	1935, 1891	1980, 1800	1973, 1792	1958, 1775	2047, 2016,1853
Ref.	[105]	[130]	[131]	[138c]	[132]	[156]

Figure 8. Views of the X-ray structures of **54c,e,f** (H atoms omitted for clarity except μ-H in **54c**), and comparison of crystallographic and IR data.

In the asymmetric aminocarbyne complex [$(CO)_4Fe(\mu\text{-}CNEt_2)Fe(CO)_2(NO)$] (**61**), the Fe-carbyne distances are 1.950(10) and 1.874(11) Å (Figure 9) [117].

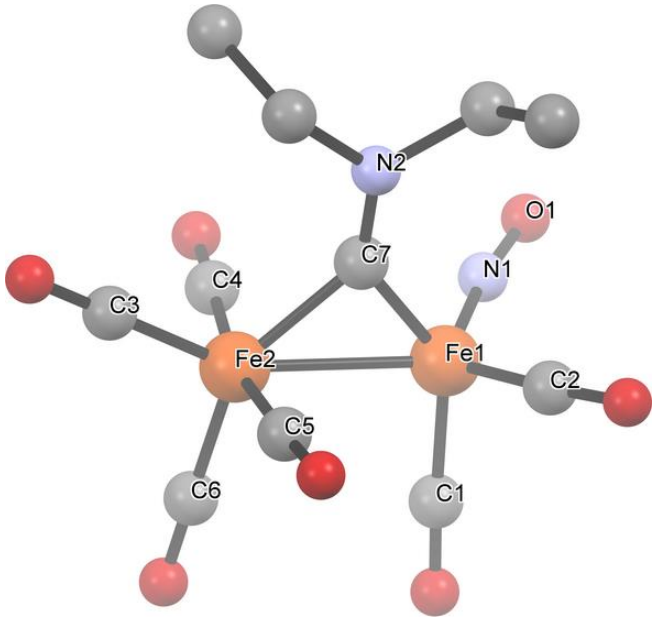


Figure 9. View of the X-ray structure of [$(CO)_4Fe(\mu\text{-}CNEt_2)Fe(CO)_2(NO)$] (**61**) [117]. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Fe2-C7 1.950(10), Fe1-C7 1.874(11), C7-N2 1.266(12), Fe2-C4 1.814(13), Fe2-C3 1.773(15), Fe2-C5 1.772(13), Fe2-C6 1.796(13), Fe1-C2 1.717(12), Fe1-C1 1.766(16), Fe1-N1-O1 169.5(11), Fe1-C2-O1 74.9(10), Fe2-C7-N2 136.2, Fe1-C7-N2 138.5(9).

In general, the infrared spectra of dimetallic bridging aminocarbyne complexes display the C-N stretching vibration as a medium-weak band in the 1500-1610 cm^{-1} region; it occurs at 1506 and 1532 cm^{-1} in the diplatinum complexes **42** and **43** [93], and in between 1512-1540 cm^{-1} in the dinickel **44** [95]. These wavenumber values approach those typical for imines/oximes (*ca.* 1650 cm^{-1}; 1640 cm^{-1} for $H_2C{=}NH$ [157]), while the C-N stretching falls at approximately 1020-1250 cm^{-1} for aliphatic

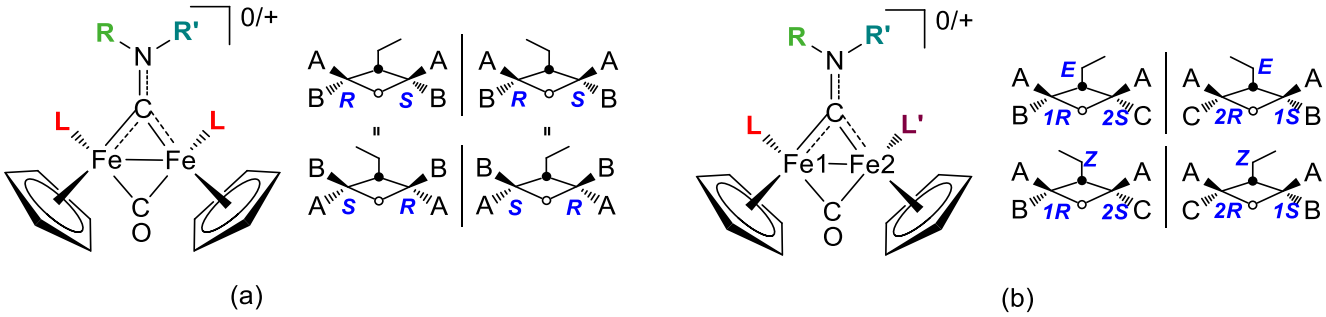
amines (methylamine: 1044 cm^{-1} [158]) and 1260-1350 cm^{-1} for aromatic amines (aniline: 1278 cm^{-1} [159]), in agreement with the substantial C-N double bond character in the bridging aminocarbyne. Within the series of diiron complexes **40**, the detected value in dichloromethane solution is slightly lower with aromatic N-substituents (1520-1540 cm^{-1}) rather than aliphatic (1550-1600 cm^{-1}) [105,106]. The stretching vibrations of the terminal CO ligands are in the ranges 2018-2030 (asymmetric stretching) and 1985-1998 cm^{-1} (symmetric stretching), while the absorption related to the bridging CO is detected at 1833-1853 cm^{-1}. For comparative purposes, the IR spectrum of $[Fe_2Cp_2(CO)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH{=}CH_2)]BF_4$ displays the corresponding CO bands at 2037, 2012 and 1863 cm^{-1} [160], while in $[Fe_2Cp_2(CO)_3(\mu\text{-}CR)]^+$ complexes the asymmetric stretching is around 2040 cm^{-1} [161]. These IR outcomes point out that the π-acceptor nature of the bridging ligand increases along the series amino-alkylidyne < vinyl < alkylidyne, in agreement with the Pombeiro's scale (see Introduction) [9].

In general, in the ^{13}C NMR spectra of dimetallic complexes, the aminocarbyne carbon resonates in the 305-390 ppm interval (Table 2). In the series of diiron complexes **40**, the chemical shift tends to increase on decreasing the electron donor properties of the N-substituents (e.g., δ = 316.4, 323.2 and 331.5 for R = Cy, 2-naphthyl and 2,6-C_6H_3MeCl, respectively) [105,106]. For comparison, the carbyne in diiron μ-alkylidyne complexes of general formula $[Fe_2Cp_2(CO)_3(CR)]^+$ (R = alkyl group) resonates around 500-530 ppm [161].

The partial double bond character of the aminocarbyne C-N bond usually prevents rotation at room temperature. Subsequently, isomerism is observed when different groups are placed on the nitrogen atom. For instance, *cis*-$[M_2Cp_2(L)_2(\mu\text{-}CO)\{\mu\text{-}CNR(R')\}]^+$ complexes (M = Fe, Ru; L = CO, CNR) exist as a racemic mixture of enantiomers, corresponding to the possible orientations of the nitrogen substituents with respect to the Fe_2C_2 diamond (Scheme 25a) [103,107b,110]. Thus, the Cp and terminal L ligands are inequivalent, giving rise to distinct $^1H/^{13}C$ signals. The ^1H spectrum does not change with temperature, indicating the absence of accessible isomerization pathways [104,136b]. The high energy of bridge-open intermediates, which would enable the isomerization following an

Adams-Cotton like mechanism [98], is reasonable on considering the strong preference of the aminocarbyne ligand for the bridging site.

Isomerism arising from hindered rotation around the C=N bond (E/Z isomerism) may add to another source of isomerism in the structure, associated to either the *cis*/*trans* mutual arrangement of the Cp ligands or a different coordination sphere at the two metal atoms. Therefore, *cis*-$[Fe_2Cp_2(L)(L')(\mu\text{-}CO)(\mu\text{-}CNRR')]^{0/+}$ complexes (L ≠ L') exist as mixtures of two diastereomers (two pairs of enantiomers), called "α" and "β" (Scheme 25b) [104,110,108 ,125,130,136b,149]. The α/β ratio is normally governed by steric factors, *i.e.* it is higher when a bulky substituent (*e.g.* Xyl) is present on the aminocarbyne [127a,131,132].



Scheme 25. Isomerism in *cis*-$[Fe_2Cp_2(L)(L')(\mu\text{-}CO)(\mu\text{-}CNRR')]^{0/+}$ complexes with (a) identical or (b) different terminal ligands.

Table 2. Spectroscopic and X-ray data related to bridging aminocarbyne ligands in homo-dimetallic complexes.

Compound [a]	**IR** [b]	**^{13}C NMR** [c]	**X-Ray**		**Ref.**
	ũ(CN) / cm^{-1}	**δ(CN) / ppm**	**d(M-C) / Å**	**d(C-N) / Å**	
$[Fe_2(CO)_6(\mu\text{-}CNEt_2)_2]$	-	-	1.902 1.909	1.284	[162]
			1.903 1.914	1.280	
$[Fe_2Cp_2(CO)_3(\mu\text{-}CNMe_2)]CF_3SO_3$ (**40a**[CF_3SO_3])	1604	315.5	1.875(2) 1.875(2)	1.297(4)	[105]
$[Fe_2Cp_2(CO)_3\{\mu\text{-}C(NC_5H_{10})\}][W_2(CO)_{10}(\mu\text{-}CN)]$ (**40b**[$W_2(CO)_{10}(\mu\text{-}CN)$])	1572	315.3	1.874(6) 1.877(6)	1.280(8)	[116]
$[Fe_2Cp'_2(CO)_3(\mu\text{-}CNMe_2)]I$ (**40c**[I])	1599	-	1.85(2) 1.85(2)	1.30(3)	[100]
$[Fe_2Cp_2(CO)_3\{\mu\text{-}CNMe(Cy)\}]CF_3SO_3$ (**40f**[CF_3SO_3])	1567	316.4	1.881(14) 1.873(15)	1.291(18)	[106]

$[Fe_2Cp_2(CO)_3\{\mu\text{-}CNMe(1H\text{-}indol\text{-}6\text{-}yl)\}]CF_3SO_3$ (**40g**$[CF_3SO_3]$)	1542	324.9	1.874(6) 1.870(6)	1.289(7)	[106]
$[Fe_2Cp_2(CO)_3\{\mu\text{-}CNMe(Xyl^{Cl})\}]CF_3SO_3$ (**40h**$[CF_3SO_3]$)	1522	331.5	1.871(4) 1.875(4)	1.295(5)	[105]
$[Fe_2Cp_2(CO)_3\{\mu\text{-}CNMe(4\text{-}C_6H_4OMe)\}]CF_3SO_3$ (**40i**$[CF_3SO_3]$)	1540	324.3	1.870(5) 1.866(5)	1.287(6)	[106], [163]
$[Fe_2Cp'_2(CO)_2(\mu\text{-}CNMe_2)_2][CF_3SO_3]_2$ (**45a**$[CF_3SO_3]_2$)	1611 1631	308.1	1.883(5) 1.879(5)	1.301(6)	[104]
			1.880(5) 1.893(5)	1.289(7)	
$[Co_2Cp_2(\mu\text{-}CNEt_2)_2]$ (**49**)	-	-	1.830(3) 1.821(3)	1.312(4)	[119]
$[W_2(S_2CNEt_2)_2(\mu\text{-}S)(\mu\text{-}S_2CNEt_2)\{\mu\text{-}S_2Sn(CHSiMe_3)_2\}(\mu\text{-}CNEt_2)]$ (**50**)	1495	312.0	2.07 (2) 2.10 (2)	1.25 (3)	[120]
$[Mo_2Cp(\mu\text{-}SMe)_3\{\mu\text{-}(\eta^5\text{-}C_5H_4)C(N^tBu)NC(^tBu)\}]$ (**51a**)	-	366.9	2.117(2) 2.006(2)	1.361(2)	[121a]
$[Mo_2Cp(\mu\text{-}SMe)_2(\eta^1\text{:}\eta^2\text{-}CCH)\{\mu\text{-}(\eta^5\text{-}C_5H_4)C(NXyl)NC(Xyl)\}]$ (**51b**)	-	362.9	1.999(6) 1.997(6)	1.369(7)	[121c]
$[Mo_2Cp(\mu\text{-}SMe)_2(\mu\text{:}\eta^2\text{-}OCNHXyl)\{\mu\text{-}(\eta^5\text{-}C_5H_4)C(NXyl)NC(Xyl)\}]$ (**52a**)	-	369.3	1.99(2) 1.97(2)	1.44(2)	[121b]
$[Mo_2Cp(\mu\text{-}SMe)_2(\mu\text{:}\eta^2\text{-}OCNH^tBu)\{\mu\text{-}(\eta^5\text{-}C_5H_4)C(NXyl)NC(Xyl)\}]$ (**52b**)	-	362.7	2.012(6) 1.993(6)	1.386(7)	[121b]
$[Mo_2Cp(\mu\text{-}SMe)_2(\mu\text{:}\eta^2\text{-}OCNMeXyl)\{\mu\text{-}(\eta^5\text{-}C_5H_4)C(NXyl)NC(Xyl)\}]$ (**52c**)	-	336.8	2.019(5) 2.004(5)	1.370(6)	[121b]
$[Mo_2Cp(\mu\text{-}SMe)_2(CNXyl)_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)C(NXyl)NC(Xyl)\}]Br$ (**52d**)	-	386.8	2.049(3) 2.032(3)	1.363(3)	[121c]
$[Fe_2Cp_2(CO)_2(CNXyl)\{\mu\text{-}CNMe(Xyl)\}]CF_3SO_3$ (**53a**$[CF_3SO_3]$)	-	332.0	1.884(7) 1.866(7)	1.303(9)	[129]
$[Fe_2Cp_2\{NH{=}C(^tBu)CCTol\}(CO)_2\{\mu\text{-}CNMe(Xyl)\}]$ (**53c**)	-	339.8	1.854(4) 1.868(4)	1.321(5)	[164]
$[Fe_2Cp_2(CO)_2(CNMe)(\mu\text{-}CNMe_2)]BPh_4$ (**53f**$[BPh_4]$)	1586	322.3	1.876(5) 1.848(5)	1.303(7)	[104]
$[Fe_2Cp_2(CO)_2(NH_2Et)(\mu\text{-}CNMe_2)]CF_3SO_3$ (**53g**$[CF_3SO_3]$)	-	331.3	1.90(1) 1.80(1)	1.31(2)	[128]
$[Fe_2Cp_2(CO)_2(PHPh_2)\{\mu\text{-}CNMe(Xyl)]CF_3SO_3$ (**53h**$[CF_3SO_3]$)	1508	331.7	1.880(3) 1.897(3)	1.302(4)	[132]
$[Fe_2Cp_2(CO)_2\{C(Me)NHPr\}(\mu\text{-}CNMe_2)]CF_3SO_3$ (**53i**$[CF_3SO_3]$) [d]	1570	330.4	1.909(3) 1.843(3)	1.284(4)	[105]
$[Fe_2Cp_2(CO)_2(\mu\text{-}CNMe_2)(\mu\text{-}CNMe)]BPh_4$ (**53j**$[BPh_4]$) [d]	1600	318.8	1.876(4) 1.884(4)	1.293(5)	[208]
$[Fe_2Cp_2(CO)_2(\mu\text{-}H)(\mu\text{-}CNMe_2)]$ (**54c**)	-	338.4	1.864(2) 1.860(3)	1.312(3)	[130]
$[Fe_2Cp_2(N_3)(CO)_2\{\mu\text{-}CNMe(Xyl)\}]$ (**54d**)	1519	313.1	1.849(3) 1.877(3)	1.304(4)	[131]
$[Fe_2Cp_2(C{\equiv}CSiMe_3)(CO)_2\{\mu\text{-}CNMe(Xyl)\}]$ (**54e**) [d]	1506	337.2	1.875(5) 1.824(5)	1.307(7)	[138c]
$[Fe_2Cp_2(Ph)(CO)_2\{\mu\text{-}CNMe(Xyl)\}]$ (**54f**)	1563	340.8	1.819(5) 1.899(5)	1.320(7)	[132]
$[Fe_2Cp_2(SPh)(CO)_2\{\mu\text{-}CNMe(4\text{-}C_6H_4OMe)\}]$ (**54g**)	1576	339.8	1.897(3) 1.841(3)	1.303(3)	[138a]
$[Fe_2Cp_2\{C(OMe)(CN)Me\}(CO)_2(\mu\text{-}CNMe_2)]$ (**54h**) [d]	1561	332.8	1.887(4) 1.845(4)	1.294(5)	[105]
trans-$[Fe_2Cp_2(NCS)(CO)_2\{\mu\text{-}CNMe(Xyl)\}]$ (**54i**)	1568	340.6	1.855(4) 1.874(4)	1.297(5)	[131]
$[Fe_2Cp_2(S_2CNEt_2)(CO)_2\{\mu\text{-}CNMe(Xyl)\}]$ (**54j**)	1500	333.5	1.864(1) 1.871(1)	1.313(2)	[132]
$[Fe_2Cp_2(CO)_2\{C(OMe)CCTol\}\{\mu\text{-}CNMe(Xyl)\}]$ (**54k**) [d]	1524	332.2	1.846(6) 1.869(6)	1.311(8)	[123]
$[Fe_2Cp_2\{C(OMe)(CN)CCPh\}(CO)_2\{\mu\text{-}CNMeXyl)\}]$ (**54l**) [d]	-	338.1	1.839(4) 1.897(4)	1.317(5)	[126]
$[Fe_2Cp_2(CO)_2\{C(OMe){=}CHC(Tol){=}C(CN)_2\}\{\mu\text{-}CNMe(Xyl)\}]$ (**54m**) [d]	-	336.3	1.834(3) 1.894(3)	1.318(4)	[126]
$[Ru_2Cp_2(NCO)(CO)_2(\mu\text{-}CNMe_2)]$ (**54n**)	-	342.5	1.940(5) 1.991(5)	1.304(6)	[131]
$[Fe_2Cp_2(CO)_2(CO^nBu)(\mu\text{-}CNMe_2)]$ (**55a**)	1544	330.9	1.843(3) 1.877(3)	1.296(4)	[125]

$[Fe_2Cp(CO)_2(CN^tBu)(\eta^4\text{-}C_5H_5CH_2CN)(\mu\text{-}CNMe_2)]$	-	330.3	1.852(2) 1.878(3)	1.305(3)	[138b]
$[Fe_2Cp_2\{C(O)C_4H_3S\}(CO)_2\{\mu\text{-}CNMe(Bn)\}]$ (**55b**)	1526	335.3	1.845(4) 1.879(4)	1.303(5)	[124]
$[Ru_2Cp_2(COPh)(CO)_2(\mu\text{-}CNMe_2)]$ (**55c**)	1573	306.7	1.938(3) 1.991(3)	1.300(4)	[108]
$[Fe_2Cp_2(CNXyl)_2(\square\text{-}CO)\{\square\text{-}CNMe(Xyl)\}]CF_3SO_3$ (**58**$[CF_3SO_3]$)	1517	336.2	-	-	[148]
$[Fe_2Cp_2(CH_2CN)(CO)_2(\mu\text{-}CNMe_2)]$ (**59a**)	-	332.7	1.843(2) 1.886(3)	1.299(3)	[149]

[a] All $M_2Cp_2(CO)_x$ complexes (M = Fe, Ru) show *cis*- arrangement of Cp ligands, unless otherwise specified. Co-crystallized solvate molecules omitted from the formulae. [b] In CH_2Cl_2 or other solvent. [c] $CDCl_3$, CD_2Cl_2 or other common deuterated solvent. Abbreviation list: Xyl = 2,6-$C_6H_3Me_2$; Xyl^{Cl} = 2,6-C_6H_3MeCl; Cp' = C_5H_4Me; Tol = 4-$C_6H_4CH_3$. [d] Prepared according to different routes and not directly from **40** (Scheme 20b).

3.4. Biological and catalytic studies on diiron bis-cyclopentadienyl complexes

The search for new effective metal drugs overcoming the limitations of the platinum drugs currently employed in chemotherapy is intense, and in this regard iron compounds are interesting due to the biological implications of such metal element [165]. Various monoiron compounds have been investigated to this purpose, and some promising ferrocene derivatives (ferrocifens) accessed pre-clinical trials [166]. In this scenario, the diiron complexes discussed in this section are among the first diiron organometallic species investigated for the anticancer potential to date. The behavior in aqueous media and the anticancer potential of a series of air-stable diiron aminocarbyne complexes has been recently evaluated [106, 167]. Thus, **40a-m** (as triflate or tetrafluoroborate salts, see Scheme 26) are substantially amphiphilic, with octanol/water partition coefficient values (Log P_{ow}) in the range +0.3 to less than -1.5, and exhibit a remarkable stability in water and in cell culture medium solution. Note that a considerable fraction (up to ca. 90%) of the starting materials was NMR detected in the latter medium after being maintained for 24 hours at 37 °C. In general, the cationic species **40a-m** and the monosubstituted **53k-m** (Scheme 26) are more robust in water than some neutral derivatives of types **54** and **56**. The antiproliferative activity was assessed against ovarian, colon, pancreatic, breast and melanoma cancer cells, and **40f** and **40i** revealed the most promising species; moreover, **40i** displayed a significant selectivity compared to a noncancerous cell line (HEK-293) [106]. Uptake experiments outlined that the observed selectivity is not ascribable to a different

penetration of the complexes into the two types of cells, therefore the superior activity against cancer cells might be dependent on their ability to interfere with a specific target.

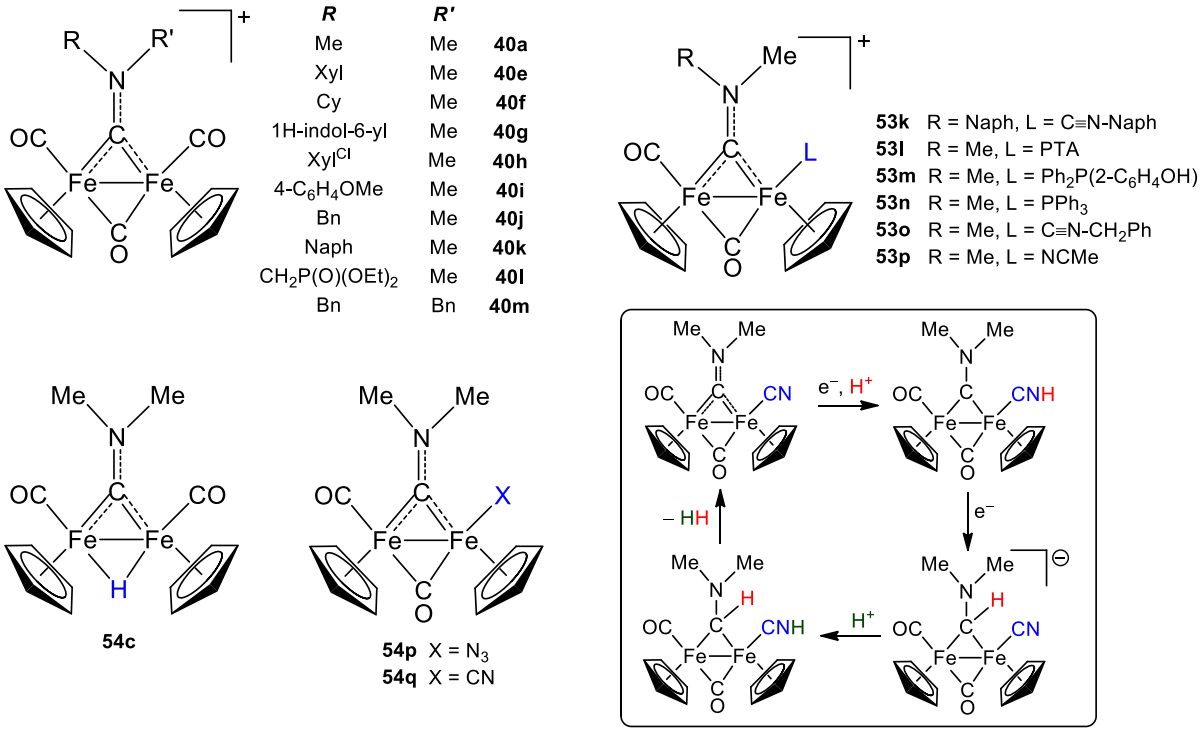
Notably, the cytotoxicity profile of the aminocarbyne complexes is substantially unaltered in 3D cell cultures, with **40i** exhibiting activity either comparable or even superior to that of cisplatin under the same conditions. Mechanistic experiments outlined the ability of **40f,i** to behave as CO-releasers (CORMs) inside the cells, to alkylate biological targets and to misbalance the cellular redox homeostasis (via ROS production and inhibition of the selenoenzyme Thioredoxin Reductase). The degradation of the inside the cell presumably contributes to the redox activity: it has been demonstrated that such degradation, in aqueous solution, slowly leads to the extensive rupture of the organometallic scaffold, accompanied by oxidation of the iron(I) centers to iron(III) oxides.

While the strongly hydrophilic salts of **40a** and **53l** are inactive against A2780 cells, **53m** (Log P_{ow} = +1.0) displayed IC_{50} value of 9.2 μM under the same conditions, indicating that the large possibility of structural functionalization of diiron aminocarbyne carbonyl complexes enables to regulate the amphiphilicity of the compounds and thus their biological activity.

Vinyliminium derivatives of **40** (see Scheme 21) are also cytotoxic, and the synthetic opportunity offered by the huge choice of alkyne reagents amplifies the possibility of structural variation/functionalization [141,142,168], including the incorporation of groups with a specific biological function [169]. The preliminary outcomes provided by diiron aminocarbyne complexes require more comments. They merit further studies and optimization, on account of the fact that they display ideal characteristics for a metal drug, and more precisely: 1) easy availability from inexpensive starting chemicals via gram-scale reactions; 2) appreciable solubility in aqueous media and amphiphilicity due to the ionic nature; 3) tunability of the physico-chemical properties by an appropriate choice of substituents and counteranion; 4) wide opportunity for structural modification exploiting the cooperativity of the diiron core; 5) multitargeted action.

In the context of the research on the development of diiron complexes as functional models of natural [FeFe]-hydrogenases, which catalyze the conversion of protons and electrons into dihydrogen and

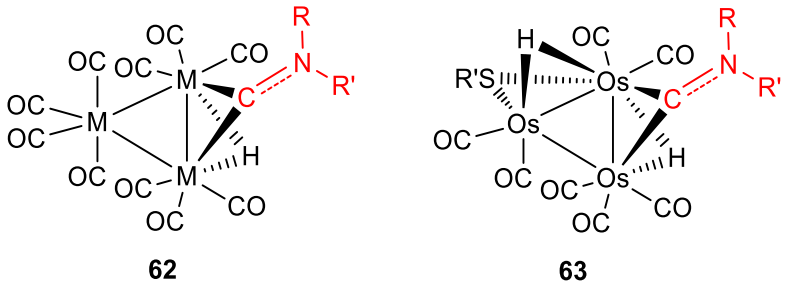
the reverse reaction [170], some diiron aminocarbyne complexes have been recently investigated as possible electro-catalysts for the H_2 production in acetonitrile solution from acetic acid [171]. Cyclic voltammetric analyses revealed the inactivity of the cationic complexes **53n-o** and the neutral ones **54c,q**, while **53p** displayed a modest activity which is probably related to the presence of the labile acetonitrile ligand, enabling the liberation of one metal site (Scheme 26). Otherwise **54q**, containing a terminal cyanide ligand, proved effective to promote H_2 evolution, with a turnover number of 15.5, which is comparable with the performance of more conventional [FeFe] hydrogenase models based on diiron dithiolate systems. DFT calculations were performed to give insight into the catalytic activity of **54q** [153], outlining a plausible mechanism consisting in the following sequence (Scheme 26, inset): 1) first electron transfer to the complex; 2) first cyanide protonation; 3) second electron transfer; 4) hydrogen migration from the {CNH} unit to the carbyne; 5) second cyanide protonation; 6) H-H bond formation. The cyanide ligand is crucial to the activity, in that it behaves both a protonation site and as a proton shuttle towards the aminocarbyne carbon, which in turn accumulates electron density in the reduced form of the complex. These findings suggest that the search for efficient, iron-based catalysts for H_2 production should not be necessarily restricted to the realm of the largely investigated iron dithiolate [FeFe] hydrogenase mimics, and evidence an uncommon catalytic mechanism which is essentially based on a suitable combination of ligands on the diiron scaffold without directly involving the metal centers.



Scheme 26. Diiron μ-aminocarbyne complexes evaluated as potential anticancer agents or H_2 evolution catalysts. $CF_3SO_3^-$ or BF_4^- as counterion for cationic complexes. Abbreviation list: Xyl = 2,6-$C_6H_3Me_2$, Cy = C_6H_11, Xyl^{Cl} = 2,6-C_6H_3MeCl, Bn = CH_2Ph, Naph = 2-naphthyl, PTA = 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane. Inset: DFT-proposed mechanism for the electrocatalytic activity of **54q** in H_2 evolution.

4. Bridging tertiary aminocarbyne ligands in homo-trinuclear and higher nuclearity complexes

Aminocarbyne ligands bridging two metal atoms are found in several trinuclear clusters derived from $[M_3(CO)_{12}]$ (M = Fe, Ru, Os) and in clusters with higher nuclearity based on group 8 metals or cobalt. Concerning the trinuclear compounds **62-63** (Scheme 27), these share a common structural motif based on one aminocarbyne and one hydride placed on the same edge of the $\{M_3\}$ triangle. Tetra-nuclear and higher nuclearity systems show variable arrangements of the metal atoms and commonly comprise bridging sulfide co-ligands.



62 **63**

Scheme 27. General structures of trinuclear group 8 metal clusters containing μ_2-bridging aminocarbyne ligands.

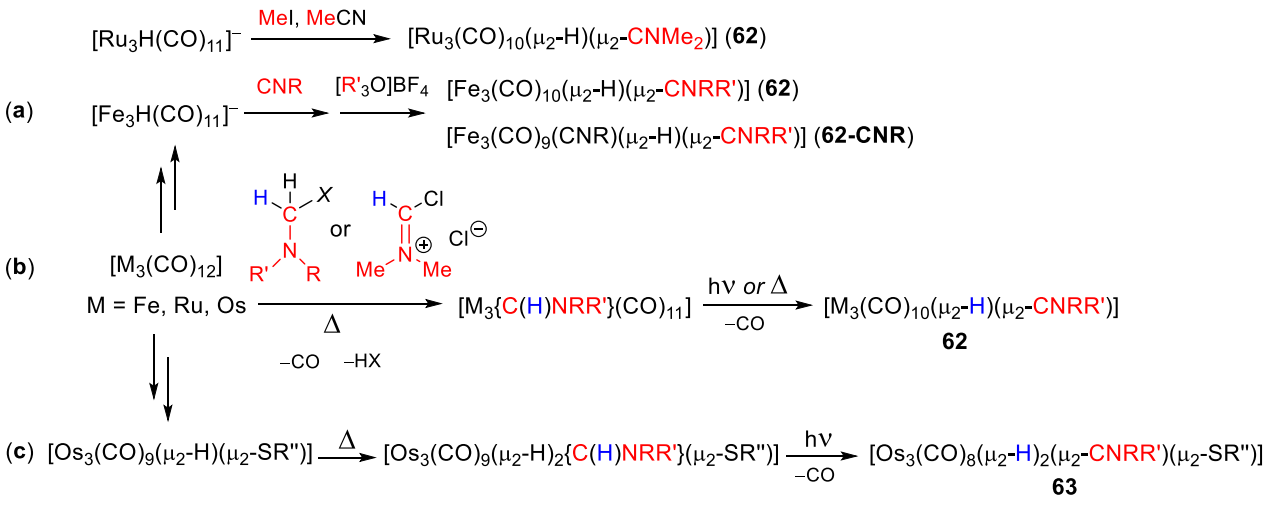
4.1. Synthetic routes and reactivity

The common synthetic routes to install aminocarbyne ligands on polynuclear carbonyl clusters rely on the same general strategy, i.e. the decarbonylation of a parent metal compound coupled with the activation of a small molecule, whereby the aminocarbyne and other coordinating fragments are generated. At variance to dimetallic complexes, the use of isocyanide ligands as precursors for aminocarbynes has been reported in a few cases only: CO/CNR substitution(s) on $[M_3H(CO)_{11}]^-$ (M = Fe, Ru) is followed by alkylation, and the overall reaction can be carried out in one-pot in the case of ruthenium (Scheme 28a) [172,173,174]; alkylation of $[Fe_3(\mu_2\text{-}H)(CO)_{19}(CNR)_2]^-$ yields mixed isocyanide-aminocarbyne derivatives (**62-CNR**) [173].

Thermal reactions of $[M_3(CO)_{12}]$ (M = Fe, Ru, Os) or $[Os_3(CO)_{10}(\mu_2\text{-}H)(\mu_2\text{-}SR)]$ with various reagents of general formula $[RR'N\text{-}CH_2X]$ proceed with cleavage of C-H e C-X bonds, providing the

bridging hydride and aminocarbyne ligands (Scheme 28b-c). However, the reactions involving tertiary amines and their silyl/stannyl-substituted derivatives (Me_3N, $BuMe_2N$, $Me_2NCH_2SnMe_3$, $Me_3SiCH_2NMe_2$) [175,176,177,178] or chloroformiminium chloride, $[Me_2N{=}CHCl]Cl$ [179], are non-selective, affording the aminocarbyne products in low yields. On the other hand, bis(dialkylamino)methanes, $H_2C(NR_2)_2$ (R = Me, Et), are more effective reagents and their straightforward reactions with triosmium clusters, $[Os_3(CO)_{10}]$ and $[Os_3(\mu_2\text{-}H)(\mu_2\text{-}SR)(CO)_8]$, have been elucidated in detail [180,181,182]. At a first stage, CO replacement and activation of the bis-amino reagent (cleavage of C-H and C-N bonds) result in the formation of a terminal diaminocarbene ligand $\{C(H)NR_2\}$. Then, UV irradiation removes another carbonyl ligand from the cluster and triggers oxidative addition of the carbene C-H bond, resulting in the formation of μ-H and μ-CNR_2 moieties within complexes of type **63**.

The photoinduced decarbonylation/C-H activation process is more selective than a thermal treatment (pyrolysis at 200 °C) [183]. On the other hand, the reaction of $[Os_3(CO)_{10}(\mu_2\text{-}H)_2]$ with $CH_2(NMe_2)_2$ gives the iminium complex $[Os_3(CO)_{10}(\mu_2\text{-}H)(\mu_2\text{-}\eta^2\text{-}CH_2{=}NMe_2)]$ in a modest yield, which can be subsequently converted into a mixture of amino-alkylidene and amino-alkylidyne derivatives, $[Os_3(CO)_{10}(\mu_2\text{-}H)(\mu_2\text{-}CNMe_2)]$ (**62b**), in refluxing heptane via formal H_2 elimination [178].



Scheme 28. Synthetic routes to μ2-aminocarbyne ligands in trinuclear group 8 clusters: (a) alkylation of coordinated isocyanide (R = Me, Et, ^{i}Pr, R' = Et; R = ^{i}Pr, R' = Me); (b-c) combined CO removal /

C-X activation (R = R' = Me, X = H, $SnMe_3$, $SiMe_3$, NMe_2; R = R' = Et, X = NEt_2; R = Me, R' = ^{n}Bu, X = H). Schematic representation of the organic reagents generating hydride and aminocarbyne ligands.

The representative X-ray structure of $[Fe_3(CO)_{10}(\mu_2\text{-}H)(\mu_2\text{-}CNMe_2)]$ (**62a**) [179b] is shown in Figure 10.

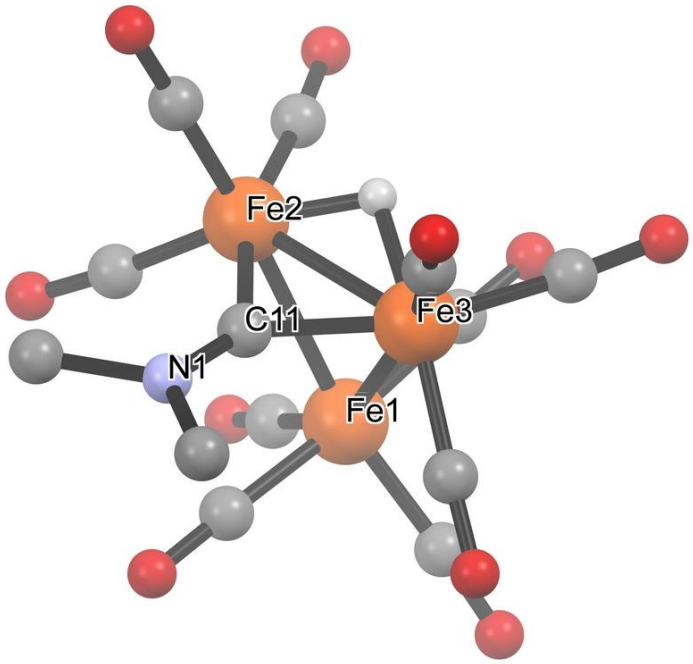
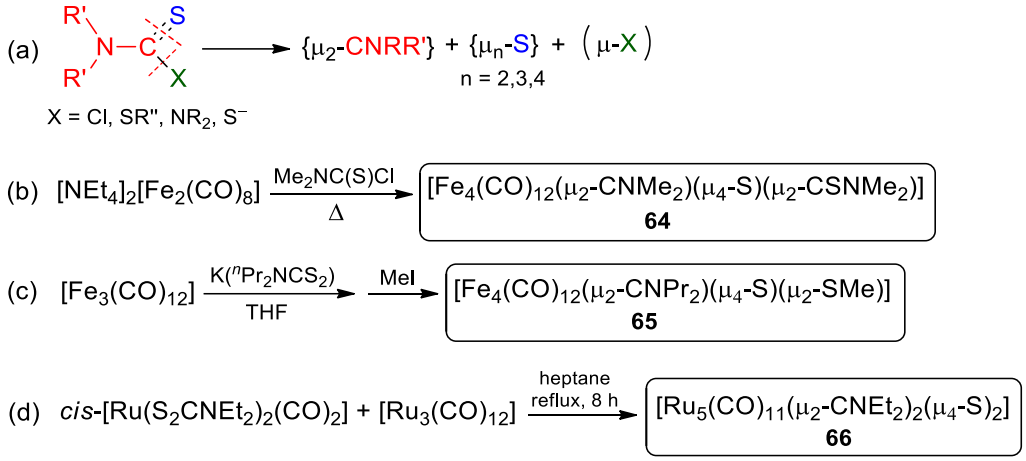


Figure 10. View of the X-ray structure of a triiron μ_2-aminocarbyne complex, $[Fe_3(CO)_{10}(\mu_2\text{-}H)(\mu_2\text{-}CNMe_2)]$ (**62a**) [179b]. H atoms (except μ-H) omitted for clarity. Selected bond lengths (Å): Fe-C11 1.89(1) and 1.91(1), C11-N1 1.30(1).

Also, the formation of μ_2-aminocarbyne ligands in tetra- and higher polynuclear clusters has been accomplished via the fragmentation of suitable organic reagents. The thermal reaction of mono-, di- or tri-metal carbonyls in the presence of [(RR'N)C(=S)X] (X = N, Cl, S) is accompanied by C-S and C-X bonds cleavage and generation of sulfide ($\mu_3\text{-}S^{2-}/\mu_4\text{-}S^{2-}$), aminocarbyne ($\mu_2$-CNRR') and possibly other bridging sulfur-containing ligands (*e.g.* thiolates, thiocarboxamide). Bridging sulfides are the key to the aggregation and the stabilization of the final metal scaffold. Possible aminocarbyne precursors are dimethylthiocarbamoyl chloride $ClC(=S)NMe_2$ [184], tetramethylthiourea $(NMe_2)_2CS$

[185], dialkyldithiocarbamates and related species [186,187,188,189,190]. All of these reactions usually show a limited/poor selectivity. Some cases are reported in Scheme 29; the X-ray structure of the bis-aminocarbyne pentaruthenium cluster **66** is depicted in Figure 11. It is worth mentioning the peculiar reduction of $CoCl_2$ by zinc metal in the presence of PPh_3 and $Na(Et_2NCS_2)$ in acetonitrile, affording the tricobalt complex $[Co_3Cl(PPh_3)_2(\mu_2\text{-}CNEt_2)(\mu_3\text{-}S)(\mu_2{:}\eta^2\text{-}SCNEt_2)]$ (**67**) in 43% yield (see the X-ray structure in Figure 11) [191].



Scheme 29. (a) General fragmentation of [RR'NC(=S)X] leading to the installation of aminocarbyne, sulfide and possibly other ligands on polymetallic species; (b-d) selected reactions affording tetra- and pentametallic complexes with μ_2-aminocarbyne ligands.

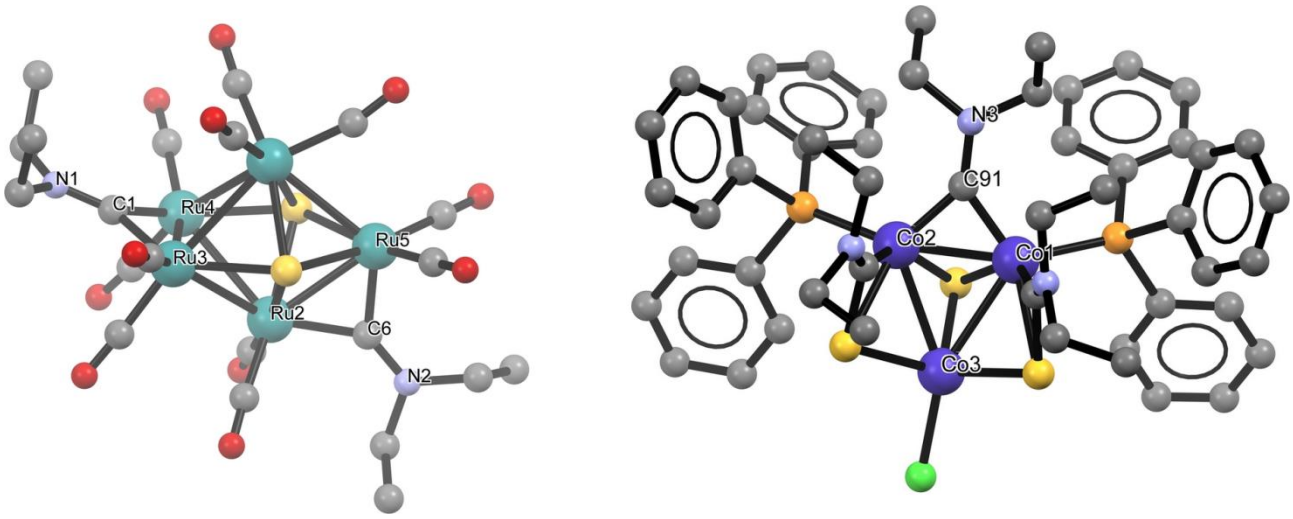
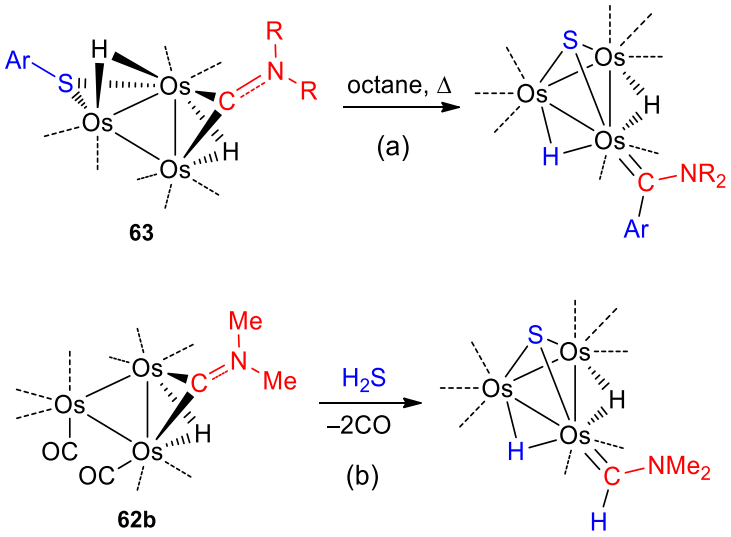


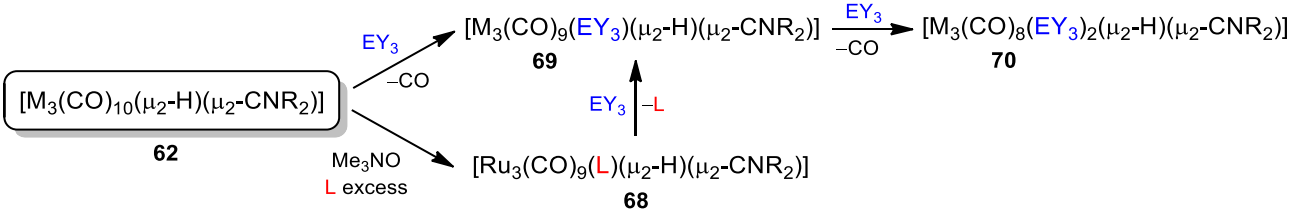
Figure 11. Views of the X-ray structures of $[Ru_5(CO)_{11}(\mu_2\text{-}CNEt_2)_2(\mu_4\text{-}S)_2]$ (**66**) [186] and $[Co_3Cl(PPh_3)_2(\mu_2\text{-}CNEt_2)(\mu_3\text{-}S)(\mu_2\text{-}SCNEt_2)]$ (**67**) [191]. H atoms omitted for clarity. Selected bond lengths (Å): **66**, Ru3-C1 1.957(9), Ru4-C1 1.949(9), C1-N1 1.29(l), Ru3-CO 1.822 and 1.827, Ru4-CO 1.833 and 1.851; **67**, Co-C91 1.823(8) and 1.833(8), C91-N3 1.323(9).

The chemistry of the trimetallic aminocarbyne complexes **62** and **63** has been significantly less explored if compared to related dimetallic species (Section 3.2). However, the aminocarbyne moiety in **62-63** appears more prone to nucleophilic addition, thus converting into amino-alkylidene derivatives. Some aryl-thiolato complexes of the type **63**, i.e. $[Os_3(CO)_8(\mu_2\text{-}H)_2(\mu_2\text{-}CNRR')(\mu_2\text{-}SAr)]$, convert into $[Os_3(CO)_8\{=C(Ar)NRR'\}(\mu_2\text{-}H)_2(\mu_3\text{-}S)]$ in refluxing octane, via intramolecular migration of the aryl group and subsequent shift of the resulting amino-alkylidene ligand to a terminal coordination site (45-60% yields, Scheme 30a) [181]. The formation of the μ_3-S unit is the driving force for the process. Similarly, Adams and co-workers reported the high temperature reaction of **62b** with an external sulfur-source (H_2S), proceeding with the complete scission of hydrogen sulfide to afford $[Os_3(CO)_8\{=C(H)NMe_2\}(\mu_2\text{-}H)_2(\mu_3\text{-}S)]$ in a moderate yield (Scheme 30b) [192].



Scheme 30. Amino-alkylidyne to amino-alkylidene conversion in triosmium clusters: (a) via intramolecular aryl migration (R = Me, Ar = Ph, C_6F_5, Tol; R = Et, Ar = Tol); (b) via H_2S scission. Spectator CO ligands represented by dotted lines.

When the aminocarbyne function in **62-63** is not directly involved in the reactions, anyway its electronic effects play a pivotal role to address the outcomes. The trinuclear clusters **62** can be modified by sequential substitution of one or two CO ligands with a variety of group 15 donor ligands (Scheme 31) [174,193,194,195]. The replacement of one carbonyl to enable the coordination of a labile N-ligand is performed by means of Me_3NO. The resulting adducts **68** represent useful intermediates for subsequent substitution reactions affording **69** and **70** [174]. The X-ray structures of two representative ruthenium complexes are drawn in Figure 12.



Scheme 31. Substitution reactions of carbonyl ligands on trinuclear group 8 μ_2-aminocarbyne complexes. R_2 = Me_2, Bn_2, MeBn. L = NCMe, pyridine. E = P, As, Sb; Y = Ph. E = P; Y = Cy, Bu, OPh, OMe, O^{i}Pr.

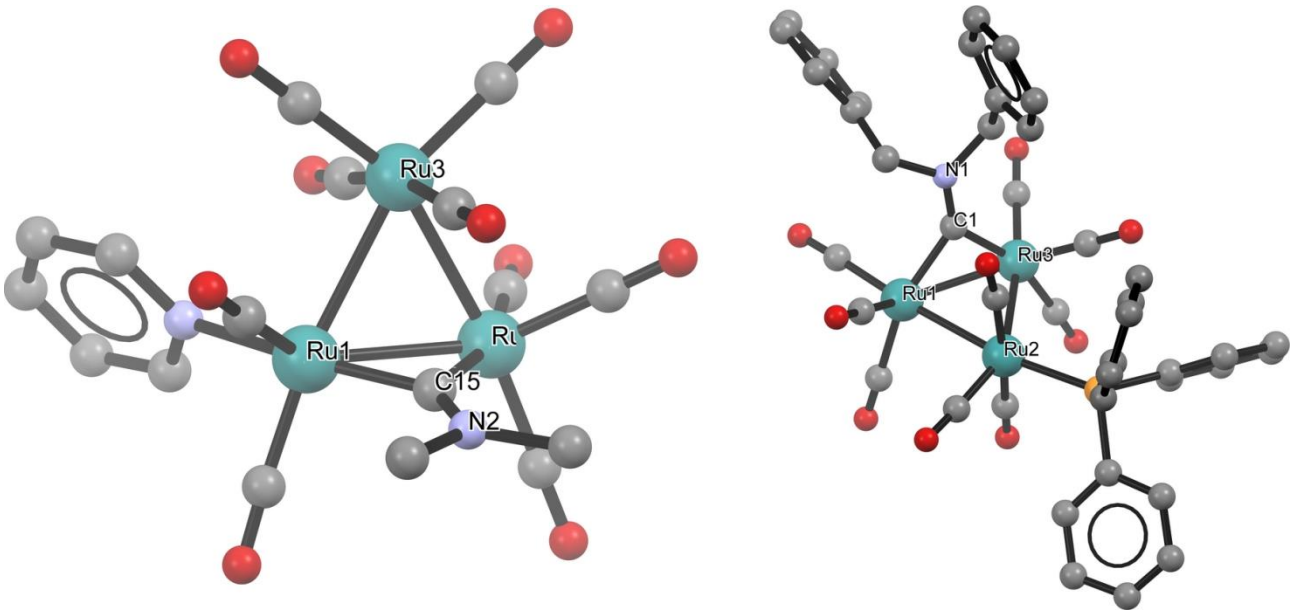
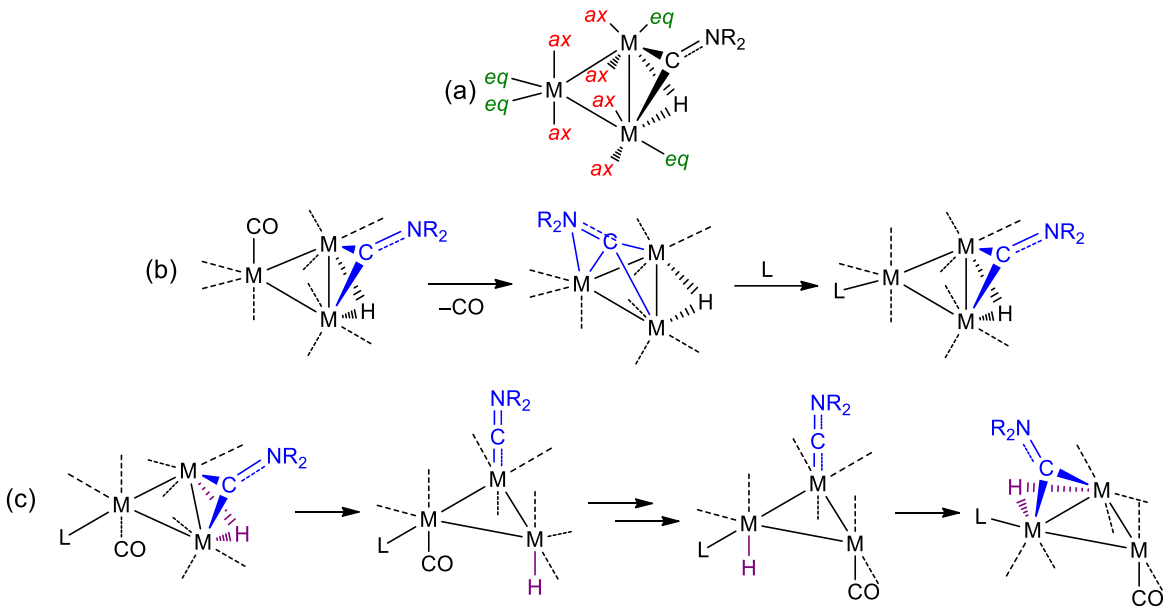


Figure 12. Views of the X-ray structures of $[Ru_3(CO)_9(Py)(\mu\text{-}H)(\mu\text{-}CNMe_2)]$, **68a** [194], and $[Ru_3(CO)_9(PPh_3)(\mu\text{-}H)(\mu\text{-}CNBn_2)]$, **69a** [194]; H-atoms omitted for clarity. Selected bond lengths (Å): **68a**) C15-N2 1.304(7), Ru1-C15 1.977(6), Ru2-C15 2.047(4), Ru2-CO(trans to C15) 1.974(5); **69a**) C1-N1 1.288(14), Ru1-C1 2.052(10), Ru3-C1 2.041(11).

The mono-substituted complexes **68-69** exist in different isomeric forms, related to the coordination mode of L (bridging or terminal) and the orientation (axial or equatorial) with respect to the M_3 triangle (Scheme 32a). The proposed mechanism for substitution is dissociative, whereby the aminocarbyne temporarily adopts a μ_3-η^1:η^2-coordination in order to compensate the electronic unsaturation, before the addition of the incoming ligand (Scheme 32b) [194,195]. Such involvement of the nitrogen in the coordination of the aminocarbyne group is rather unusual [196]. The kinetic product, resulting from the substitution on the $M(CO)_4$ site, subsequently equilibrates to a mixture of isomers. The isomer ratio is determined by steric and electronic properties associated to L and the aminocarbyne [193]. More in detail, the most stable isomer for complexes $[Ru_3(CO)_9(Py)(\mu_2\text{-}H)(\mu_2\text{-}CNRR')]$ (**68**) displays the pyridine in trans position with respect to the aminocarbyne ("bridging axial" isomer), as a consequence of the trans influence exerted by the latter (vide infra). On the other hand, phosphines, being bulkier and better π-acceptors than pyridine, occupy equatorial sites

("bridging equatorial" and "non-bridging equatorial" isomers) [194]. For a given incoming ligand L, the effect exerted by different aminocarbyne groups is mostly steric in nature. For instance, bulky amino-substituents (e.g., benzyl) enhance the stability of the substitution products at the kinetic $M(CO)_4$ site [194].

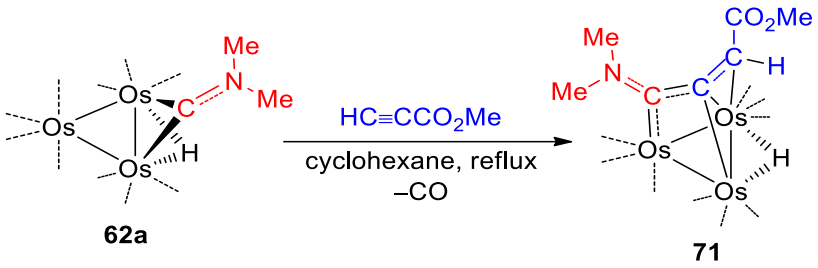
The proposed mechanism for isomerization [195] relies on the flexibility of the hydride/aminocarbyne couple, switching from bridging to terminal sites and viceversa (Scheme 28c) [193,197]. While these ligands move around the M_3 triangle, L remains bonded to the same metal atom. Such isomerization via bridge opening/closing is somehow reminiscent of the Adams-Cotton mechanism relevant to dinuclear systems.



Scheme 32. (a) Axial (*ax*) and equatorial (*eq*) sites in $[M_3(CO)_{10}(\mu_2\text{-}H)(\mu_2\text{-}CNR_2)]$ clusters (**62**); proposed pathways for CO/L substitution (b) and isomerization (c). Spectator CO ligands are represented by dotted lines.

Doubly bridging aminocarbyne ligands in trimetallic complexes may be involved in coupling reactions with unsaturated molecules [197,198]. In particular, the high temperature reaction of **62a** with methyl propiolate proceeds with CO elimination and carbyne/alkyne coupling, to give the μ_3-aminoallenyl **71** as the prevalent product (Scheme 33). In **71**, the carbyne-nitrogen bond maintains

some double-bond character, as indicated by crystallographic [C-N distance = 1.29(1) Å] and ^{1}H NMR features (non-equivalent N-Me groups).



Scheme 33. C-C coupling reaction involving aminocarbyne (red) and methyl propiolate (blue) on a triosmium cluster (CO ligands replaced by dotted lines).

The pyrolysis of {Ru_3} and {Os_3} aminocarbyne clusters promotes the elimination of carbonyls and other volatile ligands, and subsequently a dramatic rearrangement of the metal framework, leading to multiple products in low yields. Nevertheless, this approach provides the entry to otherwise non-accessible tetra- to octa-nuclear structures decorated with aminocarbyne ligands. In some cases, the initial μ_2-coordination is retained, *e.g.* in $[Ru_5(CO)_{11}(\mu_2\text{-}CNMe_2)(\mu_4\text{-}S)_2]$ (**66b**) [185], $[Ru_6(CO)_{14}(\mu_6\text{-}C)(\mu_2\text{-}CNMe_2)_2]$ (**72**) [254], $[Os_6(CO)_{12}(\mu_2\text{-}H)_2(\mu_2\text{-}CNMe_2)_2(\mu_3\text{-}SMe)_2]$ (**73**) [182], $[Os_6(CO)_{15}(\mu_2\text{-}CNMe_2)_2(\mu_3\text{-}S)(\mu_2\text{-}SPh)]$ (**74**) [183] and $[Ru_7(CO)_{19}(\mu_6\text{-}H)(\mu_2\text{-}CNMe_2)]$ (**75**) [255]. In other cases, triply and quadruply bridging aminocarbyne ligands are obtained (see Section 7). The X-ray structure of **75**, consisting of a capped octahedral Ru_7 unit with the hydride lying in the center of the octahedron cavity, is shown in Figure 13.

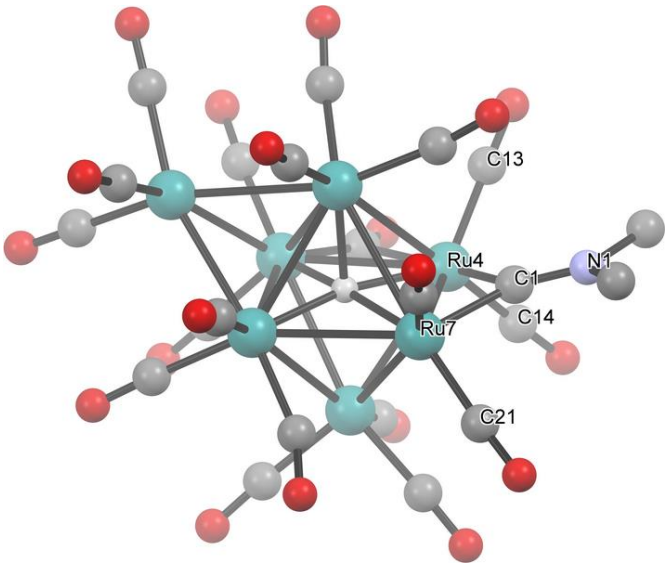


Figure 13. View of the X-Ray structure of $[Ru_7(CO)_{19}(\mu\text{-}H)(\mu_2\text{-}CNMe_2)]$ (**75**) [255]. H-atoms (except μ-H) omitted for clarity. Selected bond lengths (Å): Ru4-C1 1.992(5), Ru7-C1 1.969(5), C1-N1 1.292(6), Ru4-CO 1.882(6) and 1.866(6), Ru7-CO 1.864(6) and 1.890(6).

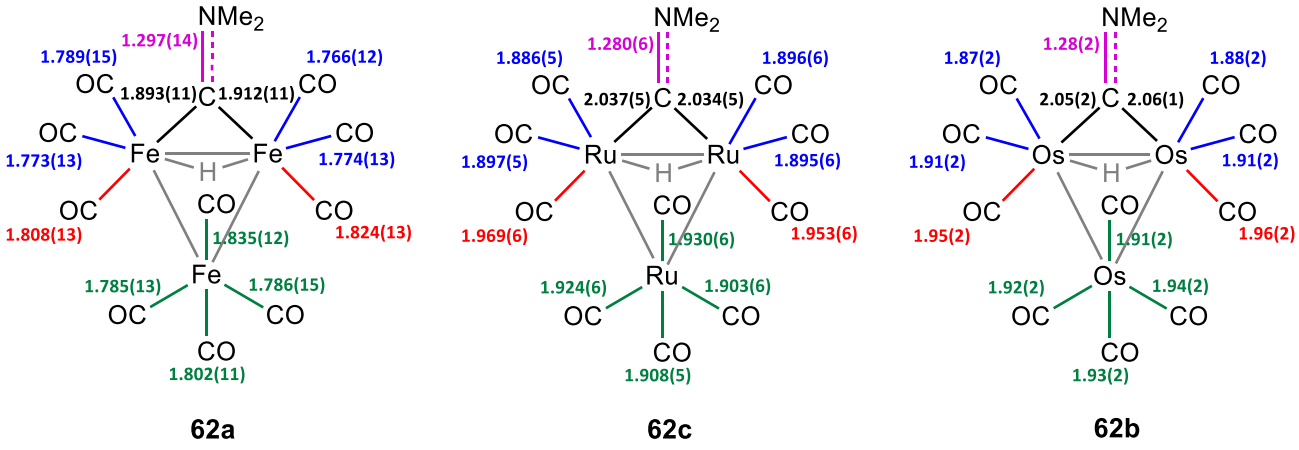
4.2. Structural and spectroscopic features

Salient crystallographic data related to $\{\mu_2\text{-}CNRR'\}$ ligands in polynuclear compounds are collected in Table 3. Similarly to what observed for dimetallic species, the carbyne-N distance (1.30 ± 0.02 Å) and the planarity around the nitrogen agree with a substantial iminium character, while metal-carbyne distances (Fe-C: 1.91 ± 0.01 Å; Ru-C and Os-C: 2.00 ± 0.04 Å) are consistent with a π-backbonding interaction [174,188,191].

Overall, the same bonding description as that shown for dimetallic μ_2-aminocarbyne complexes should be applied here for polynuclear ones, considering the aminocarbyne as a two-electron monocationic donor (Scheme 24) [172,175b,177,183] and reflecting comparable spectroscopic features (Table 4). Thus, the CN stretching vibration is found as a medium-weak band in the 1530-1600 cm^{-1} region of the IR spectra, while the ^{13}C NMR resonance of the carbyne carbon is usually detected around 320 ppm. In addition, isomerism traced back to the inhibited rotation around the carbyne-N axis has been observed [172,174,177]; based on variable temperature NMR

measurements, an activation barrier to rotation of 54 kJ mol^{-1} was reported for [$Fe_3(CO)_{10}(\mu_2$-H){μ_2-$CN^iPr(Et)$}] (**62d**) [172].

X-ray data related to the homologous group 8 trinuclear clusters **62a-c** are compared in Scheme 34: in the three structures, the effective π-acceptor ability of the aminocarbyne ligand is evidenced by an elongation of the metal-carbonyl bond in trans [175b,194]. Accordingly, CO/pyridine mono-substitution from **62c** determines a marked asymmetry in the resulting complex **68a**: the carbyne trans to the prevalently σ-donor pyridine ligand is more tightly bound to ruthenium [1.977(6) Å] than the carbyne trans to the π-acceptor CO ligand [2.047(4) Å], see Figure 12 [194].



Scheme 34. Comparative view of bond distances in the X-ray structures of [$M_3(CO)_{10}(\mu_2$-H)(μ_2-$CNMe_2$)], (M = Fe, **62a** [179b]; M = Ru, **62c** [175b]; M = Os, **62b** [178]). Data of **62c** related to one of the two independent molecules in the crystal. View of the X-ray structure of **62a** in Figure 10.

Table 3. X-ray data related to μ_2-aminocarbyne ligands in trimetallic and higher nuclearity complexes.

Compound	d(MC) / Å	d(CN) / Å	Ref.
[$Fe_3(CO)_{10}(\mu_2$-H)(μ_2-$CNMe_2$)] (**62a**)	1.89(1) 1.91(1)	1.30(1)	[179b]
[$Os_3(CO)_{10}(\mu_2$-H)(μ_2-$CNMe_2$)] (**62b**)	2.06(1) 2.05(2)	1.28(2)	[178]
[$Ru_3(CO)_{10}(\mu_2$-H)(μ_2-$CNMe_2$)] [a] (**62c**)	2.034(5) / 2.037(5) 2.018(4) / 2.034(5)	1.280(6) / 1.279(5)	[175b]
[$Os_3(CO)_8(\mu_2$-H)$_2$(μ_2-$CNMe_2$)(μ_2-SPh)] (**63a**) [a]	2.12(2) / 2.10(2) 2.00(2) / 2.00 (2)	1.27(3) / 1.32(3)	[180], [181]
[$Os_3(CO)_{10}(\mu_2$-$CNMe_2$)(μ_2-SPh)]	2.13 (2) 2.09 (2)	1.27 (2)	[183],[19 7]

[{$Fe_2(CO)_6$}$_2$(μ_2-$CNMe_2$)(η^2-$SCNMe_2$)(μ_4-S)] (**64**)	1.927(7) 1.920(8)	1.325(9)	[184]
[{$Fe_2(CO)_6$}$_3$(μ_2-$CNEt_2$)$_2$(μ_4-S)$_2$]	1.88(2) 1.92(2)	1.30(2)	[189]
	1.91(2) 1.90(2)	1.29(2)	
[{$Fe_2(CO)_6$}$_3${μ_2-$CN(CH_2CH{=}CH_2)_2$}$_2$(μ_4-S)(μ-SMe)]	1.902(4) 1.911(4)	1.296(4)	[188]
[$Ru_5(CO)_{11}$(μ_2-$CNEt_2$)$_2$(μ_4-S)$_2$] (**66**)	1.957(9) / 1.949(9) 2.009(9) / 1.936(9)	1.29(1) / 1.29(1)	[186]
[$Ru_5(CO)_{11}$(μ_2-$CNMe_2$)$_2$(μ_4-S)$_2$] (**66b**)	1.986(8) / 2.048(8) 1.999(9) / 1.984(9)	1.29(1) / 1.27(1)	[185]
[$Co_3Cl(PPh_3)_2$(μ_2-$CNEt_2$)(μ_2-$SCNEt_2$)(μ_3-S)] (**67**)	1.823(8) 1.833(8)	1.323(9)	[191]
[$Ru_3(CO)_9$(Py)(μ_2-H)(μ_2-$CNMe_2$)] (**68a**)	1.977(6) 2.047(4)	1.304(7)	[194]
[$Ru_3(CO)_9(PPh_3)$(μ_2-H)(μ_2-$CNBn_2$)] (**69a**)	2.05(1) 2.04(1)	1.29(1)	[194]
[$Os_3(CO)_7$(μ_2-H)(μ_2-$CNMe_2$)(μ_2-SPh)(η^2-CH_2NMe_2)]	2.07(2) 2.02(2)	1.30(2)	[197]
[$Os_3(CO)_7$(μ_2-H)(μ_2-$CNMe_2$)(μ_2-CH_2NMe_2)(μ_2-SPh)]	2.01(2) 2.03(1)	1.28(2)	[197]
[$Ru_6(CO)_{14}$(μ_6-C)(μ_2-$CNMe_2$)$_2$] (**72**)	1.925(6) 2.053(6)	1.307(8)	[254]
[$Os_6(CO)_{12}$(μ_2-H)$_2$(μ_2-$CNMe_2$)$_2$(μ_3-SMe)$_2$] (**73**)	1.99(3) 2.04(3)	1.39(4)	[182]
	2.00(3) 2.03 (3)	1.32(4)	
[$Os_6(CO)_{15}$(μ_2-$CNMe_2$)$_2$(μ_3-S)(μ_2-SPh)] (**74**)	1.98 (2) 2.04 (2)	1.30 (3)	[183]
[$Ru_7(CO)_{19}$(μ_6-H)(μ_2-$CNMe_2$)] (**75**)	1.969(5) 1.992(5)	1.292(6)	[255]
[$Fe_4(CO)_{12}$(μ-η^1,κ^1-$SCNEt_2$)(μ_4-S)(μ_2-$CNEt_2$)]	1.917(2) 1.910(2)	1.297(3)	[190]
[$Ru_8(CO)_{15}$(μ_2-$CNMe_2$)$_2$(μ_5-S)$_2$(μ_4-S)(μ_3-S)]	2.038(6) 1.964(7)	1.303(8)	[187]

[a] Two crystallographically independent molecules.

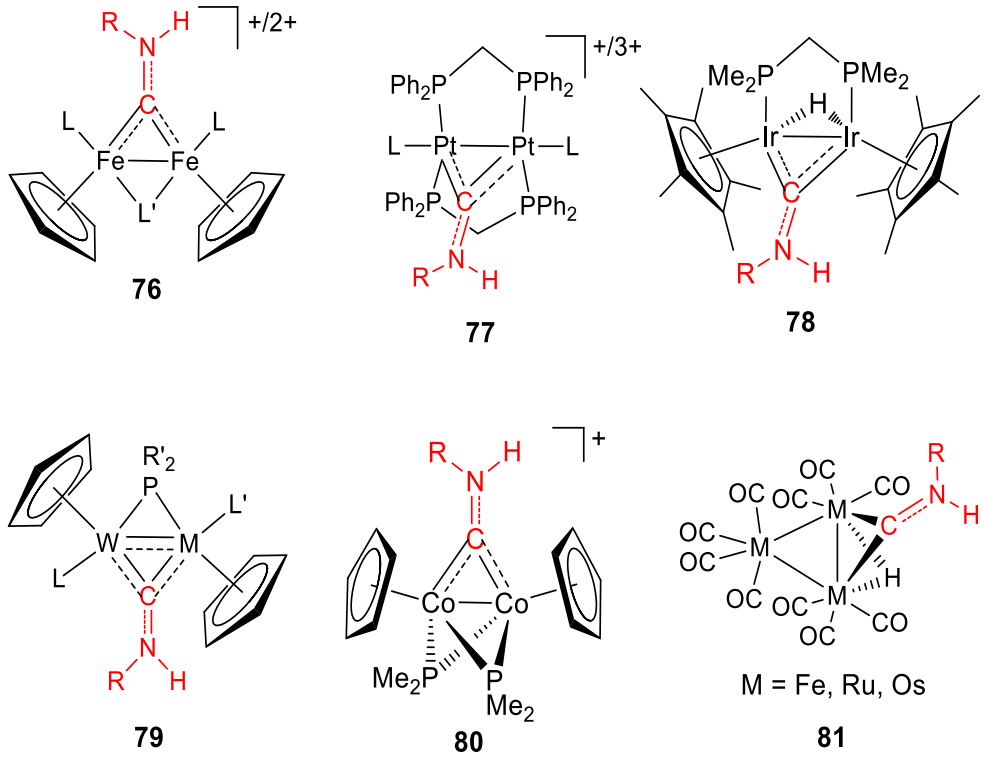
Table 4. Spectroscopic data related to μ_2-aminocarbyne ligands in trimetallic and higher nuclearity complexes.

Compound	**IR [a]**	**^{13}C NMR [b]**	**Ref.**
	$\tilde{\nu}$(CN) / cm^{-1}	**δ(CN) / ppm**	
[$Ru_3(CO)_{10}$(μ_2-H)(μ_2-$CNMe_2$)] (**62c**)	-	312.6	[174]
[$Fe_3(CO)_{10}$(μ_2-H)(μ_2-$CNEt_2$)] (**62d**)	-	317.3	[173]
[$Fe_3(CO)_{10}$(μ_2-H){μ_2-$CN^iPr(Et)$}] (**62e**)	-	318.3	[173]
[$Fe_3(CO)_{10}$(μ_2-H){μ_2-CNMe(Et)}] (**62f**)	1540	316.6	[173]
[$Fe_3(CO)_9$(CNEt)(μ_2-H){μ_2-CNMe(Et)}] (**62a-CNEt**)	-	318.1, 319.6, 322.3	[173]
[$Ru_5(CO)_{11}$(μ_2-$CNMe_2$)(μ_4-S)$_2$] (**66b**)	1594, 1568	-	[185]
[{$Fe(CO)_6$}{$Fe_3(CO)_9$}(μ_2-$CNEt_2$)(μ_4-S)(μ-SEt)]		311.0	[189]
[{$Ru_4(CO)_{10}$(μ_2-$CNMe_2$)(μ_3-S)}{$Ru(CO)_3(Me_2NCN(CH_2Me)$}(μ_4-S)]	1606, 1532	-	[185]
[$Ru_3(CO)_9(PPh_3)$(μ_2-H)(μ_2-$CNBn_2$)] (**69a**)	-	318.8	[174]
[$Fe_3(CO)_9(PPh_3)$(μ_2-H)(μ_2-$CNMe_2$)] (**69b**)	-	327.9	[195]
[$Ru_3(CO)_9(PPh_3)$(μ_2-H)(μ_2-$CNMe_2$)] (**69c**)	-	318.6	[174]
[$Ru_3(CO)_9(AsPh_3)$(μ_2-H)(μ_2-$CNMe_2$)] (**69d**)	-	318.9	[174]
[Ru_3(μ_2-H)$(CO)_9(AsPh_3)$(μ_2-$CNBn_2$)] (**69e**)	-	318.6	[174]

[a] Solid-state or solution. [b] $CDCl_3$, CD_2Cl_2 or other common deuterated solvent.

5. Secondary and primary bridging aminocarbyne ligands

Aminocarbyne ligands bearing one or two hydrogen atoms on nitrogen are named '*secondary*' or '*primary*', respectively [11]. From a structural point of view, secondary and primary aminocarbynes are strictly related to the tertiary homologues, but the NH_x function provides a peculiar reactivity deserving a separate discussion. Several examples of {μ_2-CNHR} ligands in di- and trinuclear complexes have been reported (Scheme 35), and some of them belong to the metal scaffolds described in Sections 3 and 4.



Scheme 35. Common metal structures hosting secondary μ_2-aminocarbyne ligands (red). **76**: L = CO, CNR; L' = CO, CNR, CNR_2^+. **77**: L = Cl, I, CNR. **79**: M = Mo, W; R' = Ph, Cy; L/L' = CO, CNR, NO.

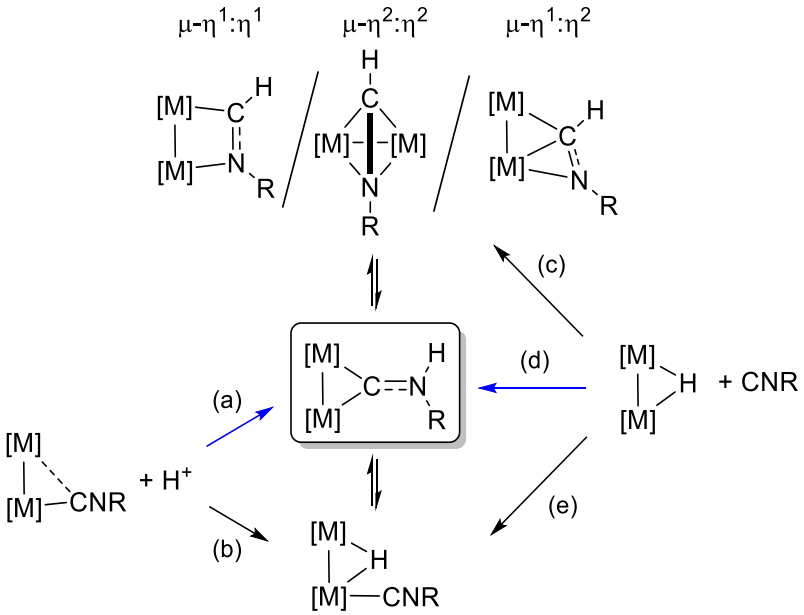
5.1. Synthetic routes

The double protonation of a cyanide ligand yields the {μ-CNH_2}$^+$ moiety (see also Section 2.2), while {μ-CNHR}$^+$ ligands are accessible via isocyanide/hydrogen assembly. The latter can be realized in

two ways, i.e. the reaction of a metal isocyanide complex with a Brønsted acid (protonation) or the reaction of a metal hydride complex with an isocyanide (isocyanide insertion). Despite the apparent simplicity, both routes may involve multiple intermediates, depending on the specific metal system (Scheme 36). In fact, di- and tri-metallic isocyanide complexes possess at least two competing basic sites: the nitrogen atom and the metal-metal bond(s) (Scheme 36a-b). The relative basicity of the two sites, hence the thermodynamic stability of the two derived products and their interconversion, depend on the metal scaffold and the isocyanide substituent. Moreover, the outcome of the reaction will be influenced by the strength of the Brønsted acid and the nature of the solvent.

On the other hand, the insertion of an isocyanide into a bridging hydride can occur according to 1,1 (C-H bond formation) or 1,2 (N-H bond formation) insertion types, affording respectively a formimidoyl (Scheme 36c) or an aminocarbyne (Scheme 36d). In addition, the formimidoyl ligand may adopt different coordination modes. The occurrence of formimidoyl/aminocarbyne isomerism and the relative stability of the isomers vary depending on the system.

The two preparative routes, and ensuing mechanistic considerations, will be discussed below.



Scheme 36. Possible arrangements of CNR/H fragments on a dimetallic core: protonation of isocyanide (a) or M-M bond (b); isocyanide insertion into bridging hydride affording formimidoyl

(c) or aminocarbyne (d); isocyanide coordination (e). The three commonly observed coordination modes for formimidoyl ligands are shown on top.

Beside the above described general methods to access secondary aminocarbyne ligands, it should be mentioned that the dirhenium complex $[Re_2Cl_2(CN^tBu)_2(\mu\text{-}Cl)(dppm)_2\{\mu\text{-}CNH(^tBu)\}]PF_6$, **82**$[PF_6]$, was serendipitously isolated as a by-product (13% yield) of the synthesis of $[Re_2Cl_3(dppm)_2(CN^tBu)_3]PF_6$ in dichloromethane (formal H^+ addition) [199].

5.1.1. Isocyanide protonation

Protonation of an isocyanide ligand leans on the same conceptual background as the alkylation (or other electrophilic additions). Hence, it takes advantage of the increased Brønsted basicity of the isocyanide coming from π-backbonding interaction, especially when the isocyanide bridges two metal atoms. In polynuclear complexes, the resulting secondary aminocarbyne ligand typically adopts a bridging coordination, regardless of the site (either bridging or terminal) occupied by the isocyanide in the precursor.

Protonation of isocyanides in di- and tri-metallic compounds is usually carried out with strong, poorly coordinating, Brønsted acids such as CF_3SO_3H, HPF_6, HBF_4, $HClO_4$, HI, HCl or $[HOEt_2][BAr^F]$, in mixed aqueous-organic or in strictly anhydrous organic solvents [93,103,112,113,172,173,200,201,202,203,204]. Selected examples are shown in Scheme 37. Both the electron rich dinuclear Ni^0 complex $[Ni_2(CNMe)_2(\mu\text{-}CNMe)(\mu\text{-}dppm)_2]$ (p$K_a \approx 10$ in THF for the conjugate acid) [94] and the related bis-cationic Ni^{+I} $[Ni_2(CNMe)_3(\mu\text{-}CNMe)(\mu\text{-}dppm)_2][PF_6]_2$ [205] are protonated to give the respective aminocarbyne derivatives **83-84** (Scheme 37b,c). Analogously, cationic diiron aminocarbyne complexes $[Fe_2Cp_2(L)(L')(CNR)(\mu\text{-}CNMe_2)]^+$ (L/L' = CO, CNR; R = Me, Et, ^{t}Bu, 2,6-$C_6Et_2H_3$; R' = Me, Et) and $[Fe_2Cp_2(CNEt)_2(\mu\text{-}CNEt_2)]^+$ **53** promptly react with strong acids (HPF_6, CF_3SO_3H) to produce the bis-aminocarbyne **85-86**, while weaker acids like CF_3CO_2H or CH_3CO_2H are ineffective (Scheme 37e) [109b,208].

It is interesting to compare the attitude towards protonation and alkylation of $[Fe_2Cp_2(CO)(\mu\text{-}CO)(CNMe)(\mu\text{-}CNMe_2)]^+$ (**53f**): the terminal methyl isocyanide ligand is protonated by CF_3SO_3H but does not react with CF_3SO_3Me [111]. In other terms, the absence of fluxionality in **53f** (Adams-Cotton mechanism not working) does not forbid the protonation to occur, which is followed by an exchange of position between the newly formed aminocarbyne and the μ-CO, yielding the thermodynamically stable product $[Fe_2Cp_2(CO)_2(\mu\text{-}CNHMe)(\mu\text{-}CNMe_2)]^+$ (**85a**). Indeed, the ease of protonation of $[Fe_2Cp_2(L)(\mu\text{-}CO)(CNR)(\mu\text{-}CNMe_2)]^+$ (**53**; L = CO, isocyanide) complexes increases in the order R = Et < Me < Xyl, according to the *thermodynamic* preference of EWD-substituted isocyanides for the bridging coordination in this system ("*migratory aptitude*") [109b,208].

(a) $[Pt_2X_2(\mu\text{-}CNR)(\mu\text{-}dppm)_2] \xrightarrow[X = Cl, I]{HClO_4} [Pt_2X_2(\mu\text{-}CNHR)(\mu\text{-}dppm)_2]^+$ (**77**)

(b) $[Ni_2(CNMe)_2(\mu\text{-}CNMe)(\mu\text{-}dppm)_2] \xrightarrow[THF]{[HOEt_2]PF_6} [Ni_2(CNMe)_2(\mu\text{-}CNHMe)(\mu\text{-}dppm)_2]^+$ (**83**)

(c) $[Ni_2(CNMe)_3(\mu\text{-}CNMe)(\mu\text{-}dppm)_2]^{2+} \xrightarrow[Et_2O]{[HOEt_2]BF_4} [Ni_2(CNMe)_3(\mu\text{-}CNHMe)(\mu\text{-}dppm)_2]^{3+}$ (**84**)

(d) $[M_2Cp_2(CO)_3(CNR)] \xrightarrow[M = Fe, Ru]{HPF_6} [M_2Cp_2(CO)_3(\mu\text{-}CNHR)]^+$ (**76**)

(e) $[Fe_2Cp_2(L)_2(CNR)(\mu\text{-}CNMeR)]^+ \xrightarrow[\text{or } HPF_6 / Et_2O]{CF_3SO_3H / CHCl_3} [Fe_2Cp_2(L)_2(\mu\text{-}CNHR)(\mu\text{-}CNMeR)]^{2+}$
L = CO, **85**
L = CNR, **86**

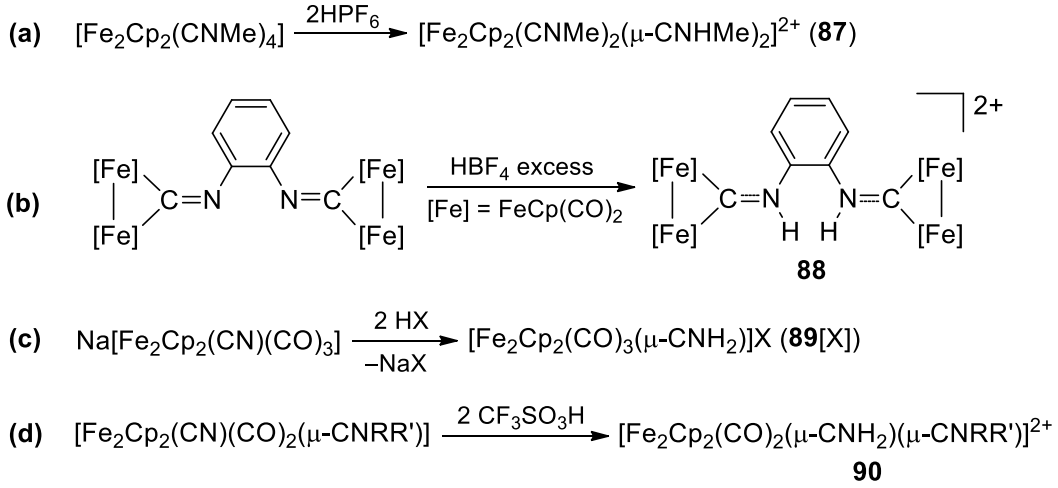
(f) $[Fe_3(CO)_{10}(CNR)(\mu\text{-}H)]^- \xrightarrow{CF_3SO_3H} [Fe_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}CNHR)]$ (**81**)

Scheme 37. Protonation reactions of isocyanide ligands on various di- and tri-metallic complexes.

Neutral diiron bis-cyclopentadienyl compounds with either a bridging diisocyanide [112,113,202] or two (or more) isocyanide ligands, $[Fe_2Cp_2(CO)_{4-x}(CNR)_x]$ ($x \geq 2$), are susceptible to double protonation. When isocyanides with secondary alkyl substituents (e.g. R = Cy, ^{i}Pr) are involved, the resulting bis-aminocarbyne species may be rather unstable [111,203,206]. This feature, together with the lack of reactivity of $[Fe_2Cp_2(CO)_3(CN^tBu)]$ (Equation 13) with Brønsted acids [203], has been

explained on the basis of a combination of the steric bulk of the nitrogen substituent, weakening the N-H bond, and the relatively low tendency of the secondary alkyl isocyanide to reach a bridging site. The protonation of *cis*-$[Fe_2Cp_2(CNMe)_4]$ can be regulated with the strength of the acid: the selective, single protonation to $[Fe_2Cp_2(CNMe)_3(\mu\text{-}CNHMe)]^+$ (**87**) is achieved using acetic acid or benzoic acid, while HPF_6 affords the bis-aminocarbyne $[Fe_2Cp_2(CNMe)_2(\mu\text{-}CNHMe)_2]^{2+}$ (**86a**, Scheme 38a), and acids of intermediate strength (Cl_3CCO_2H or Cl_2CHCO_2H) give a mixture of **86a** and **87** [109b]. Compound $[\{Fe_2Cp_2(CO)_3\}_2(\mu\text{-}1,2\text{-diisocyanobenzene})]$ is another stark example of different behavior towards protonation and alkylation. Indeed, this complex is converted into the bis-aminocarbyne dication **88** if treated with excess HBF_4 (Scheme 38b), whereas steric issues prevent the bis-methylation (section 3.1.1).

Double protonation of the cyanide in $[Fe_2Cp_2(CO)_3(CN)]^-$ and related complexes affords the primary aminocarbyne ligand (see Scheme 38c-d and Figure 14) [207,208]. Note that {Fe-CNH} intermediates are elusive and could not be detected even using one equivalent of acid. Therefore, the basicity of coordinated *hydrogen isocyanide* appears superior to that of its cyanide precursor.



Scheme 38. Double protonation of isocyanide (a, b) and cyanide (c, d) ligands affording diiron complexes with bridging secondary/primary aminocarbyne ligands.

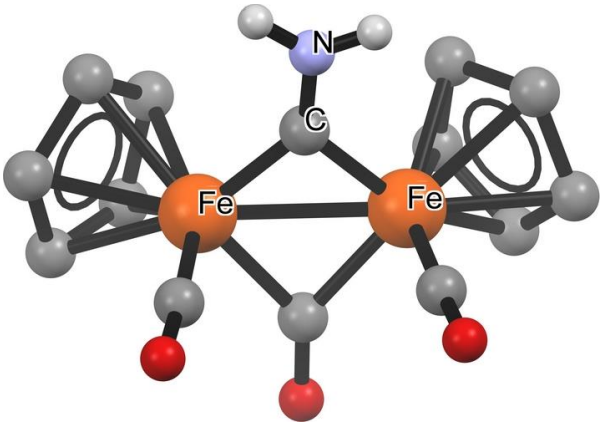
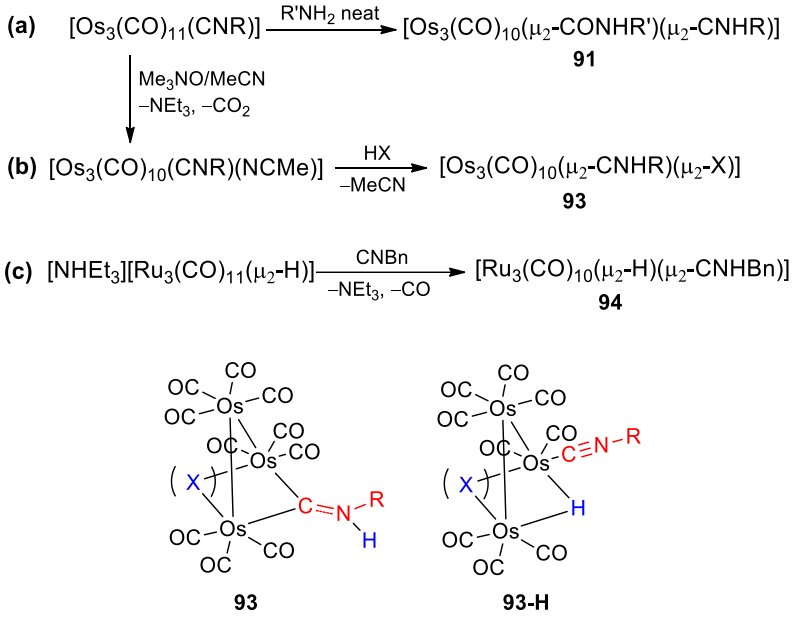


Figure 14. View of the X-ray structure of $[Fe_2Cp_2(CO)_3(\mu\text{-}CNH_2)]^+$ (**89**) [207]; H atoms (except NH) omitted for clarity. Selected bond lengths (Å): Fe-carbyne 1.862(3) and 1.867(3), carbyne-N 1.279(4), Fe-CO(terminal) 1.777(4) and 1.769(4), Fe-CO (bridging) 1.947(4) and 1.926(4).

Another strategy to produce secondary aminocarbyne ligands makes use of protic species, enabling isocyanide protonation coupled to nucleophilic substitution/addition on carbonyl ligands. For instance, addition of primary amines to $[Os_3(CO)_{11}(CNR)]$ leads to aminocarbyne and carboxamido ligands, via amine to isocyanide hydrogen transfer and nucleophilic CO-attack of the resulting amido group (Scheme 39a, compounds **91**) [209,210]. Further CO substitution is possible, and the X-ray structure of $[Os_3(CO)_9(NH_2{}^i\text{Pr})(\mu{:}\eta^1{:}\eta^1\text{-}CONH{}^i\text{Pr})(\mu\text{-}CNHPh)]$ (**92a**) is shown in Figure 15. Analogous reactions were performed with $[Os_3(CO)_{10}(CNR)(NCMe)]$ and propiolic acid [211], 1-hydroxybenzotriazole [212], 1-hydroxypyridine-2-thione [213] and hydrogen chloride in aprotic solvents (Scheme 39b) [200]. In the products **93**, the deprotonated reagent is found as a ligand bridging two osmium atoms which are no longer connected by a metal-metal bond. A related case of CO/CNR substitution coupled to protonation from the ammonium counter cation has been described on a triruthenium cluster (Scheme 39c) [214]. In certain cases, the triosmium aminocarbyne **93** form in admixture with hydride isomers derived from metal protonation, especially when aliphatic isocyanides are involved (structure **93-H** in Scheme 39) [211,213].



Scheme 39. Isocyanide protonation coupled with either (a) nucleophilic addition or (b-c) substitution, involving one CO ligand in trimetallic complexes. Generic structures of open-cluster triosmium species (**93**, **93-H**).

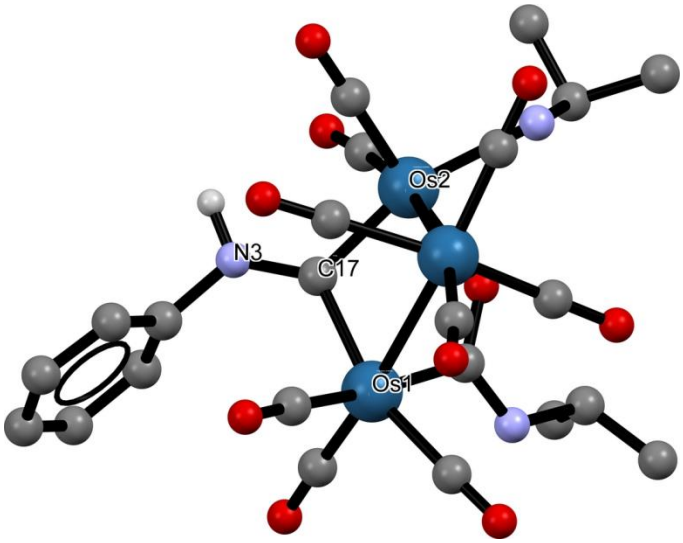


Figure 15. View of the X-ray structure of $[Os_3(CO)_9(NH_2{}^iPr)(\mu{:}\eta^1{:}\eta^1\text{-}CONH{}^iPr)(\mu\text{-}CNHPh)]$ (**92a**) [209]; H atoms (except NH) omitted for clarity. Selected bond lengths (Å): Os1-C17 2.098(11), Os2-C17 1.991(13), C17-N3 1.339(18).

Protonation reactions of $[Os_3(CO)_{10}(CNR)(NCMe)]$ [200] and $[Fe_2(CNR)_6(pdt)]$ [215] (pdt = κ^2S-1,3-propanedithiolate) have been studied in detail, revealing to what extent the strength of the acid, the polarity of the solvent and the isocyanide substituent (R) may direct the proton attack to either CNR or the M-M bond. These systems are good models for the fine-tuning of site-selective protonation in metal complexes. Thus, the reaction of $[Fe_2(CNMe)_6(pdt)]$ with the strong acid $[HOEt_2][BAr^F]$ leads to exclusive formation of the bridging hydride, whereas the aminocarbyne $[Fe_2(CNMe)_5(\mu\text{-}CNHMe)(pdt)]^+$ (**95**) is selectively formed under carefully controlled conditions ($[Et_3NH][BAr^F]$ at −78 °C). However, subsequent isomerization of **95** to $[Fe_2(CNMe)_6(\mu\text{-}H)(pdt)]^+$ takes place at room temperature, **95** is the more stable product according to DFT calculations [215]. The protonation of $[Fe_2(CNR)_6(pdt)]$ complexes bearing aryl substituents (R = 4-C_6H_4OMe, 4-C_6H_4Cl) directly leads to the hydride.

The triosmium clusters $[Os_3(CO)_{10}(CNR)(NCMe)]$ react with strong acids (HBF_4, CF_3SO_3H) to give the hydride derivative $[Os_3(CNR)(NCMe)(CO)_{10}(\mu_2\text{-}H)]^+$, but in this case the Os-Os bond is the kinetic site of protonation. Thus, a weaker acid, such as HCl in dichloromethane, initially affords the hydride product which then equilibrates with the aminocarbyne isomer. In a less polar solvent (cyclohexane), the product ratio shifts towards the aminocarbyne [200]. Concerning the nature of the isocyanide substituent, electron-withdrawing groups (Ph > Bn > Pr) favor the formation of the aminocarbyne.

In general, the effect of the nature of the isocyanide on the reactivity is rationalized in relation to its tendency to adopt a bridging coordination and to the extent of π-backbonding offered by the metal scaffold. It is apparent that, in the diiron-pdt system, the net effect supplied by aryl substituents on the isocyanide is a decrease of the N-basicity (see above).

In diiron bis-cyclopentadienyl compounds, although the isocyanide protonation always leads to the aminocarbyne, protonation of the [Fe-Fe] core might be of some relevance to the reaction mechanism, especially when bridging/terminal ligand exchange processes are viable [208].

5.1.2. Isocyanide insertion into dimetal-μ-hydride

The alternative method for the building of secondary aminocarbyne groups is the insertion of an isocyanide into a bridging hydride ligand. This strategy has been successfully applied to various dimetallic bis-cyclopentadienyl complexes comprising bridging phosphide or diphosphine ligands. The representative structures of ditungsten (**79a**) and diiridium products (**78a**) are shown in Figure 16.

The reactions are very sensitive to the type of isocyanide and to electronic factors related to the metal centers. For instance, $[W_2Cp_2(CO)_2(\mu\text{-}H)_2]$ and $[W_2Cp_2(CO)_2(\mu\text{-}H)(\mu\text{-}PCy_2)]$ react with methyl isocyanide and xylyl isocyanide, respectively, to afford the aminocarbynes $[W_2Cp_2(CO)_2(\mu\text{-}H)(\mu\text{-}CNHR)]$ (**96**) and $[W_2Cp_2(CO)(CNXyl)(\mu\text{-}CNHXyl)(\mu\text{-}PCy_2)]$ (**79b**) [216, 217]. In the latter case, the kinetic formimidoyl species $[W_2Cp_2(CO)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CHNXyl)(\mu\text{-}PCy_2)]$ was obtained at 0 °C in dichloromethane, and isomerized to **79b** during alumina chromatography or more efficiently in hot toluene solution [218]. Likewise **79b**, the hybrid molybdenum-tungsten complex $[WMoCp_2(CO)_2(\mu\text{-}CNHXyl)(\mu\text{-}PCy_2)]$ (**79c**) was produced via a formimidoyl intermediate from isocyanide insertion into metal-hydride bond [219]. Conversely, the reactions of $[W_2Cp_2(CO)_2(\mu\text{-}H)(\mu\text{-}PCy_2)]$ with 4-methoxyphenyl isocyanide and tert-butyl isocyanide led to the almost quantitative isolation of the $\mu\text{-}\eta^2\text{:}\eta^2$-formimidoyl products. Moreover, the nitrosyl adduct $[W_2Cp_2(NO)_2(\mu\text{-}H)(\mu\text{-}PPh_2)]$ adds tert-butyl isocyanide to give a ca. 3:1 mixture of formimidoyl and aminocarbyne isomers [220]. DFT calculations pointed out that the ditungsten aminocarbyne complexes are the thermodynamically stable products in every cases [218,220].

Isomerization towards the opposite direction has been reported for $[Co_2Cp_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]^+$ (hexafluorophosphate salt): the reaction with methyl isocyanide at –78 °C forms the aminocarbyne $[Co_2Cp_2(\mu\text{-}CNHMe)(\mu\text{-}PMe_2)_2]^+$ (**80a**) which quantitatively turns into the formimidoyl $[Co_2Cp_2(\mu\text{-}CHNMe)(\mu\text{-}PMe_2)_2]^+$ in the presence of a catalytic amount of methylamine [221,222].

An intermolecular case has been described for $[Fe_3H(CO)_{10}(CN^iPr)]^-$: this complex is stable at room temperature and undergoes protonation to afford the aminocarbyne {CNH(^{i}Pr)}, which then rearranges to formimidoyl upon heating at 40 °C in THF [172,173].

Otherwise, aminocarbyne complexes **78** have been prepared from $[Ir_2Cp^*_2(\mu\text{-}H)_2(\mu\text{-}dmpm)_2]^{2+}$ (triflate salt) via reaction with cyclohexyl isocyanide or phenyl isocyanide; on the same system, addition of tert-butyl isocyanide simply affords the adduct $[Ir_2(H)Cp^*_2(CN^tBu)(\mu\text{-}H)(\mu\text{-}dmpm)_2]^{2+}$ [223].

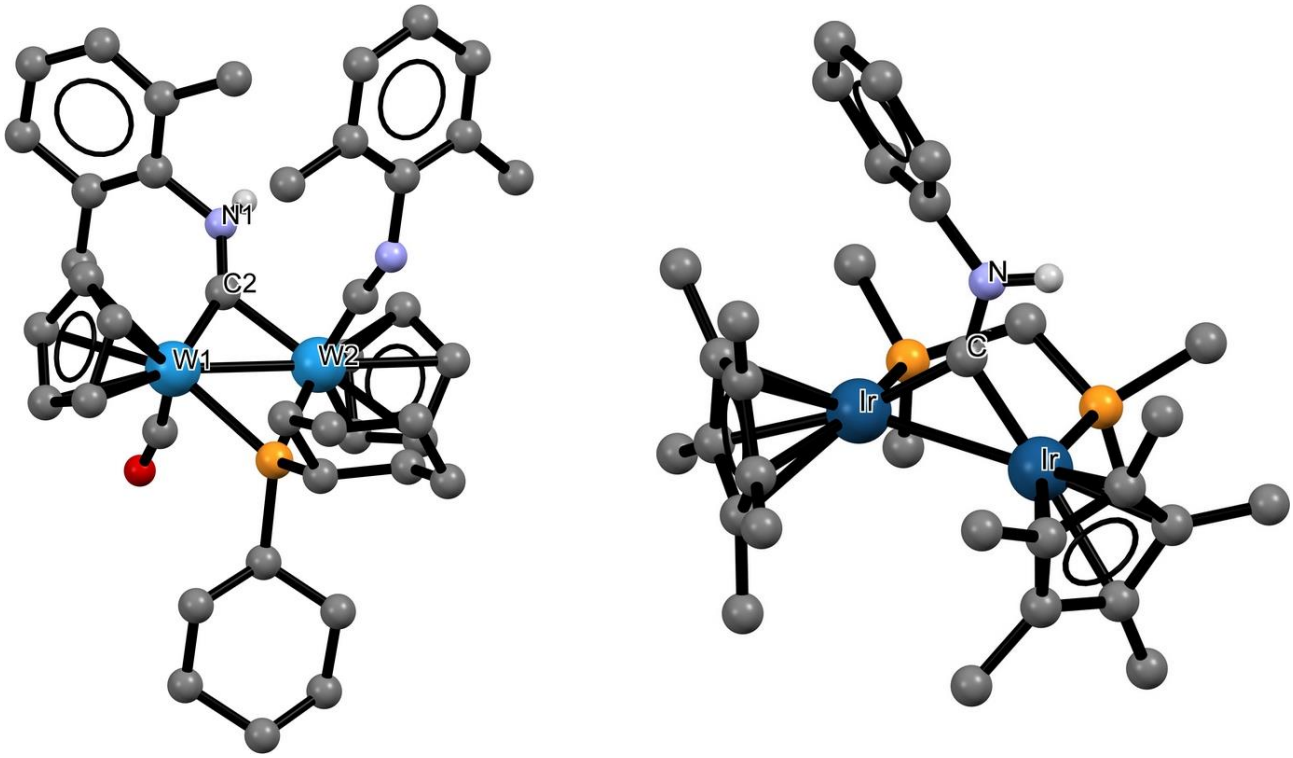


Figure 16. Views of the X-Ray structures of $[W_2Cp_2(CO)(CNXyl)(\mu\text{-}CNHXyl)(\mu\text{-}PCy_2)]$ (**79a**) [217] and $[Ir_2Cp^*_2(dmpm)(\mu\text{-}CHNPh)]^+$ (**78a**) [223]. H atoms (except NH) omitted for clarity. Selected bond lengths (Å): **79a**, W1-C2 1.97(3), W2-C2 2.06(2), C2-N1 1.31(3), W1-CO 1.93(3); **78a** (average values on three independent cations): Ir-carbyne 1.99(3) and 1.98(3), carbyne-N 1.31(3).

5.2. Reactivity

The Brønsted acidity of secondary aminocarbyne ligands is the central aspect governing the chemistry of the related complexes, since the sensitivity to even mildly basic species usually inhibits addition

or substitution reactions. As a matter of fact, only a few CO substitution reactions have been reported for the triosmium clusters **91** [209,210] and the diiron complex **85a** [136]. Besides, dinuclear group 6 metal complexes with secondary aminocarbyne ligands have been invoked as intermediates in isocyanide/alkylidyne coupling reactions [218,224].

In principle, H^+ removal from the {μ-CNHR} moiety (re)generates the isocyanide, however the outcome of this process depends on the employed Brønsted base. In some cases, deprotonation equilibria are established in polar solvents such as water, acetone or methanol. Most frequently, the deprotonation is not reversible and is associated to the degradation of the compound via side reactions; for this reason, many μ-CNHR complexes are poorly stable in solution [93,203,208] sometimes even at low temperature [103,113], with consequent experimental drawbacks in their isolation and characterization. For instance, $[Fe_2Cp_2(CNMe)_3(\mu\text{-}CNHMe)]^+$ (**87**) decomposes upon dissolution in water with formation of several products including the mononuclear $[FeCp(CNMe)_3]^+$ [109b].

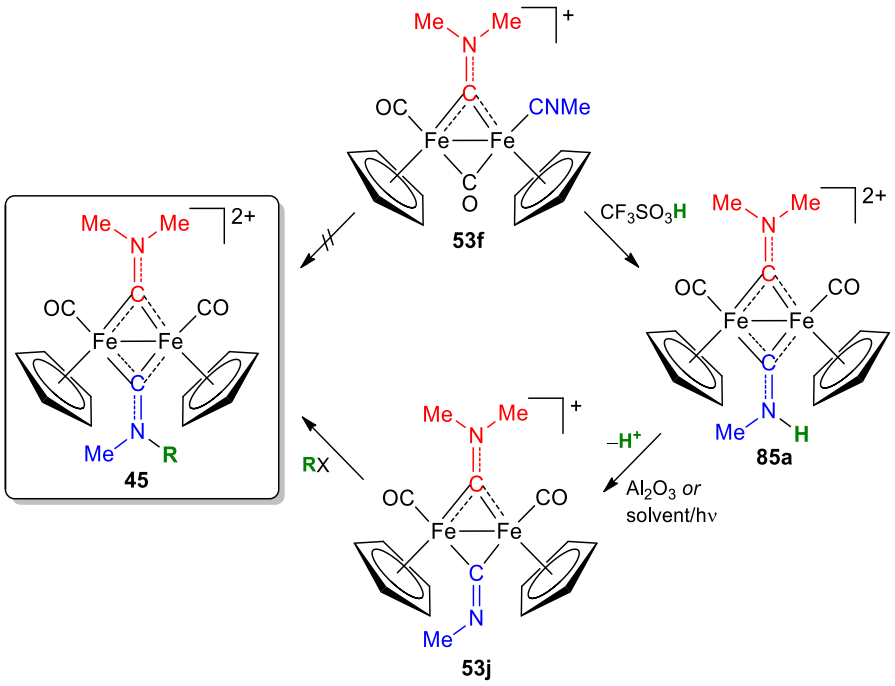
Remarkably, $[Fe_2Cp_2(CO)_2(L)(\mu\text{-}CNHMe)]^+$ (**76**; L = CO, CNMe) and $[Fe_2Cp_2(CO)_2(\mu\text{-}CNH(Me)_2]^{2+}$ (**85b**) undergo oxidative cleavage of the Fe-Fe bond by silver salts in methanol or acetonitrile [206]. Such sensitivity to protic solvents and oxidants is not observed in analogous {μ-CNR_2} diiron complexes **40**, which instead are rather stable in water (see Section 3.4) [167] and display high oxidation potentials [171b]. Therefore, the diiron-{μ-CNR_2} scaffold is tolerant to Ag^+ salts, which are conveniently used for halide abstraction from **54-Cl** (see Scheme 21) [139].

Furthermore, secondary aminocarbyne complexes might be intrinsically unstable in the presence of basic co-ligands or counter-anions [109b,203]. For instance, $[Fe_3(CO)_{10}(\mu\text{-}H)(CNHR)]$ (**81**; R = Me, Et, ^{i}Pr) decompose in the solid state over a period of hours to yield, *inter alia*, $[Fe_3(CO)_{11}(CNMe)]$ via H_2 release [172,173] Similarly, the reaction of $[W_2Cp_2(CO)_2(\mu\text{-}H)_2]$ with tert-butyl isocyanide leads directly to H_2 and $[W_2Cp_2(CO)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CN^tBu)]$, presumably via a μ-$CNH^tBu$ intermediate [216].

The efficient *secondary aminocarbyne* to *isocyanide* conversion may be realized using an appropriate Brønsted base under stoichiometric conditions. For instance, triethylamine has been successfully employed with $[Pt_2Cl_2(\mu\text{-dppm})_2(\mu\text{-CNHR})]^+$ (**77**) and $[Fe_2Cp_2(CO)_2(\mu\text{-CNHR})]^+$ (**76**) [93,97], and a mild base such as a tertiary phosphine is effective towards the bis-cationic $[Fe_2Cp_2(CO)_2(\mu\text{-CNHR})(\mu\text{-CNR'}_2)]^{2+}$ (**86**) [136].

Silica and alumina may induce both mono- and bis-deprotonation respectively from secondary and primary aminocarbyne ligands in diiron bis-cyclopentadienyl complexes [111,136,208]. Conversely, Ru_3/Os_3 aminocarbyne clusters are resistant to deprotonation under the same conditions, so they can be generally purified via chromatography [212,213].

The feasible deprotonation of secondary aminocarbyne complexes can be exploited to synthesize bis-alkylated derivatives. For instance, $[Ru_3(CO)_{10}(\mu_2\text{-H})\{\mu_2\text{-CNR(Bn)}\}]$ (**62**; R = Me, Bn) have been prepared from $[Ru_3(CO)_{10}(\mu_2\text{-H})\{\mu_2\text{-CNH(Bn)}\}]$ (**81a**) via one-pot deprotonation/alkylation (NaOMe/MeI) or two-step reduction/alkylation (Na/BnCl) [174,214]. Similarly, bis-aminocarbyne complexes $[Fe_2Cp_2(CO)_2\{\mu\text{-CNMe(R)}\}(\mu\text{-CNMe}_2)]^{2+}$ (**45**) can be obtained from $[Fe_2Cp_2(CO)(CNMe)(\mu\text{-CO})(\mu\text{-CNMe}_2)]^+$ (**53f**), see Scheme 40. Direct alkylation of the terminal methylisocyanide ligand is not viable (vide infra), but a protonation/deprotonation sequence provides a straightforward access to the thermodynamically less stable isomer $[Fe_2Cp_2(CO)_2(\mu\text{-CNMe})(\mu\text{-CNMe}_2)]^+$ (**53j**, see Table 2), which in turn can be alkylated [111,208].



Scheme 40. Three-step synthesis of diiron bis-(tertiary)aminocarbyne complexes from aminocarbyne-methylisocyanide precursor via protonation/deprotonation/alkylation route.

Secondary aminocarbyne moieties may be involved in intramolecular H-shift rearrangements. For example, passing the triosmium clusters **92** through a silica gel column promotes the displacement of the labile amine ligand and the subsequent formation of hydride species in 60-75% yields (Equation 17) [209,210].

$$[Os_3(CO)_9(NH_2{}^iPr)\{\mu_2\text{-}C(O)NH{}^iPr\}\{\mu_2\text{-}CNH(R)\}] \xrightarrow[-NH_2{}^iPr]{SiO_2} [Os_3(\mu_2\text{-}H)(CO)_9\{\mu_2\text{-}C(O)NH{}^iPr\}(\mu_2\text{-}CNR)] \quad (17)$$

(**92**) R = Ph, CH_2Ph, Pr

5.3. Structural and spectroscopic features

Selected structural and spectroscopic data for secondary and primary aminocarbyne ligands in di- and tri-metallic complexes are collected in Table 5. Salient features resemble those of analogous tertiary aminocarbyne complexes and recall the same bonding description (Section 3.3). The ^{13}C NMR signal for the carbyne carbon is observed in the 315−344 ppm range for Fe_2, W_2 and MoW complexes, while

it is considerably more shielded (255−270) in Ir_2 and Os_3 derivatives. The CN stretching vibration is found as a medium intensity band around 1500-1600 cm^{-1} and isomerism due to restricted rotation around the C-N bond has been reported [209,212,214,219,220]. In other cases, the observation of a single set of ^1H NMR signals has been traced back to a rapid E-Z isomerization on the NMR timescale, proceeding through a reversible proton exchange with the solvent [208].

In addition, spectroscopic fingerprints of μ-CNHR ligands are the infrared NH stretching vibration around 3300 cm^{-1} and a broad NH resonance in the ^1H spectrum in the 9-12 ppm interval; the latter has sometimes been reported in the high field range (≈ 3 ppm).

Interestingly, complexes $[Os_3(CO)_9(L)(\mu:\eta^1:\eta^1\text{-}CONH^iPr)\{\mu\text{-}CNH(R)\}]$ (L = CO, **90**; L = $NH_2{}^iPr$, **91**; R = Pr, Bn) were characterized by ^{15}N NMR spectroscopy [225], and the resonance related to the aminocarbyne group was detected around −170 ppm (liquid NH_3 as reference), this value being intermediate between those typical of aliphatic amines (*ca*. −400 ppm) and imines (−20 to −100 ppm range). This experimental evidence corroborates the hybrid aminocarbyne/iminium nature of the ligand.

A comparison between data available for the homologous complexes $[Fe_2Cp_2(CO)_3(\mu\text{-}CNH_2)]^+$ (**89**, Figure 14) [207] and $[Fe_2Cp_2(CO)_3(\mu\text{-}CNMe_2)]^+$ (**40a**, Figure 6) [105] suggests the higher π-acceptor character of the (μ-CNH_2) ligand compared to (μ-$CNMe_2$), e.g. Fe-carbyne distances are 1.862(3) and 1.867(3) Å in **89** and 1.875(2) Å in **40a**.

Table 5. Spectroscopic and X-ray data related to μ_2-CNHR and μ_2-CNH_2 ligands in homo-dimetallic complexes.

Compound [a]	IR [b]		^{13}C NMR [c]	^1H NMR [c]	X-ray		Ref.
	ũ(NH) / cm^{-1}	ũ(CN) / cm^{-1}	δ(CN) / ppm	δ(NH) / ppm	d(MC) / Å	d(CN) / Å	
$[Fe_2Cp_2(CO)_3(\mu\text{-}CNHMe)]BF_4$ (**76a**[BF_4])	-	1598	--	-	1.87(1) 1.88(1)	1.28(1)	[203]
$[Fe_2Cp_2(CO)_3(\mu\text{-}CNHMe)]PF_6$ (**76b**[PF_6])	-	-	320.6	3.22	-	-	[103]
$[Fe_2Cp_2(CO)_3(\mu\text{-}CNHEt)]PF_6$ (**76c**[PF_6])	-	-	318.6	3.07	-	-	[103]
$[Fe_2Cp_2(CO)_3(\mu\text{-}CNH^iPr)]PF_6$ (**76d**[PF_6])	-	-	315.4	3.17	-	-	[103]
$[Fe_2Cp_2(CO)_3(\mu\text{-}CNH^iPr)]PF_6$ (**76e**[PF_6])	-	-	314.1	3.26	-	-	[103]

$[Fe_2Cp_2(CO)_3\{\mu\text{-}CNH(CH_2OCO_2H)\}]BF_4$ (**76f**[BF_4])	3268	1574	-	13.8-12.0	-	-	[201]
$[Pt_2Cl_2(dppm)_2(\mu\text{-}CNHTol)]ClO_4$ (**77a**[ClO_4])	-	1509 1504	-	-	-	-	[93]
$[Pt_2I_2(dppm)_2(\mu\text{-}CNHTol)]ClO_4$ (**77b**[ClO_4])	-	1503, 1499	-	-	-	-	[93]
$[Ir_2Cp^*_2(dmpm)(\mu\text{-}CHNPh)]CF_3SO_3$ (**78a**[CF_3SO_3]) [d]	-	1595	255	11.5	1.99(2) 1.98(2) 2.00(2) 1.99(2) 1.96(2) 1.98(2)	1.31(2) 1.33(2) 1.29(2)	[223]
$[W_2Cp_2(CO)(CNXyl)(\mu\text{-}CNHXyl)(\mu\text{-}PCy_2)]$ (**79a**)	-	-	335.4 337.5	9.85 9.76	2.06(2) 1.97(3)	1.31(3)	[217]
$[W_2Cp_2(CO)_2(\mu\text{-}CNHXyl)(\mu\text{-}PCy_2)]$ (**79b**)	-	-	333.6	9.92	-	-	[218]
$[MoWCp_2(CO)_2(\mu\text{-}CNHXyl)(\mu\text{-}PCy_2)]$ (**79c**, two isomers)	-	-	344.4, 343.2	10.31, 10.09	-	-	[219]
$[W_2Cp_2(\mu\text{-}CO)(\mu\text{-}CNHXyl)(\mu\text{-}PCy_2)]$	3300	-	318.8	7.22	2.016(4) 2.032(4)	1.344(5)	[218]
trans-$[W_2Cp_2(NO)_2(\mu\text{-}CNH^tBu)]$	-	-	336.0	9.99	2.086(6) 2.086(6)	1.311(8)	[220]
$[Re_2Cl_2(^tBuCN)_2(dppm)_2\{\mu\text{-}CNH(^tBu)\}(\mu\text{-}Cl)]PF_6$ (**82**[PF_6]) [d]	3350	-	-	-	1.96(2) 2.03(2) 2.03(2) 1.92(3)	1.40(3) 1.36(3)	[199b]
$[Ni_2(CNMe)_2(\mu\text{-}CNHMe)(\mu\text{-}dppm)_2][PF_6]_2$ (**83**[PF_6]$_2$)	3338	1525	-	-	1.854(8) 1.854(8)	1.30(2)	[94]
$[Fe_2Cp_2(CNMe)_2(\mu\text{-}CNHMe)_2][X]_2$ (**86a**[X]) [f]	3318	1593	-	3.52	-	-	[109b]
$[Fe_2Cp_2(CNEt)_2(\mu\text{-}CNHEt)_2][X]_2$ (**86b**[X]) [f]	3300	1580	-	3.77	-	-	[109b]
$[Fe_2Cp_2(CNMe)_3(\mu\text{-}CNHMe)]PF_6$ (**87**[PF_6])	3335	1568	-		-	-	[109b]
$[Fe_2Cp_2(CO)_3(\mu\text{-}CNH_2)]X$ (**89**[X]) [e]	2825	1582	328.1	12.3	1.862(3) 1.867(3)	1.279(4)	[207]
$[Os_3(CO)_9(NH_2{}^iPr)(\mu\text{:}\eta^1\text{:}\eta^1\text{-}CONH{}^iPr)(\mu\text{-}CNHPh)]$ (**92a**)	-	-	-	10.6 10.4	2.10(1) 1.99(1)	1.34(2)	[209]
$[Os_3(CO)_{10}(\mu\text{:}\eta^1\text{:}\eta^1\text{-}CONH{}^iPr)(\mu\text{-}CNHBn)]$ (**92b**)	-	-	-	9.26 9.11	2.13(3) 2.13(3)	1.26(4)	[210]
$[Os_3(CO)_{10}(\mu\text{-}CNHBn)(\mu\text{-}Cl)]$ (**93a**)	-	-	-	9.20	2.12(4) 2.10(3)	1.30(6)	[200]
$[Os_3(CO)_{10}(\mu\text{-}CNHBn)(\mu\text{:}\eta^1\text{-}SC_5H_4NO)]$ (**93b**)	-	-	-	11.4	2.09(2) 2.05(2)	1.30(2)	[213]
$[Os_3(CO)_{10}(\mu\text{-}CNHPh)(\mu\text{:}\eta^1\text{-}O_2CC{\equiv}CH)]$ (**93c**)	-	-	269.2	9.07	2.11(2) 2.09(2)	1.29(3)	[211]
$[Os_3(CO)_{10}(\mu\text{-}CNHPr)(\mu^2\text{:}\eta^1\text{:}\eta^1\text{-}$hydroxybenzotriazolate$)]$ (**93d**)	-	-	258.9	9.37	2.10(1) 2.08(1)	1.32(1)	[212]
$[Os_3(CO)_{10}(\mu\text{-}CNHBn)(\mu^2\text{:}\eta^1\text{:}\eta^1\text{-}$hydroxybenzotriazolate$)]$ (**93e**)	-	-	267.6	9.22	2.12(1) 2.08(1)	1.32(2)	[212]

[a] All $[M_2Cp_2(CO)_x]$ complexes are *cis*-, unless otherwise specified. Co-crystallized solvate molecules omitted from the formulae. [b] Solid-state or solution. [c] $CDCl_3$, CD_2Cl_2 or other common deuterated solvent. [d] Two or three independent molecules in the crystal structure. [e] X = Cl for X-ray and IR data, X = BF_4 for NMR data. [f] X = PF_6 for IR data, X = CCl_3CO_2 for NMR data. Abbreviation list: Cy = cyclohexyl C_6H_{10}, Xyl = 2,6-$C_6H_3Me_2$, Tol = 4-$C_6H_4CH_3$, dppm = $CH_2(PPh_2)_2$, dppe = $Ph_2PCH_2CH_2PPh_2$, dmpm = $CH_2(PMe_2)_2$, Cp* = C_5Me_5.

6. Special aminocarbyne ligands in polynuclear complexes

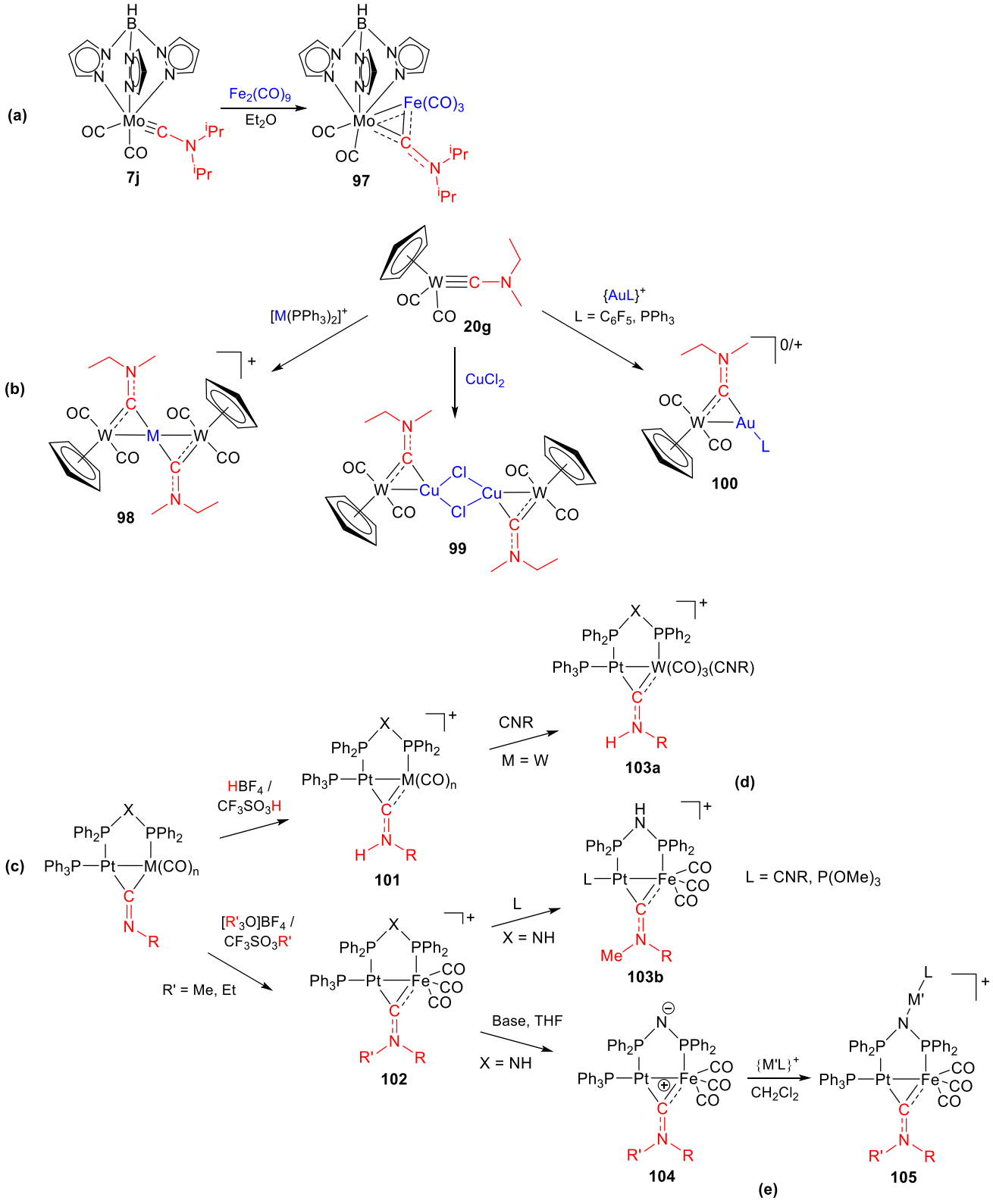
6.1. Bridging aminocarbynes in hetero-dimetallic complexes

Some aminocarbyne complexes based on two different metal elements have appeared in the literature, and these are useful to discuss bonding features, particularly when two rather different metal atoms are implicated, as in the case of early/late combination.

The reaction of a monometallic aminocarbyne complex with a second metal fragment gives a possible access to heterometallic aminocarbyne. In particular, [Mo(Tp){CN(^{i}Pr)$_2$}(CO)$_2$] (**7j**, Tp = trispyrazolylborate) and [Ru$_3$(CO)$_{10}$(μ-H)(μ$_2$-CNMe$_2$)] (**62c**) are convenient starting materials for coupling with iron carbonyls [Fe$_2$(CO)$_9$, Fe(CO)$_5$] to access [MoFe] and [Ru$_2$Fe] assemblies [195,226,227]. For instance, the reaction of **7j** with Fe$_2$(CO)$_9$ at room temperature affords the heterodinuclear [MoFe(Tp)(CO)$_5$(μ-CN^{i}Pr$_2$)] (**97**) in 70% yield (Scheme 41a).

Similarly, the reactions of [WCp{CNMe(Et)}(CO)$_2$] (**20g**) with group 11 metal fragments afford variable polymetallic structures (**98-100**) wherein each pair of metal atoms is bridged by the aminocarbyne unit (Scheme 41b) [228].

An alternative approach consists in the construction of the aminocarbyne moiety directly on a heterodimetallic scaffold. To this category also belongs 79c, presented above (Section 5.1). Moreover, [Fe-Pt] and [Mo-Pt] complexes of general formula [{Pt(PPh$_3$)}{M(CO)$_n$}(μ-CNXyl)(μ-dppm)] (M = Fe, n = 3; M = Mo, n = 4; Xyl = 2,6-C$_6$H$_3$Me$_2$), and their bis(diphenylphosphanyl)amine (dppa) analogues, undergo attack at the bridging isocyanide by alkylating agents [229,230,231] or Brønsted acids [229,230,232,233,234] to give the corresponding bridging aminocarbyne species **101-102** (Scheme 41c). Analogously to homodimetallic systems, the electrophilic addition is favored when a bridging coordination site is available for the isocyanide ligand. In contrast to CNXyl, CN^{t}Bu occupies a terminal position and is not alkylated even under forcing conditions [231]. The representative X-ray structures of [W-Au] (**100a**) and [Fe-Pt] (**102a**) complexes are depicted in Figure 17.



Scheme 41. Preparation of (a) [Mo-Fe], (b) [W-M] (M = group 11 metal) and (c) [Pt-M] [M = Fe, n = 3; M = Mo or W, n = 4; X = CH_2 (dppm) or NH (dppa)] heterometallic complexes with bridging aminocarbyne ligands (red). (e) Base = NEt_3, $K(OSiMe_3)$, KH; M'L = $AuPPh_3$, $CuAsPh_3$, HgMe.

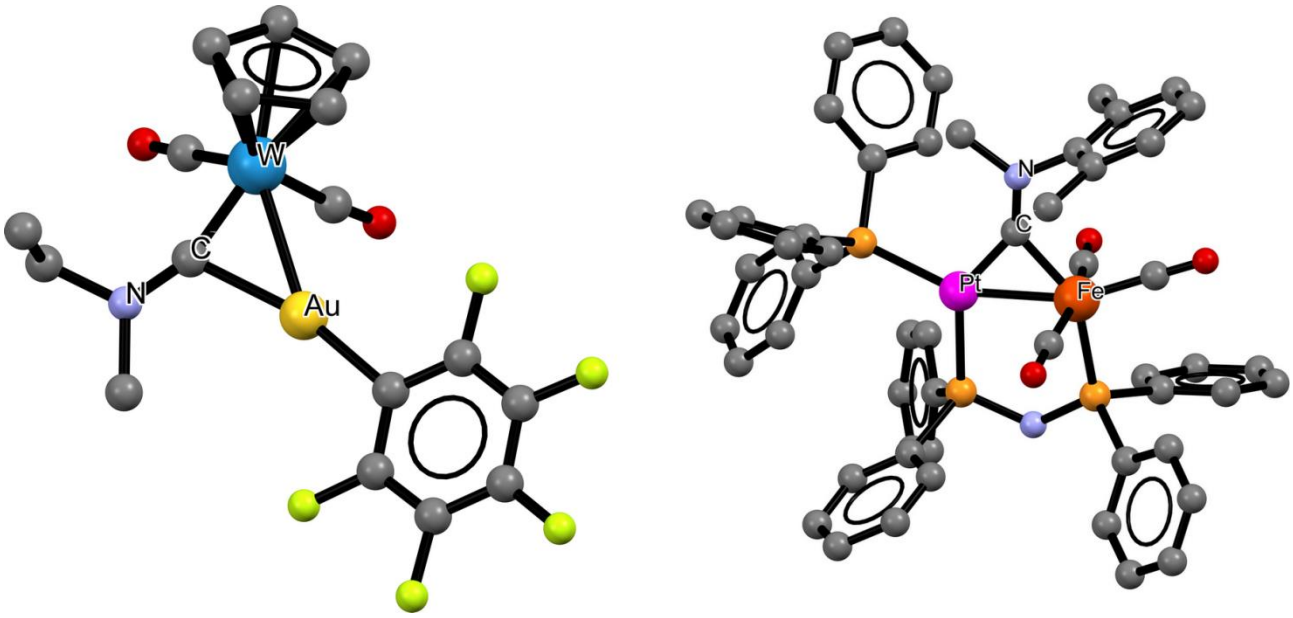


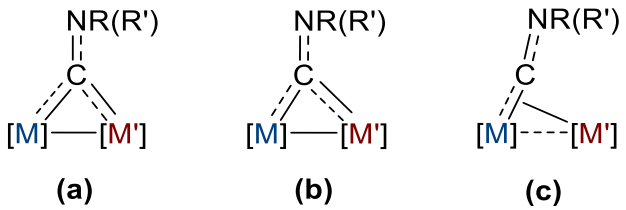
Figure 17. Views of the X-Ray structures of [{WCp(CO)$_2$}{AuPhF}{μ-CNMe(Et)}] (**100a**) [228] and [{Fe(CO)$_3$}{Pt(PPh$_3$)}{μ-CNMe(Xyl)}(μ-dppa)]$^+$ (**102a**, [BF$_4$]$^-$ salt) [230] H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): **100a**, W-carbyne 1.90(1), W-CO 1.95(1) and 1.96(1), Au-carbyne 2.13(2), carbyne-N 1.29(2), N-carbyne-W 160(1), N-carbyne-Au 115(1), carbyne-Au-C$_6$F$_5$ 162.9(6), W-Au-C$_6$F$_5$ 150.3(4); **102a**, Pt-carbyne 1.996(5), Fe-carbyne 1.918(4), carbyne-N 1.296(6), C-Pt-Fe 48.6(1), C-Fe-Pt 51.3(2).

Structural and spectroscopic data for heterometallic aminocarbyne complexes are in Table 6. X-ray and IR results confirm a substantial aminocarbyne/iminium hybridism, regardless of the metal/metal combination. Consequently, E/Z isomerism may be observed due to inhibited C-N bond rotation, unless the formation of one of the two isomers is sterically disfavored due to a bulky substituent on the nitrogen (e.g. Xyl) [230,231]. Secondary aminocarbyne ligands display the typical infrared N-H stretching at ca. 3300 cm^{-1} and the related ^{1}H NMR signal around 8-10 ppm (see Section 5.3) [229,230,232].

The coordination fashion of bridging aminocarbyne ligands in heterodimetallic complexes is affected by the different atomic size and properties of the two metal centers. Thus, in platinum-iron complexes **102-105** there is no bonding asymmetry (Scheme 42a), in that the M-C-N angles and M-C distances

are comparable (*ca* 140° and 1.93 ± 0.03 Å, respectively); this situation evidences a certain degree of π-backbonding from both the low-valent metals. It is remarkable that bonding asymmetry is instead rather common when the electron densities on the two metal atoms (even identical elements) are significantly different (Scheme 42b).

Conversely, in tungsten/group 11 metal complexes **98-100**, the bonding pattern is dramatically changed. The W-C bond is notably short [1.90(1) Å in **100a**], evidencing a considerable π-backdonation from the tungsten. Besides, the W-C-N unit approaches linearity [160(1)° in **100a**, 154.6(9) in **99a**]. Thus, from the perspective of the group 11 M^{+I} center, the connection with the aminocarbyne ligand is best viewed as a η^2 donation from the $W{=}CNR_2$ group, thus resembling the picture in classical η^2-alkene group 11 complexes (Scheme 42c) [228].



Scheme 42. Bonding modes for bridging aminocarbyne ligands on heterodimetallic scaffolds: (a) μ_2-η^1:η^1 symmetric; (b) μ_2-η^1:η^1 asymmetric; (c) η^1:η^2 alkene-like.

The peculiar nature of the aminocarbyne ligand in [W-M] complexes (M = Cu, Ag, Au) has deep consequences on the reactivity. Thus, addition of nucleophiles (L = CN^-, H^-, PR_3, NR_3) to **100a** proceeds with cleavage of the W-Au bond, leading to $[Au(C_6F_5)L]$ and regeneration of the precursor **20g** [228]. Conversely, [Fe-Pt] and [W-Pt] aminocarbyne complexes (**101**, **102**) react with Lewis bases while maintaining the dimetallic core, selectively affording carbonyl or triphenylphosphine substitution products **103a-b** (Scheme 41d) [231,232].

Interestingly, Brønsted bases deprotonate **102** at the bis-phosphine ligand to give **104** in 80-95% yields (Scheme 41e) and the resulting zwitterion **104** can be N-alkylated or N-metallated to give heterotrimetallic derivatives **105** [231].

Table 6. Spectroscopic and X-ray data related to bridging aminocarbyne ligands in heterometallic complexes.

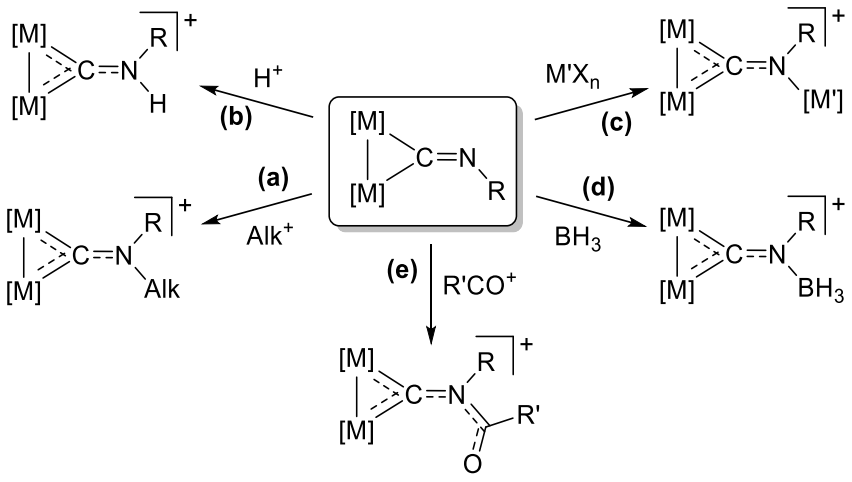
Compound [a]	IR [b]	^{13}C NMR [c]	X-Ray				Ref.
	ũ(CN) / cm^{-1}	δ(CN) / ppm	d(MC) / Å	d(CN) / Å	α(MCN) / °	α(MCM') / °	
[M{WCp(CO)$_2$(μ-CNEtMe)}$_2$]PF$_6$ (**98**[PF$_6$])	Cu:1563 Ag:1564 Au:1567	Cu:268.1 Ag:265.7 Au:266.9	-	-	-		[228]
[{WCp(CO)$_2$}$_2${CuCl}$_2${μ-CNMe(Et)}$_2$(μ-Cl)] (**99a**)	1555	263.4	W: 1.89(1) Cu: 2.01(1)	1.30(1)	Cu:120.6(9) W:155(1)	84.1(5)	[228]
[{WCp(CO)$_2$}{AuPh^F}{μ-CNMe(Et)}] (**100a**)	1555	259.6	W: 1.90(1) Au: 2.13(2)	1.29(2)	Au:115(1) W:160(1)	84.8(6)	[228]
[{M(CO)$_4$}{Pt(PPh$_3$)}(μ-dppa)(μ-CNHCH$_2$SO$_2$Tol)]BF$_4$ (**101**[BF$_4$])	Mo:1519 W:1515	Mo:321.9 W:318.5	-	-	-		[232]
[{Fe(CO)$_3$}{Pt(PPh$_3$)}(μ-dppm){μ-CNH(Xyl)}]BF$_4$ (**101a**[BF$_4$])	1527	313.7	-	-	-		[233]
[{Fe(CO)$_3$}{Pt(PPh$_3$)}(μ-dppa){μ-CNMe(Xyl)}]BF$_4$ (**102a**[BF$_4$])	1542	311.7	-	-	-		[230]
[{Fe(CO)$_3$}{Pt(PPh$_3$)}(μ-dppa){μ-CNMe(2-C$_6$H$_4$OMe)}]CF$_3$SO$_3$ (**102b**[CF$_3$SO$_3$])	1532	-	Pt: 1.923(5) Fe: 1.975(6)	1.263(7)	Pt:141.2(5) Fe:137.9(5)	80.9(2)	[230]
[{Fe(CO)$_3$}{Pt(PPh$_3$)}(μ-dppa){μ-CNMe(Bn)}]BF$_4$ (**102c**[BF$_4$])	1572	-	Pt: 1.99(2), Fe: 1.91(1)	1.33(2)	Pt:142(1) Fe:137(1)	80.5(5)	[231]
[{Fe(CO)$_3$}{Pt(PPh$_3$)}(μ-dppm){μ-CNMe(4-C$_6$H$_4$OMe)}]BF$_4$ (**102d**[BF$_4$])	1532	306.8	-	-	-		[233]
[{Fe(CO)$_2$(CNR*)}{Pt(PPh$_3$)}(μ-dppa){μ-CNMe(R*)}]BF$_4$ (**103a**[BF$_4$]) R* = 1,2-C$_6$H$_4$OCH$_2$CH$_2$	1528	315.7	-	-	-		[231]
[{Fe(CO)$_2$(CN^{t}Bu)}{Pt(PPh$_3$)}(μ-dppa){μ-CNMe(Xyl)}]BF$_4$ (**103b**[BF$_4$])	1539	-	Pt: 1.992(9) Fe:1.909(11)	1.27(1)	Fe:136.0(7) Pt: 144.2(7)	79.7(3)	[231]
[{W(CO)$_3$(CNXyl)}{Pt(PPh$_3$)}(μ-dppa)(μ-CNHCH$_2$SO$_2$Tol)]BF$_4$ (**103c**[BF$_4$])	1596	314.7	-	-	-		[232]
[{Fe(CO)$_3$}{Pt(PPh$_3$)}(μ-dppa-*H*){μ-CNMe(Xyl)}] (**104a**)	1538	312.0	Pt:1.996(5) Fe:1.918(4)	1.296(6)	Pt:144.3(3) Fe:135.7(3)	80.0(2)	[230]
[{Fe(CO)$_3$}{Pt(PPh$_3$)}(μ-dppa-*H* AuPPh$_3$){μ-CNMe(Xyl)}]CF$_3$SO$_3$ (**105a**[CF$_3$SO$_3$])	1544	-	Pt: 1.987(4) Fe: 1.929(4)	1.276(5)	Fe:136.8(3) Pt:143.7(3)	79.1(2)	[231]

[a] Co-crystallized solvate molecules omitted from the formulae. [b] Solid-state or solution. [c] $CDCl_3$, CD_2Cl_2 or other common deuterated solvent. Abbreviation list: Xyl = 2,6-C$_6$H$_3$Me$_2$, Tol = 4-C$_6$H$_4$Me, dppm = CH$_2$(PPh$_2$)$_2$, Ph^F = C$_6$F$_5$; dppa = Ph$_2$P(NH)PPh$_2$; dppa-*H* = Ph$_2$P(N)PPh$_2$.

6.2. N-acyl aminocarbynes

Lewis acids other than protonating and classical alkylating agents may react with isocyanide complexes to form aminocarbyne-like species. The addition to isocyanides of a range of metal dihalides and boranes yield, respectively, 'metallaaminocarbynes' and 'borataaminocarbynes', which might be viewed as bi- or tri-metallic units bridged by a κ*C,N* isocyanide moiety and will not be discussed further [112,113,235,236,237,238,239]. An overview of μ_2-aminocarbyne-like ligands derived from the possible isocyanide-Lewis acid combinations is given in Scheme 43.

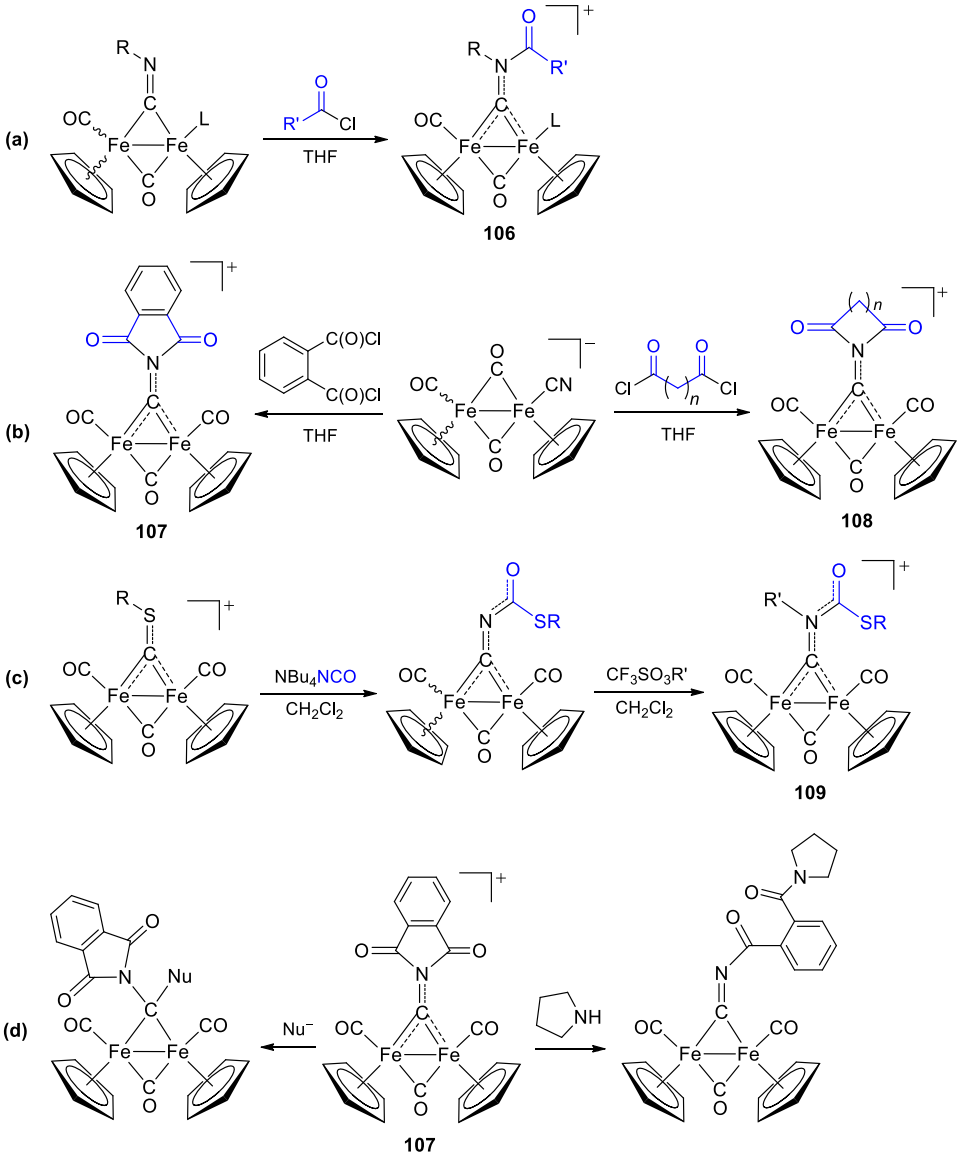
In this section, we will focus on *N*-acyl aminocarbynes (carboxamidocarbynes), and related species, which have been reported on the diiron bis-cyclopentadienyl scaffold. The introduction of the acyl function provides peculiar features in terms of synthetic procedures, reactivity and structural/spectroscopic characterization.



Scheme 43. Categories of electrophilic addition to isocyanide ligands in dimetallic complexes. (a) alkylation; (b) protonation; (c) metalation; (d) boration; (e) acylation.

The reactions of $[Fe_2Cp_2(CO)_2(L)(CNR)]$ (L = CO, CNR) with acetyl or benzoyl chlorides afford the respective N-monoacyl derivatives **106** (Scheme 44a) [240]. On the other hand, the addition of an excess of dicarboxylate acid dichlorides to the cyanide complex $[Fe_2Cp_2(CO)_3(CN)]^-$ produces N,N'-diacylated aminocarbynes (imidocarbynes) **107**-**108** in variable yields (Scheme 44b) [241]. A view of the structure of the phthalimido complex **107** is shown in Figure 18. N-thiocarboxamido derivatives

109 were obtained by Busetto et al. via a two-step synthesis, consisting in the initial insertion of the cyanate ion into the carbyne-S bond in diiron thiocarbyne complexes (yields 60-65%), followed by electrophilic addition (Scheme 44c) [242]. The alkylation works with alkyl triflates but not with methyl iodide, affording the products **109** in ca. 80% yield, while CF_3SO_3H protonation is less efficient (54%).



Scheme 44. Routes for the installation of N-acyl aminocarbyne ligands on the $\{Fe_2Cp_2(CO)_x\}$ scaffold: (a) isocyanide acylation (L = CO or CNR, R = Me, Et, Bn; R' = Me, Ph); (b) cyanide acylation (n = 2, succinimido; n = 3, glutarimido); (c) sequential cyanate insertion into carbyne-S bond and protonation/alkylation (R = Me, Et; R' = H, Me, Et). (d) Nucleophilic additions to diacylated

aminocarbyne: ring opening affording an isocyanide or alkylidene formation (Nu = CN^- from NaCN in DME or $[W(CN)(CO)_5]^-$ from NEt_4^+ salt in CH_2Cl_2).

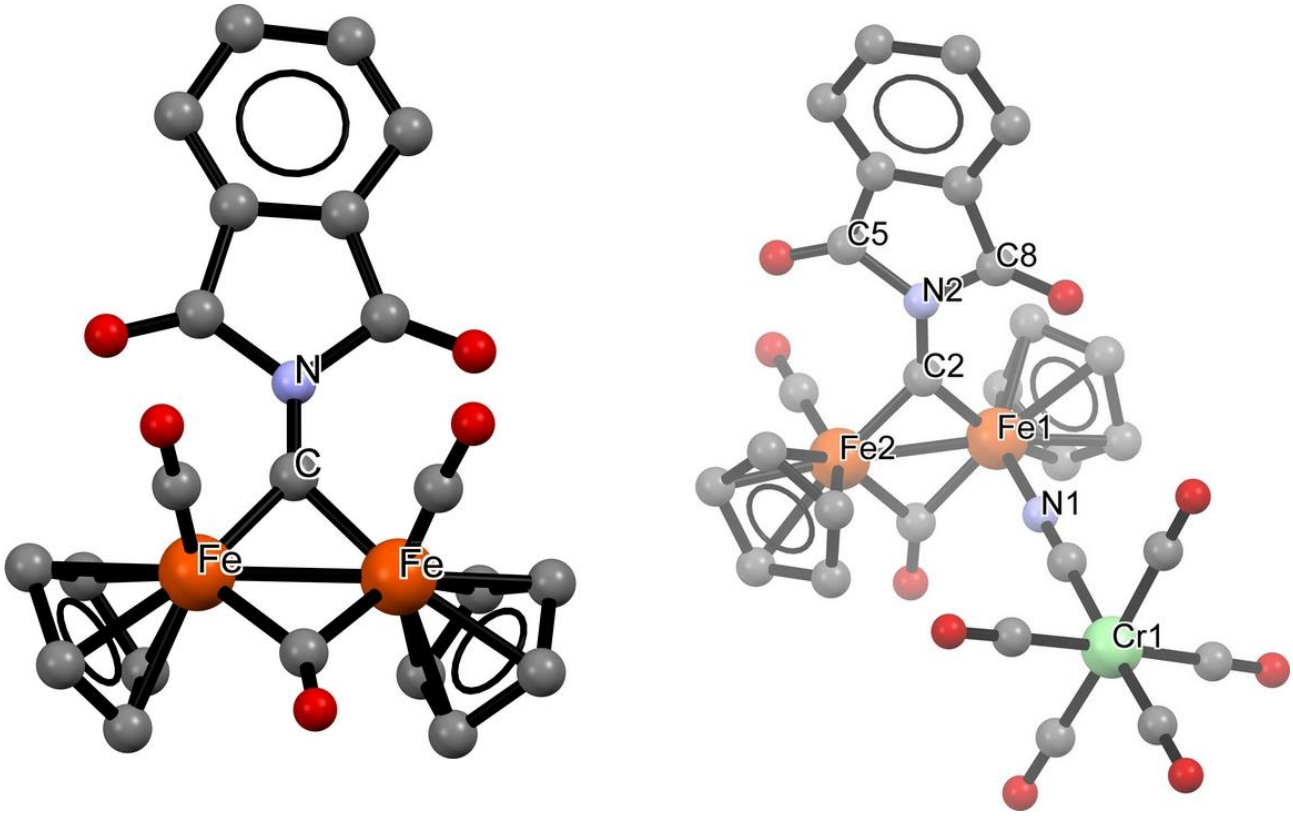
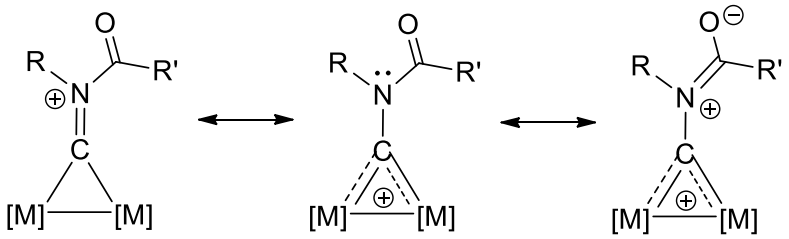


Figure 18. Views of the X-ray structures of $[Fe_2Cp_2(CO)_3(\mu\text{-C-phthalimido})]^+$ (**107** (PF_6^- salt) [241] and *trans*-$[Fe_2Cp_2(CO)_2(\mu\text{-C-phthalimido})\{NCCr(CO)_5\}]$ (**110**). H atoms omitted for clarity [243] Selected bond lengths (Å) and angles (°): **107**, Fe-carbyne 1.86(3), carbyne-N 1.31(4), Fe-μ-CO(av.) 1.98, Fe-CO(av.) 1.71, Fe-carbyne-Fe 85(1); **110**, Fe1-C2 1.80(1), Fe2-C2 1.86(1), C2-N2 1.37(1), N2-C5 1.45(2), N2-C8 1.45(2), Fe1-μ-CO 1.89(1), Fe2-μ-CO 1.93(2), Fe2-CO 1.77(1), Fe2-C2-Fe1 86.6(5).

Salient spectroscopic and structural data related to aminocarbyne complexes **106-109** are compiled in Table 7. With respect to classical aminocarbyne ligands, here the nitrogen lone pair has an additional possibility of π donation with the adjacent acyl group, resulting in an extensive electron charge delocalization (Scheme 45). This appears true especially for complexes **109** bearing the strong

electron-withdrawing {C(O)SR} substituent, whose IR spectra display a carbyne-N stretching band in the 1460-1490 cm^{-1} range, which is consistent with a limited π-overlapping [242].

The bonding pattern in the other cases is not so clear-cut. Compared to N,N-dialkyl aminocarbynes, the μ-C-N stretching band in the IR spectra of **106** falls within the typical range of wavenumbers (ca. 1590 cm^{-1}) [240]. The carbyne-N bond distance in **107** and **108** is only slightly elongated (1.31-1.37 Å) and N-C(O) are pure single bonds (1.45-1.47 Å), therefore it may be concluded that the two acyl groups do not cause a significant decrease of the carbyne-N bond order. On the other hand, the downfield shifted ^{13}C NMR resonances (340-360 ppm) in both **107** and **109** are in alignment with the deshielding provided by electron acceptor N-substituents on analogous systems (Section 3.3, Table 2) and highlight an enhanced carbyne character.



Scheme 45. Resonance structures for bridging N-acyl aminocarbyne ligands in dimetallic complexes.

In general, N-acyl aminocarbyne ligands in diiron complexes possess a superior electrophilic character compared to ordinary aminocarbynes. This can be explained on considering that, at the same time, the carbyne is slightly more electrophilic and the carbonyl group provides an additional site for nucleophilic attack. The regioselectivity is determined by the nature of nucleophile: thus, cyanide and hydride add to the carbyne carbon of **109** affording the corresponding alkylidenes, while methoxide reacts on the thiocarboxyl with regeneration of the isocyanide function (deacylation) [242]. For **107**, various nucleophilic additions have been reported to occur at either the acyl group (ring opening), the carbyne carbon (alkylidene formation) and iron (carbon monoxide substitution), Scheme 44d [241,243]. In particular, the reaction of **107** with the pentacarbonylcyanochromate anion allowed to insert a chromium center within the organometallic core (**110**), Equation 18. Although

obtained in a very low yield, **110** provides a useful structural comparison with **107** (Figure 18): the steric (cis to trans rearrangement of the Cp ligands) and electronic (strengthened iron to carbyne backbonding) effects consequent to the CO/chromate substitution are evident from the X-ray parameters.

$$[Fe_2Cp_2(CO)_3(\mu\text{-C-phthalimido})]PF_6 + NEt_4[Cr(CN)(CO)_5] \rightarrow [Fe_2Cp_2(CO)_2\{NCCr(CO)_5\}(\mu\text{-C-phthalimido})] + [NEt_4]PF_6 \quad (18)$$

107[PF_6] **110**

The enhanced reactivity of the diiron N-acyl aminocarbynes render them sensitive to moisture and to protic solvents, an aspect which is not encountered for related N,N-dialkyl derivatives (see Sections 3.2 and 3.4) [167]. Thus, the former compounds are often poorly stable in solution, undergoing degradation via multiple routes and causing difficulties in their manipulation [240,242]. For instance, **106** and the related CO/isocyanide mono-substituted adducts decompose rapidly in air and are unstable even in the solid state at −25 °C under N_2 atmosphere.

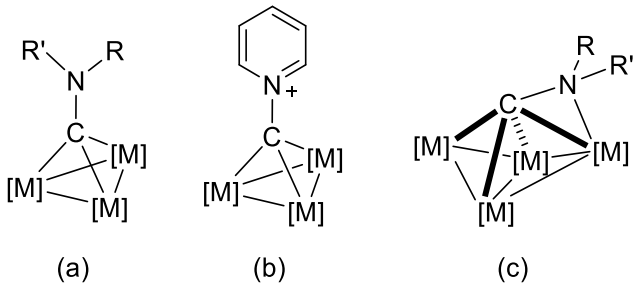
Table 7. Spectroscopic and X-ray data related to bridging *N*-acyl and *N*,*N*-diacyl aminocarbyne ligands.

Compound [a]	**IR** [b]	**^{13}C NMR** [c]	**X-ray**			**Ref.**
	ũ(CN) / cm^{-1}	**δ(CN) / ppm**	**d(MC) / Å**	**d(NC) / Å carbyne**	**d(NC) / Å carbonyl**	
$[Fe_2Cp_2(CO)_3\{\mu\text{-CN(Me)C(O)Ph}\}]Cl$ (**106a**[Cl])	1594	-	-	-	-	[240]
$[Fe_2Cp_2(CO)_3\{\mu\text{-CN(Et)C(O)Me}\}]Cl$ (**106b**[Cl])	1593	-	-	-	-	[240]
$[Fe_2Cp_2(CO)_3\{\mu\text{-CN(Bn)C(O)Ph}\}]Cl$ (**106c**[Cl])	1590	-	-	-	-	[240]
$[Fe_2Cp_2(CO)_3(\mu\text{-C-phthalimido})]PF_6$ (**107**[PF_6])	-	356.5	1.86(3)	1.31(4)	1.45(4)	[241]
$[Fe_2Cp_2(CO)_3(\mu\text{-C-glutarimido})]PF_6$ (**108a**[PF_6], n = 3)	-	-	1.87(1)	1.31(2)	1.47(2)	[241]
$[Fe_2Cp_2(CO)_3\{\mu\text{-CN(Me)C(O)SMe}\}]CF_3SO_3$ (**109a**[CF_3SO_3])	1460	343.4				[242]
trans-$[Fe_2Cp_2(CO)_2(\mu\text{-C-phthalimido})\{NCCr(CO)_5\}]$ (**110**)	-	-	1.80(1) 1.86(1)	1.37(1)	1.45(2) 1.45(2)	[243]

[a] All $Fe_2Cp_2(CO)_x$ complexes (M = Fe, Ru) show *cis*- arrangement of Cp ligands, unless otherwise stated. Co-crystallized solvate molecules omitted from the formulae. [b] Solid-state or solution. [c] $CDCl_3$, CD_2Cl_2 or other common deuterated solvent. Abbreviation list: Bn = $CH_2C_6H_5$, phthalimido = 1,2-$C_6H_4(CO)_2N$; glutarimido = $(CH_2)_3(CO)_2N$.

7. Multibridging aminocarbyne ligands

Triply-bridging aminocarbyne ligands with alkyl/aryl substituents possess a peculiar nature, and have been described on trimetallic (Scheme 46a) and, less frequently, tetrametallic complexes based on Cr, Fe, Co and Rh. An interesting type of μ_3-aminocarbyne ligand is found in a number of triosmium clusters, wherein the nitrogen atom belongs to a heterocyclic ring ("N-heterocyclic carbynes", Scheme 46b). Aminocarbyne ligands bridging four metal atoms (Scheme 46c) are significantly rarer and will be only briefly described.



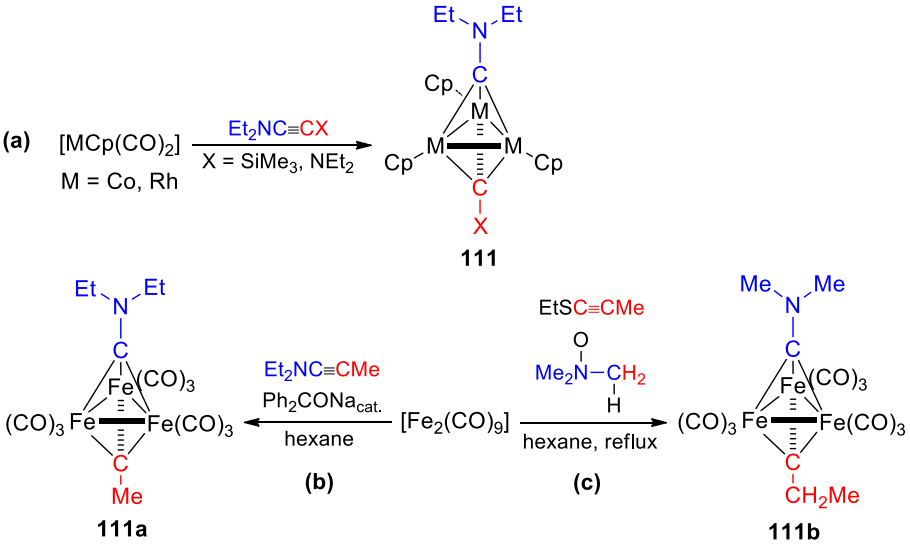
Scheme 46. Structures of tri- and tetrametallic complexes with multibridging aminocarbyne ligands.

7.1. Synthetic routes

Three different methods have been developed for the synthesis of μ_3/μ_4 aminocarbyne complexes: 1) thermal activation of small unsaturated molecules by suitable metal precursors; 2) electrophilic addition to isocyanide ligand; 3) growing/rearrangement of metal fragments containing μ_2-CNR_2 ligands. Except for the isocyanide protocol, these reactions are generally not selective and the final aminocarbyne complexes are isolated in low yields.

The first method involves the thermal activation of various nitrogen-organics by mono- and dimetallic carbonyl complexes, e.g. $Fe_2(CO)_9$, $Co_2(CO)_8$, $[MCp(CO)_2]$ (M = Co, Rh) and $[CrCp(CO)_3]_2$. Therefore, both the trimetallic core and the μ_3-CNRR' ligand are generated in one-pot fashion. Within this framework, aminoalkynes and related species ($R_2NC{\equiv}CX$; X = alkyl, SiR_3, NR_2; R = alkyl) are convenient precursors of two alkylidyne fragments upon C≡C bond cleavage (structure **111**, Scheme 47a,b and Figure 19) [119,162,244,245]. Quite often, cycloaddition products (η^4-cyclobutadiene / η^5-cyclopentadienone) are also formed under these conditions. A related fragmentation occurs

intermolecularly in the tetrairon clusters $[Fe_4(Cp')_4(C_2H_2)(XC{\equiv}CBr)]$ (X = H; Br), where the (di)bromoacetylene ligands are first transformed into a (di)aminoacetylene and then split into two μ_3-carbyne ligands upon monoelectronic oxidation [246,247]. Chloroformamidinium chloride ($[Me_2N{=}CHCl]Cl$) [248], coordinated thiocarboxamide (R_2NCS) [249] and Me_3NO [250] have also been employed as sources for the formation of μ_3-CNRR' ligands. In particular, the reaction of $Fe_2(CO)_9$ with an alkynyl-alkyl sulfide and trimethylamine-N-oxide was conducted at ca. 70 °C and yielded **111b** as a minor product along with diiron complexes (Scheme 47c). The unexpected formation of **111b** involves the unusual multiple C-H activation of a Me_3NO methyl group.



Scheme 47. Selected examples of thermal activation of small molecules by metal carbonyl complexes affording a triply bridging aminocarbyne (blue) and another carbyne ligand (red).

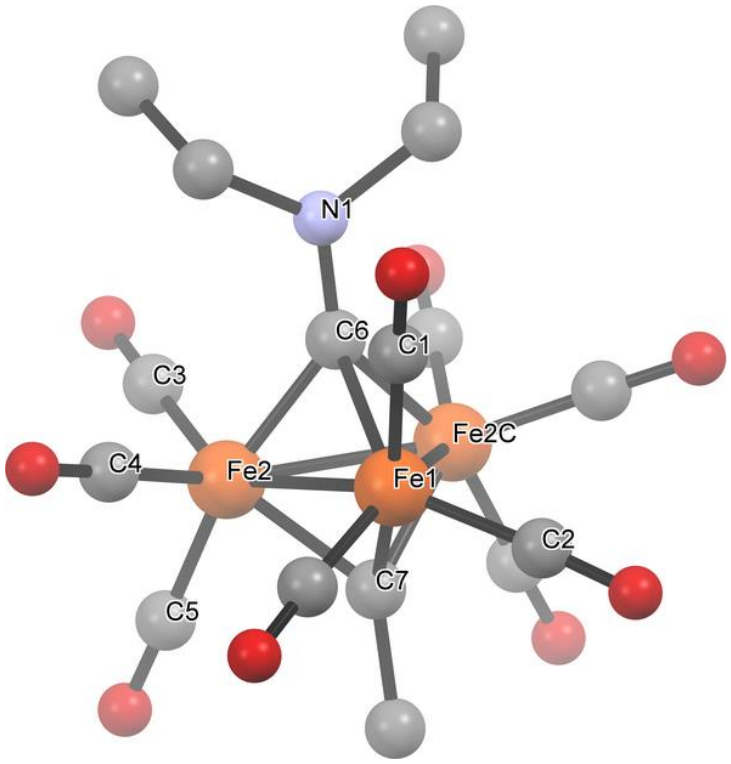
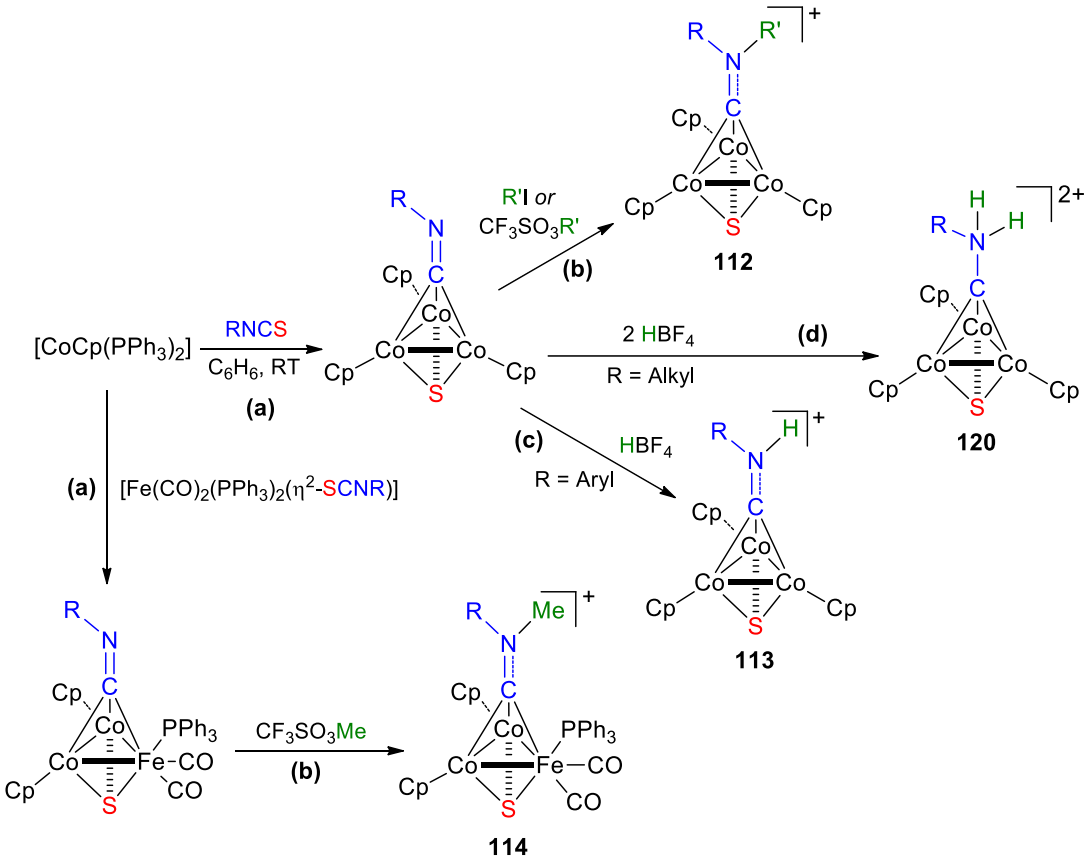


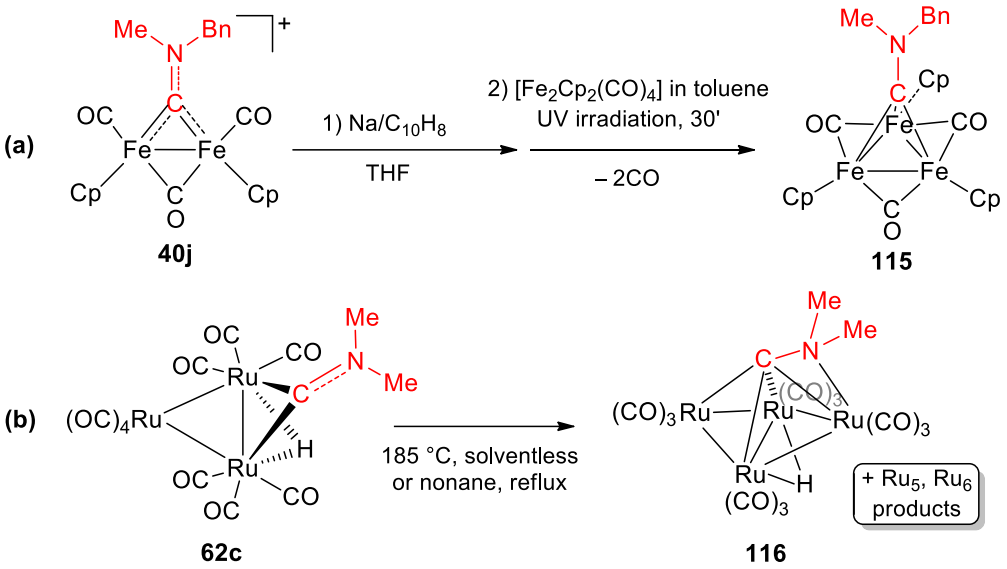
Figure 19. View of the X-ray structure of [$Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}CNEt_2)$] (**111a**) [244]. H atoms omitted for clarity. Selected bond lengths (Å): Fe1-C6 2.215(4), Fe2-C6 1.931(3), C6-N1 1.317(5), Fe1-C7 1.853(4), Fe2-C7 1.999(3), Fe2-C3 1.782, Fe2-C4 1.756, Fe2-C5 1.778, Fe1-C1 1.839, Fe1-C2 1.769.

The triply-bridging isocyanide complexes [$Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)$] and [$FeCo_2Cp_3(CO)_2(PPh_3)(\mu_3\text{-}S)(\mu_3\text{-}CNR)$] (R = alkyl or aryl) are obtained in good yields by C=S cleavage of isothiocyanates (Scheme 48a) [251,252]. Subsequent treatment with various alkylating/protonating agents affords the corresponding μ_3-aminocarbyne complexes **112** and **114** (Scheme 48b-c). Aliphatic isocyanides (CNMe, CNEt) are alkylated by relatively weak electrophiles such as methyl iodide, while aromatic isocyanides require the use of trifluoromethanesulfonates [251]. This feature is ascribable to the decrease of basicity induced by aryl substituents, associated to both electronic and steric reasons, which appears to be the dominant factor.



Scheme 48. Electrophilic additions at trinuclear μ_3-isocyanide complexes. R = Me, Et Ph, 4-C_6H_4Me, 2-C_6H_4Cl, 4-C_6H_4Br, 4-$C_6H_4CF_3$, 4-$C_6H_4NH_2$; R' = Me, Et).

A further synthetic approach relies on the elimination of a CO or NO ligand from μ_2-CNRR' aminocarbyne complexes by thermal or photolytic treatment, triggering the rearrangement of the metal scaffold and in particular a switch in the coordination mode of the aminocarbyne from μ_2 to μ_3 [117,214,253]. This is exemplified in Scheme 49a, where the nuclearity of the diiron complex **40j** is increased by reaction with $[Fe_2Cp_2(CO)_4]$ via a reduction/UV irradiation sequence, to give **115** in 5% yield. Pyrolysis of **62c**, either in the presence of $M(CO)_5$ (M = Fe, Ru) or not, provides mixtures of higher nuclearity products (Ru_3Fe, Ru_4, Ru_5, Ru_6, Ru_7), some of them featuring a tetracoordinated μ_4:η^2-aminocarbyne ligand (**116**, Scheme 49b) [254,255,256]. In the X-ray structure of **116** (Figure 20), the $\{CNR_2\}$ fragment is lying in the fold of a M_4 butterfly unit.



Scheme 49. Triply (a) and quadruply (b) bridging aminocarbyne ligands obtained by rearrangement of polymetallic structures.

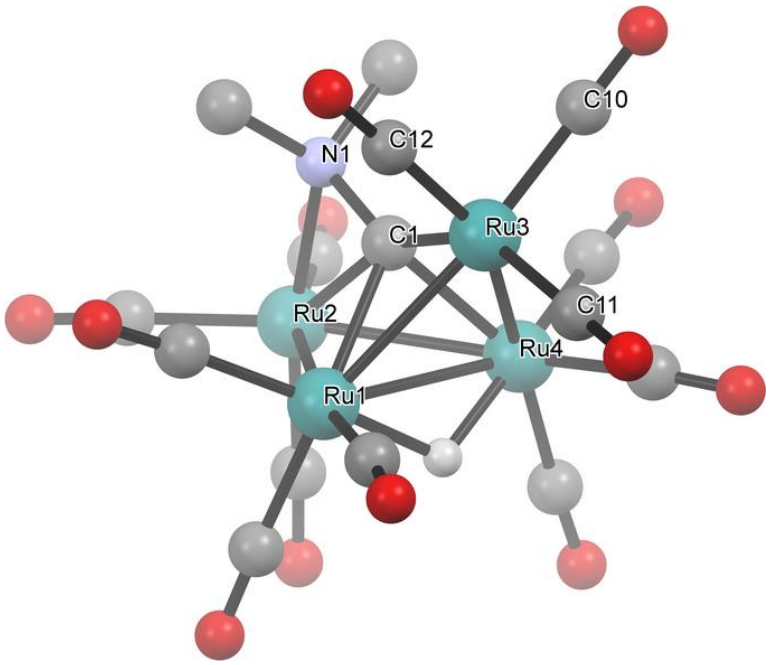
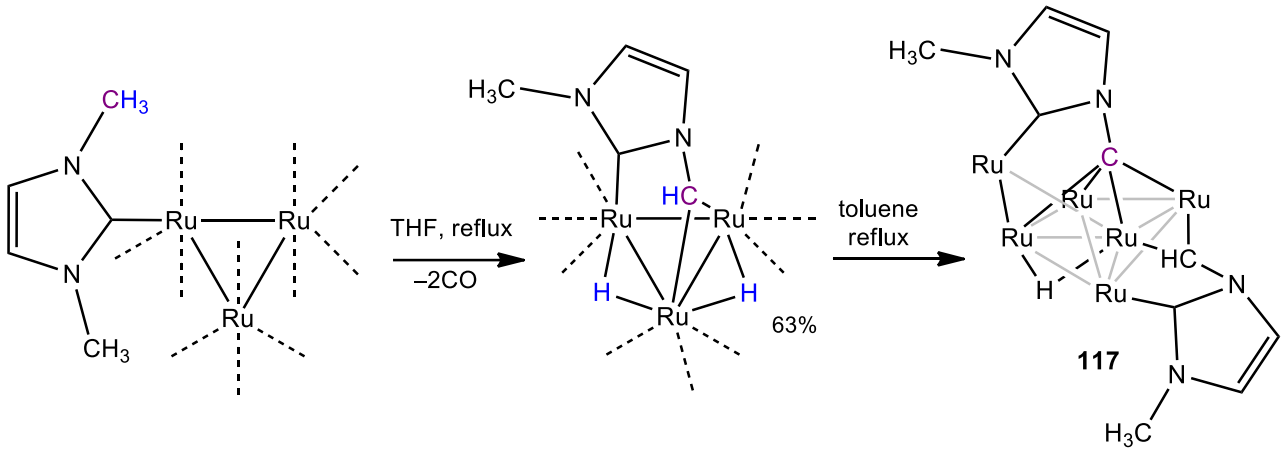


Figure 20. View of the X-ray structure of. H atoms (except Ru-H) omitted for clarity. Selected bond lengths (Å) and angles: Ru1-C1 2.161 (5), Ru2-C1 2.316 (5), Ru3-C1 1.964 (5), Ru4-C1 2.146 (5), C1-N1 1.434 (6), Ru2-N1 2.149 (4), Ru3-C10 1.883, Ru3-C11 2.002, Ru3-C12 1.875, Ru4-C1-N1 125.5(3), Ru2-C1-N1 65.1(2), Ru2-N1-C1 77.7(2) [254].

The only other case of quadruply bridging aminocarbyne ligand was obtained from $[Ru_3(NHC)(CO)_{11}]$ (NHC = 1,3-dimethylimidazol-2-ylidene) via the stepwise oxidative additions of the three C-H bonds belonging to one N-methyl substituent of NHC [257]. The first two additions produce an alkylidene intermediate, then heating in toluene at reflux temperature leads to a mixture of penta- and hexa-ruthenium species, comprising respectively an interstitial carbide (μ_5-C) and an unusual μ_4-aminocarbyne capping a square of metal atoms (**117**, Scheme 50).

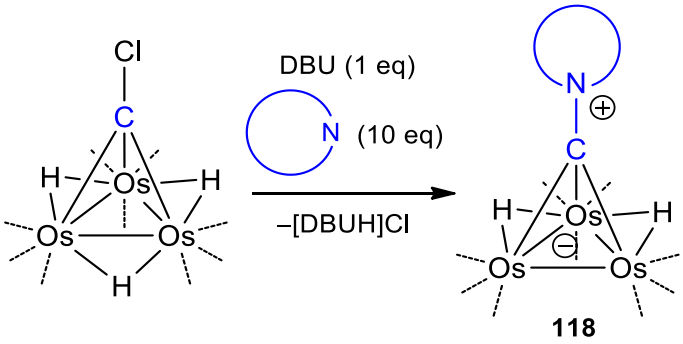


Scheme 50. Formation of Ru_6-μ_4-aminocarbyne structure via sequential activation of a methyl-substituted NHC ligand (spectator CO ligands represented as dotted lines).

"N-heterocyclic" carbynes (**118**, Scheme 51) are accessible from the triosmium chlorocarbyne $[Os_3(CO)_9(\mu\text{-}H)_3(\mu^3\text{-}CCl)]$ upon reaction with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), in the presence of an excess of the selected N-heterocyclic compound [258]. It is assumed that DBU abstracts a hydride ligand, and subsequent chloride elimination generates a highly reactive "carbenium" intermediate, $[Os_3(CO)_9(\mu\text{-}H)_2(\mu^3\text{-}C)]$, undergoing nucleophilic addition by the N-donor [258]. The reaction is rather general concerning the nature of the N-heterocyclic nucleophile: various substituted pyridines, (iso)quinolines, 2,2'- and 4,4'-bipyridines, and even DBU itself (in the absence of competing N-donors) have been successfully employed [258,259,260,261,262]. The introduction of functionalized pyridines enables a fine regulation of the optical properties of the resulting extended π-systems, as well as to incorporate a further metal fragment [263,264,265,266]. An analogous

product obtained from the isostructural ruthenium chlorocarbyne $[Ru_3(CO)_9(\mu\text{-}H)_3(\mu^3\text{-}CCl)]$ has been also reported [267]. Note that a first example of this kind of reaction was claimed in an early report on the reactivity of tricobalt halocarbynes: treatment of $[Co_3(\mu_3\text{-}CBr)(CO)_9]$ with pyrrole and triethylamine gave a product interpreted as a N-pyrrole μ_3-carbyne [268].

A view of the X-ray structure of the vinyl-pyridine derivative **118a** is shown in Figure 21.



Scheme 51. General synthesis of Os_3 carbonyl clusters with triply bridging N-heterocyclic carbyne ligands from chlorocarbyne and N-heterocyclic donors (spectator CO ligands as dotted lines).

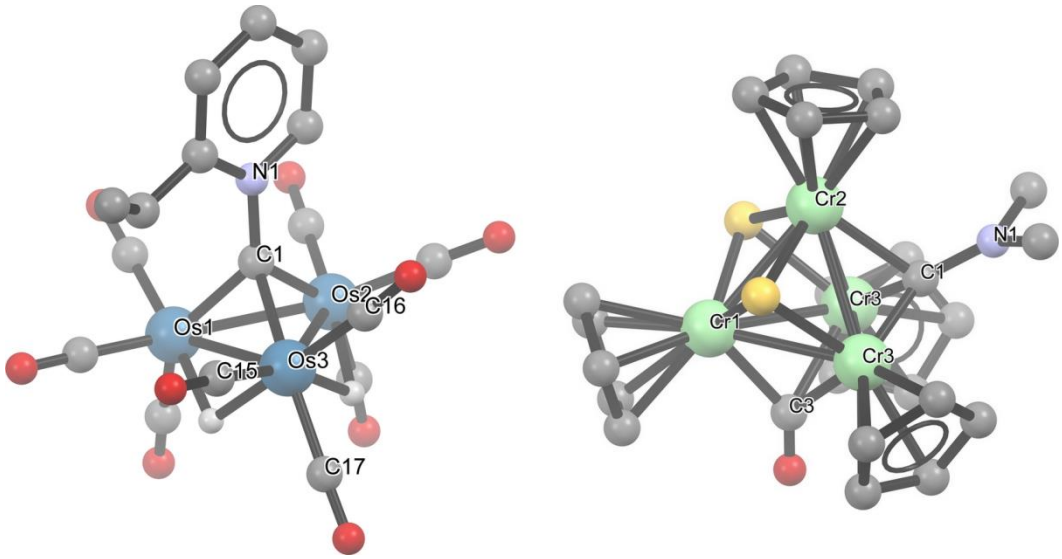


Figure 21. Views of the X-ray structures of $[Os_3(CO)_9(\mu\text{-}H)_2\{\mu\text{-}C(2\text{-}NC_5H_4CH{=}CH_2)\}]$ (**118a**) [259] and $[Cr_4Cp_4(\mu_3\text{-}S)_2(\mu_3\text{-}CNMe_2)(\mu_3\text{-}CO)]$ (**119**) [79]. H atoms (except Os-H) omitted for clarity. Selected bond lengths (Å) and angles as follows. **118a**: Os1-C1 2.12(1), Os2-C1 2.10(2), Os3-C1 2.12(1), C1-N1 1.49(2), Os3-C15 1.857, Os3-C16 1.887, Os3-C17 1.913, Os3-C1-N1 128.0(8), Os2-C1-N1 126.3(7). **119**: Cr3-C1 1.962(7), Cr3-C3 2.209(9), Cr1-C3 2.020(13), C1-N1 1.365(14).

7.2. Bonding description, characterization and reactivity

In triply bridging aminocarbyne ligands, crystallographic and spectroscopic data evidence a C-N bond order usually higher than one (Table 8). In Fe_3 (**111**, **115**) and Cr_4 clusters, an elongated carbyne-N bond length is observed (1.32-1.37 Å) but yet far from a pure single bond (1.46 Å). Note that some cases of isomerism due to hindered rotation around the C-N axis have been reported [245,253]. Interestingly, the typical bonding of the aminocarbyne ligand with respect to the M_3 triangle is dissymmetric. For instance, both $[Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}\mathbf{C^*}NEt_2)]$ (**111a**) and $[Cr_4Cp_4(\mu_3\text{-}S)_2(\mu_3\text{-}\mathbf{C^*}NMe_2)(\mu_3\text{-}CO)]$ (**119**, a view of the X-ray structure is given in Figure 21) display two shorter (1.96 Å) and one longer (2.21 Å) metal-C* bonds. Complex $[Fe_3(CO)_9(\mu_3\text{-}CEt)(\mu_3\text{-}\mathbf{C^*}NMe_2)]$ (**111b**), exhibits the opposite situation (2.02, 2.06, 1.90 Å). All distances are considerably longer than M-C bonds in related doubly-bridging aminocarbyne ligands (Table 2), where a significant metal-to-ligand π-backbonding is present. In the literature, there is no detailed description for the bonding of triply bridging aminocarbyne ligands. However, an interesting explanation can be drawn by looking at the bonding analysis of the related alkylidyne ligand in the tricobalt cluster $[Co_3(CO)_9(\mu_3\text{-}CCH_3)]$ as proposed by Chisholm [269]. According to X-ray and theoretical studies, the carbyne is viewed as *sp* hybridized, thus the three bonds with the metal atoms are formed employing one *sp* orbital and two *p* orbitals, but the combinations of the two *p* orbitals and metal orbitals are not symmetric with respect to the M_3 triangle. Therefore we might assume that, when an amino substituent is placed on the carbyne, coordination asymmetry arises since one of the two carbyne *p* orbitals is involved in π-bonding with the nitrogen atom.

In this respect, a rather wide range of CN stretching wavenumbers has been reported (1640-1300 cm^{-1}). In particular, compounds $[Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CNRR')]^+$ (**112**) are very sensitive to the nature of the N-substituents, showing a CN band around 1500 cm^{-1} with alkyl groups, moving down to 1300 cm^{-1} with electron-withdrawing aryl groups [251].

In tricobalt μ_3-CNRR' complexes, the lower participation of the nitrogen in π-bonding with the carbyne is probably responsible for the increase in the nitrogen basicity, and in complexes **112** the nitrogen atom is susceptible to protonation to give ammonium-carbyne ligands μ^3-CNH(R)(R') [248,251]. With aliphatic substituents, the nitrogen basicity is so pronounced that the ammonium-carbyne is directly obtained by double protonation of the isocyanide in $[Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$, skipping the intermediate aminocarbyne step (structure **120**, Scheme 48d). The ammonium-carbynes in **120** closely resemble a classical alkylidyne ligand, showing a ^{13}C NMR signal around 240-260 ppm, to be compared with 290 ppm for related Co_3 alkylidynes [270]. Moreover, complexes **120** display a C-N stretching band around 1400 cm^{-1} and the equivalence of identical nitrogen substituents in the ^1H NMR spectra down to − 50° C, as expected for a C-N single bond.

In triply bridging N-heterocyclic carbynes, the nitrogen lone pair is fully integrated in the π aromatic system, thus the carbyne-N interaction is essentially a single bond (1.46 ± 0.02 Å). The three Os-C bonds are close to each other and similar (2.10 ± 0.02 Å) to those found in μ_2-aminocarbyne complexes (Table 3; 2.09 ± 0.04 Å). Therefore, the best bonding description for these systems is a zwitterionic structure, with the positive charge distributed over the aromatic ring and the negative charge on the $Os_3\{\mu_3\text{-}C\}$ fragment [258]. This is reflected in an unusually shielded ^{13}C NMR resonance for the carbyne carbon (*ca*. 30 ppm for $[Os_3(CO)_9(\mu\text{-}H)_2\{\mu\text{-}C(4\text{-}NC_5H_4CH{=}CH_2)\}]$, **118b** [260]), which is very far from the situation in related μ_3-alkylidyne triosmium compounds (*e.g.* 154 ppm for $[Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CMe)]$ and 252.5 ppm for $[Os_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}CCOMe)]$) [271,272]. As a matter of fact, examples of C-N bond cleavage have been reported, causing either the detachment of the N-heterocyclic group via carbyne-alkyne coupling [273] or loss of the carbyne center as a $\{CH_2\}$ fragment [274].

In μ_4:η_2-quadruply bridging aminocarbyne ligands, three short (2.03-2.16 Å) and one long M-C (2.26-2.33 Å) connections can be found, the latter corresponding to the nitrogen-bonded metal atom. When the μ_4-aminocarbyne caps a M_4 square, all four bonds are equal and midway (2.13-2.19 Å) with

respect to the previous case. In all quadruply bridging systems, the C-N interaction is essentially a single bond (≈ 1.44 Å).

Table 8. Spectroscopic and X-ray data related to multibridging aminocarbyne ligands.

Compound	IR [a]	^{13}C NMR [b]	X-Ray		Ref.
	ũ(CN) / cm^{-1}	δ(CN) / ppm	d(MC) / Å	d(CN) / Å	
[$Fe_3(CO)_9(\mu_3$-CMe)(μ_3-CNEt_2)] (**111a**)	-	-	2.215(4), 1.931(3), 1.931(3)	1.317(5)	[244]
[$Fe_3(CO)_9(\mu_3$-CEt)(μ_3-CNMe_2)] (**111b**)	-	-	2.019(3), 2.055(3), 1.895(3)	1.329(4)	[250]
[$Co_3Cp_3(\mu_3$-S)(μ_3-CNMe_2)]I (**112a**[I])	1506	-	-	-	[251]
[$Co_3Cp_3(\mu_3$-S){μ_3-CNMe(Ph)}]I (**112b**[I])	1325	-	-	-	[251]
[$Co_3Cp_3(\mu_3$-S)(μ_3-CNHMe)]BF_4 (**112b**[BF_4])	1494	-	-	-	[251]
[$Fe_3Cp_3(CO)_3${μ_3-CNMe(Bn)}] (**115**)	1640	-	-	-	[253]
[$Ru_4(CO)_{12}(\mu_2$-H)(μ_4:η^2-CNMe_2)] (**116**)	-	-	2.161(5), 2.316(5), 1.964(5), 2.146(5)	1.434(6)	[254]
[$Ru_6(CO)_{15}(\mu_3$-H){MeIm(μ_4-C)} {MeIm(μ_2-CH)}] (**117**)	-	-	2.161(7), 2.127(7), 2.186(7) 2.185(8)	1.45(1)	[257]
[$Os_3(CO)_9(\mu$-H)$_2${μ_3-C(2-$NC_5H_4CH{=}CH_2$)}] (**118a**)	-	-	2.12(1), 2.12(1), 2.10(2)	1.49(2)	[259]
[$Os_3(CO)_9(\mu$-H)$_2${μ_3-CN(4-$NC_5H_4CH{=}CH_2$)}] (**118b**)	-	30.1	2.09(2), 2.10(2), 2.06(2)	1.48(3)	[260]
[$Ru_3(CO)_9(\mu$-H)$_2${μ_3-C(NC_5H_5)}] (**118c**)	-	-	2.06(8), 2.08(1), 2.06 (2)	1.46(1)	[267]
[$Os_3(CO)_9(\mu$-H)$_2${μ_3-CN(*DBU*)}] (**118d**)	-	-	2.12(2), 2.14(2), 2.14(2)	1.44(2)	[258]
[$Os_3(CO)_9(\mu$-H)$_2${μ_3-C(quinuclidine)}] (**118e**)	-	-	2.16(2), 2.13(2), 2.11(2)	1.44(3)	[258]
[$Os_3(CO)_9(\mu$-H)$_2${μ_3-C(4,4'-bpy)}] (**118f**)	-	-	2.08(2), 2.07(2), 2.07(2)	1.48(2)	[261]
[$Os_3(CO)_9(\mu$-H)$_2${μ_3-C(2,4'-bpy)}] (**118g**) [c]	-	-	2.12(2), 2.06(1), 2.09(1) / 2.08(1), 2.07(1), 2.07(2)	1.47(2) 1.48(2)	[261]
[$Os_3(CO)_9(\mu$-H)$_3${μ_3-C(4,4'-bpyH)}][BF_4]$_2$ (**118h**[BF_4]$_2$)	-	-	2.10(1), 2.10(2), 2.09(2)	1.44(2)	[262]
[$Cr_4Cp_4(\mu_3$-S)$_2$(μ_3-CNMe_2)(μ_3-CO)] (**119**)	1567	-	2.212(1), 1.962(7), 1.962(7)	1.37(1)	[79]
[M_3Cp_3{μ_3-CNMe(Et)}$_2$]	1446?	321 (Co) 281 (Rh)	-	-	[245]
[$Ru_5(CO)_{13}(\mu_2$-CNMe_2)(μ_4:η^2-CNMe_2)]	-	-	2.012(6), 2.107(6), 2.114(6), 2.289(6)	1.435(7)	[254]
[$Ru_5(CO)_{12}(PMe_2Ph)(\mu$-H)($\mu_4$:η^2-CN$Me_2$)]	-	-	2.12(1), 2.26(1), 2.03(1), 2.12(1)	1.43(1)	[255]

[a] Solid-state or solution. [b] $CDCl_3$, CD_2Cl_2 or other common deuterated solvent. [c] Two independent molecules in the crystal._Abbreviation list: DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene, bpy = bipyridine, Bn = $CH_2C_6H_5$, Me_2Im = 1,3-dimethylimidazol-2-ylidene.

Concluding remarks

Aminocarbynes represent a sub-class of carbyne ligands, wherein the amino-substituent provides a unique behavior which does not find equivalence in other hetero-substituted carbyne species. Following pioneeristic studies on group 6 monometallic compounds in the last century, many aminocarbyne complexes with different nuclearity and based on early to late transition metals (usually low valent) have been reported. They are accessible via a variety of synthetic routes, and exhibit in general a moderate reactivity compared to classical alkylidyne species. Nevertheless, the amino group and its potential variability offers the opportunity for a versatile chemistry that has been developed especially on some metal frameworks, leaving the space for a further significant advance in the next future. An accurate choice of nitrogen substituents provides a control of steric and electronic factors which, especially in diiron/diruthenium bis-cyclopentadienyl complexes, address regio- and stereoselective addition reactions leading to functionalized organic fragments. Although in their infancy, diiron cyclopentadienyl μ-aminocarbyne complexes represent a promising tool in view of their potential medicinal and catalytic applications.

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References

[1] According to IUPAC rules, metal compounds containing a carbyne ligand are named "alkylidyne" complexes regardless of the nature of both the carbyne substituents and the metal fragment. See: F. R. KreiBl in “Transition Metal Carbyne Complexes”, Ed. Springer (1993). On considering that the term “aminocarbyne”, rather than “aminoalkylidyne”, is largely used in the literature, the former will be generally adopted in this review.

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