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Reactions of transition metal-coordinated nitriles

Rino A. Michelin *, Mirto Mozzon, Roberta Bertani

Istituto di Chimica Industriale and Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., Facoltà di Ingegneria, Università di Padova, Via F. Marzolo 9, 35131 Padova, Italy

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* Corresponding author.

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Abstract

The reaction chemistry of nitriles, R—C≡N, where R is usually an organyl group, with transition metal complexes is reviewed. The review surveys data published during the period 1977–early 1994 on new reaction processes such as insertion into metal–hydrogen and –carbon bonds, coupling between one nitrile and an unsaturated metal fragment or between two nitriles, reduction to amines, attack by protic and aprotic nucleophiles and electrophilic attack as well as some catalytic transformations, which result from the ability of nitriles to coordinate to transition metal centres with a consequent change in the electrophilicity or nucleophilicity of the coordinated ligand.

Keywords: Nitriles: transition metal complexes

List of abbreviations

acac	acetylacetonate
bipy	2,2′-bipyridine
Cp	cyclopentadienide, η^5-C_5H_5
Cp*	pentamethylcyclopentadienide, η^5-C_5Me_5
Cp′	methyl- or ethylcyclopentadienide, η^5-C_5H_4R (R = Me, Et)
DIPP	2,6-diisopropylphenoxide
dmpe	1,2-bis(dimethylphosphino)ethane
DMSO	dimethyl sulphoxide
dppb	1,4-bis(diphenylphosphino)butane
dppbe	1,2-bis(diphenylphosphino)benzene
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
enolate	2-oxoalkyl, CH_2COR (R = OEt, Me, Ph)
ind	indenyl
mes	mesityl, 2,4,6-$Me_3C_6H_2$
py	pyridine
tedip	(tetraethyl)diphosphite, $(EtO)_2POP(OEt)_2$
THF	tetrahydrofuran
Tp′	hydridotris(3,5-dimethylpyrazolyl)borate

1. Introduction

Nitriles, R—C≡N, which are isolectronic with other unsaturated ligands such as dinitrogen, carbon monoxide, isocyanides and alkynes, are extensively used for the preparation of transition metal complexes from which, owing to their weak σ donor and π acceptor ability, they can be readily displaced to afford novel coordination and organometallic complexes. Reviews on structures, spectroscopic properties and some aspects of the reactions of transition metal coordinated nitriles have appeared [1].

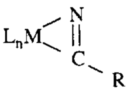
The principal aim of this review, with the exception of a brief report on some unusual coordination modes of nitriles, is to survey most of the literature from 1977 onwards on those reactions of nitriles in transition metal complexes which lead to their conversion into other organic ligands as a consequence of chemical processes such as insertion, coupling, and nucleophilic or electrophilic attack; references to papers which have been already reported in the earlier reviews are kept to a minimum, but are given each time they are required. A special emphasis will be given on some stoichiometric and catalytic transformations of these ligands since they have been recognized as convenient substrates in the synthesis of organic compounds as well as, when appropriate, on some mechanistic aspects of these reactions. On the contrary, processes which do not involve modification of the carbon–nitrogen triple bond such as novel synthetic routes to coordinated nitrile complexes and their displacement reactions or their use in different fields of application and research such as catalysis, photoluminescence and enzymatic transformations, although an active and interesting field of research, are in general beyond the scope of this review. Gas phase reactions [2] of organonitriles and the coordination chemistry of unsaturated polynitriles [3] also will not be covered.

2. π and σ,π modes of coordination of nitriles

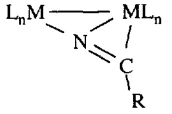
Nitriles can interact with metal centers in several different ways, i.e. as (i) terminal (end-on) σ-bonded, η^1-NCR, (ii) π-bonded (side-on), η^2-NCR or (iii) bridging σ,π-bonded, μ-η^1,η^2-NCR:

$L_nM \leftarrow :N \equiv C-R$

σ-bonding, η^1-NCR



π-bonding, η^2-NCR



σ,π-bonding, μ-η^1,η^2-NCR

Type (i) is the more common mode of nitrile coordination, which occurs by σ bonding through the nitrogen lone pair; although η^1-coordination is often accompanied by an increase in ν-(C≡N), in several transition metal nitrile complexes the ν(C≡N) values have been found to remain virtually unchanged or even are at lower frequencies (20–100 cm^{-1}) than those observed for the corresponding free nitriles and this has been ascribed to significant "back bonding" between the metal *d* orbitals and the π* orbitals of the nitriles in these compounds. On the contrary, η^2 coordination is rather uncommon and it is generally accompanied by a large decrease in the C≡N stretching frequency (up to ≈500 cm^{-1}). Among the complexes that exhibit type (ii) coordination there are the metallocene nitrile complexes [$MCp_2(\eta^2$-NCMe)] (M = Mo [4a], M = W [4b]) and the diphosphino complex [MoCl(η^2-NCMe)(dmpe)$_2$][BPh$_4$] [5]. The Mo derivatives represent the first structurally characterized η^2-nitrile complexes, but recently cationic and neutral side-on nitrile complexes of the type [WCl(bipy)(PMe$_3$)$_2$(η^2-NCCH$_3$)][PF$_6$] [6a] and [WCl$_2$(PMe$_3$)$_3$(η^2-NCCH$_3$)] [6] respectively have been also structurally characterized. The formation and structural characterization of η^2 side-bonded aryl nitrile complexes of iridium of the type $[IrCp(PPh_3)(\eta^2\text{-}NCAr)]$ and $[IrCp^*(CO)(\eta^2\text{-}NCAr)]$ (Ar = p-ClC_6H_4) [7], derived on thermolysis of 4-metallaisoxazolin-5-one metallacycles $[Ir\{C(Ar){=}NOC({=}O)\}Cp(PPh_3)]$ and $[Ir\{C(Ar){=}NOC({=}O)\}\text{-}Cp^*(CO)]$ respectively have been also reported. Structural data for η^2-nitrile complexes show that the M—N and M—C bond distances are almost similar ranging from 2.01 to 2.22 Å; the N—C bond distance is found in the range 1.22–1.27 Å, typical of a double bond, and the N—C—C nitrile angle in the range 128°–141°, indicating substantial sp^2 character in the ligand.

The σ,π coordination (type (iii)) is also uncommon and is encountered on interaction of a nitrile with di- or polynuclear systems. The X-ray structures of $[Mn_2(\mu\text{-}\eta^1,\eta^2\text{-}NCMe)(CO)_6(\mu\text{-}dppm)]$ [8] and $[Zr_2Cl_6(py)_3(\mu\text{-}\eta^1,\eta^2\text{-}NC\text{-}t\text{-}Bu)]$ [9] show that the nitrile ligand is σ coordinated via the nitrogen atom to one metal centre and π coordinated to the other. Related examples are constituted by dimolybdenum compounds $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^1,\eta^2\text{-}NCNR_2)]$ (M≡M) (R = H, Me) [10] and $[Mo_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}\eta^1,\eta^2\text{-}NCNMe_2)]$ (M≡M) [11] containing σ,π-coordinated cyanamide, $N{\equiv}C{-}NR_2$, ligands and the structures of the methyl derivatives have been reported. In the case of the trinuclear clusters $[Fe_3(CO)_9(NCR)]$ (RCN = butyronitrile [12] or benzonitrile [12b]), the X-ray structures show that the nitrile ligand is present as a triply bridging six-electron donor with the nitrogen lone pair σ bonded to one metal and the two orthogonal nitrile π bonds bridging the two other metal centres [12]. Also in the tetranuclear cluster $[Fe_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}NCPh)]$ the nitrile ligand behaves as a six-electron donor, being coordinated to the iron atoms formally via three σ-bonds and one π-bond [12b]. Finally, σ,π-nitrile coordination has been found to occur in some tetrameric Ni(0) complexes such as $[Ni(NCPh)(PPh_3)]_4\cdot 2toluene$ [13a] and $[Ni(NCMe)(PCy_3)]_4$ [13b]. In most cases the N—C—R framework in the σ,π coordination is significantly bent (≈127–135°) or slightly bent (≈163° [8]) and with a C—N bond distance of ≈1.25 Å corresponding to that expected for a double bond.

3. Insertion reactions

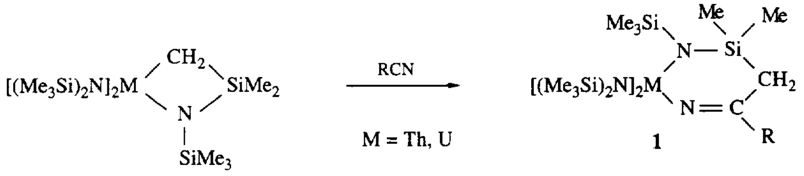
3.1. Metal–carbon bonds

3.1.1. Metal–alkyl and –aryl complexes

Insertion of the C≡N bond of an organonitrile, RCN, into a transition metal–carbon σ bond, M—R′, is not a common process, but has been found to occur with an electron-deficient metal centre, in particular an early transition or f block element, which polarizes the C≡N triple bond, thus facilitating the alkyl transfer; the strong metal–nitrogen interaction that eventually results is often invoked as providing for much of the driving force for many of these reactions. The product of the insertion is the —N=C(R′)R ligand, which is called, following Werner et al.'s suggestion [14], azaalkenylidene, although terms such as azavinylidene, methyleneamido, alkylideneamido, ketimido or azomethine have been used.

Insertion of RCN (R = Me, n-Pr, t-Bu, Ph) into an actinide–carbon bond has been reported for Th and U four-membered ring-strained metallacycles $[\{(Me_3Si)N)_2\}MCH_2Si(Me)_2NSiMe_3]$ to give six-membered ring compounds

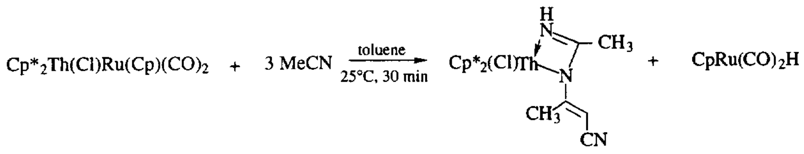
[15a,15b] (Eq. (1)) and of RCN (R = Me, *n*-Pr) into the U—Me bond of $[\mathrm{U(Me)\{N(SiMe_3)_2\}_3}]$ to give the azaalkenylidene derivatives $[\mathrm{U\{N{=}C(Me)R\}\{N(SiMe_3)_2\}_3}]$ [15b].



(1)

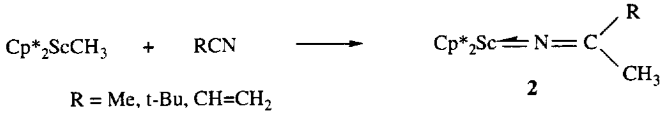
Subsequent hydrolysis with diluted HCl of the U metallacycle **1** gives specific, high yield formation of methyl ketones [15c].

The reaction of $[\mathrm{Cp^*_2Th(Cl)Ru(Cp)(CO)_2}]$ with acetonitrile affords in a quantitative yield a diazathoracyclobutene (amidinate) complex via heterobimetallic C–H functionalization and actinide-centred substrate insertion–oligomerization [16]:



(2)

Apparently, the first example of the insertion of a nitrile into a *d* block transition metal–carbon bond is that of the electron-deficient methyl complex $[\mathrm{Cp^*_2Sc(Me)}]$, which was found to react rapidly at room temperature with stoichiometric amounts of nitriles RCN (R = Me, *t*-Bu, $\mathrm{CH{=}CH_2}$) to form directly the azaalkenylidene insertion complexes $[\mathrm{Cp^*_2Sc\{N{=}C(Me)R\}}]$ [17] (Eq. (3)), whose structures have been determined by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy



(3)

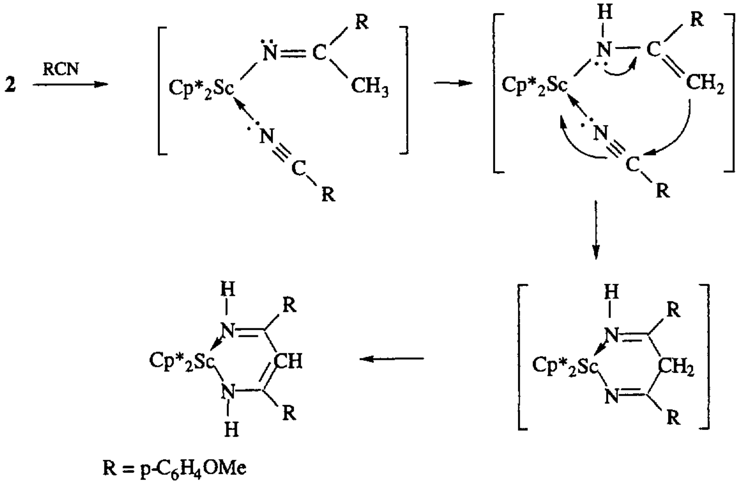
Also $[\mathrm{Cp^*_2Sc(R')}]$ (R′ = *p*-$\mathrm{MeC_6H_4}$, H) complexes react similarly with RCN (R = *p*-tolyl, *t*-Bu) and, for R′ = *p*-tolyl, an intermediate nitrile–aryl complex $[\mathrm{Cp^*_2Sc(}p\text{-}\mathrm{MeC_6H_4)(NCC_6H_4Me\text{-}}p)]$ could be isolated, which was found to isomerize slowly at room temperature to the corresponding azaalkenylidene derivative through a 1,3-alkyl shift from scandium to the coordinated nitrile carbon. This mechanism is analogous to that proposed for the insertion of nitriles into aluminium–alkyl bonds [18] and also for that of *t*-BuCN on the yttrium–carbon bond of permethylyttrocene complex $[\mathrm{Cp^*_2YCH(SiMe_3)_2}]$ to give the azaalkenylidene derivative $[\mathrm{Cp^*_2Y\{N{=}C(}t\text{-}\mathrm{Bu)CH(SiMe_3)_2\}\cdot NC{-}}t\text{-}\mathrm{Bu}]$ [19].

In contrast to these reactions, neither four-coordinate d^0 alkyls such as $[\mathrm{Cp_2M(R)(X)}]$ and $[\mathrm{Cp^*_2M(R)_2}]$ (M = Ti, Zr; R = alkyl, aryl; X = halide) nor the d^1 complexes $[\mathrm{Cp_2Ti(R)}]$ (with the exception of certain neutral $\mathrm{Cp_2M}$–hydride, –benzyne and related complexes that insert–couple with nitriles; see later) insert nitriles under mild conditions, although the latter form nitrile adducts [20]. However, the cationic titanium complexes $[Cp_2Ti(Me)(N{\equiv}CR)][BPh_4]$ and $[(Ind)_2Ti(Me)(N{\equiv}CR)][BPh_4]$ (R = Me, *n*-Pr, *t*-Bu, Ph) [21] and the zirconium complexes $[Cp'_2Zr(R)(THF)][BPh_4]$ ($Cp' = \eta^5\text{-}C_5H_4R'$, R′ = H, Me; R = H [22a,22b], Me [22a]) in the presence of MeCN or the nitrile complexes $[Cp_2Zr(R)(MeCN)_n][BPh_4]$ (R = H, Ph, CH_3, $\eta^2\text{-}CH_2Ph$) [22c,22d]) are converted to the corresponding azaalkenylidene derivatives as products of migratory insertion of RCN into the metal–carbon or metal–hydrogen bond. For the Zr reactions it is observed that the qualitative trend in the migratory aptitude is as follows: H, Ph (seconds at 23 °C) ≫ Me (hours at 23 °C) ≫ $\eta^2\text{-}CH_2Ph$ (no reaction at 60 °C) [22c]. The rates of the insertion of nitriles into the Ti—Me bond were measured by ^1H NMR with $[Cp_2Ti(Me)(NCR)]^+$ and $[(Ind)_2Ti(Me)(NCR)]^+$ (R = Me, *t*-Bu, Ph, *n*-Pr) complexes. The kinetic studies [21b] show that these reactions proceed by rate-limiting alkyl migration to the coordinated nitrile, yielding the azaalkenylidene intermediate, $[Ti\{N{=}C(Me)R\}]$, which is rapidly trapped by a second nitrile molecule. However, the results of similar kinetic studies of MeCN insertion into the Zr—Me bond in $[(C_5H_4R')Zr(Me)(MeCN)_n]^+$ (R′ = H, Me) are best explained by a mechanism in which the reactive species is the bis(acetonitrile) ($n = 2$) adduct [22c,22d]; it is also observed that electron donor groups on the Cp ring accelerate the insertion process. The bis-MeCN adduct $[Cp_2Hf(Me)(MeCN)_2]^+$ does not undergo MeCN insertion, but rather partially disproportionates to $[CpHf(Me)_2]$ and the dication $[Cp_2Hf(MeCN)_3]^{2+}$ [22d]. It is of interest to note that for higher alkyl complexes of the type $[Cp'Zr(CH_2CH_2R)(MeCN)_n]^+$ (R = CH_3, CH_2CH_3, Ph, *t*-Bu) the β-H elimination process predominates over the MeCN insertion into the Zr—C bond [22e].

The structure of the complex $[(Ind)_2Ti(Me)\{N{=}C(Me)Ph\}(NCPh)][BPh_4]$ was determined by X-ray crystallography [21b]; the azaalkenylidene ligand is η^1 coordinated and the Ti–azaalkenylidene arrangement, as well as in other reported cases [23], is close to linear (171.6(4)°) with a short Ti—N bond (1.851 Å), indicating substantial double-bond ($d_\pi - p_\pi$) character and sp hybridization of the nitrogen. The C=N distance of 1.244(8) Å indicates also the presence of a double bond as well as $\nu(C{=}N)$ at 1645 cm^{-1} as otherwise reported [23].

With an excess of nitrile (bearing hydrogen atoms on the α-carbon) the azaalkylidene derivative **2** (Eq. (3)) undergoes further reaction to give azametallacyclic complexes and a possible mechanism for their formation (Scheme 1) involves initial coordination of a second nitrile molecule to **2** followed by imine–enamine tautomerism that generates an intermediate with a nucleophilic methylene centre [17]. Attack at the electrophilic carbon of the coordinated nitrile and a second 1,3-hydrogen shift would provide the observed β-diketimino product.

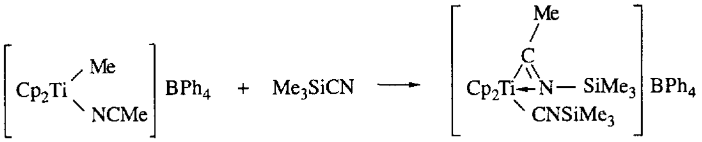
Also, dimeric paramagnetic Cr(III) alkyls $[Cp^*Cr(\mu\text{-}Cl)R]_2$ (R = Me, Et, Ph, CH_2Ph), with a 15-electron configuration of the chromium atoms, which renders them electronically unsaturated and highly Lewis acidic, react with an excess of nitrile (MeCN, EtCN) to yield similar mononuclear β-diketimino complexes by initial insertion of nitrile into the chromium–carbon bond; with stoichiometric amounts of RCN, dinuclear complexes with bridging azaalkenylidene ligands are



Scheme 1.

formed [24] and one of the latter complexes has been also structurally characterized [24a]. The Ti and Zr complexes $[Cp_2M(Me)(NCR)]^+$ are less reactive than their Sc counterparts and coupling of two nitriles with formation of metallaheterocycles (Scheme 1) is not observed [21,22].

Attempts to extend the nitrile insertion reaction of $[Cp_2Ti(Me)(NCMe)]^+$ to Me_3SiCN did not yield an azaalkylidene derivative, but instead the η^2-iminoacyl isocyanide complex was produced [21b]:

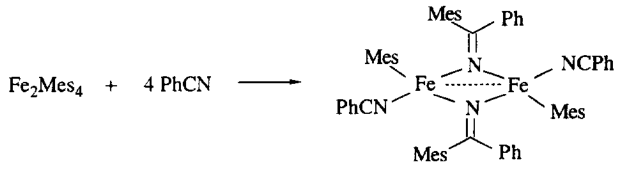


(4)

Trimethylsilyl cyanide is known to exist in equilibrium with small amounts of the isocyanide Me_3SiNC [25], which reacts preferentially with the Ti complex.

2-oxoalkyl (enolate) rhenium complexes of the type $[Re(CH_2CO_2Et)(CO_5)]$ have been found to insert RCN (R = Me, Et, *i*-Pr, Ph) into the Re—C(enolate) bond at 120 °C only in the presence of excess PPh_3 to give the complexes *trans*-$[(PPh_3)_2(CO)_2ReNHC(R)C(H)CO(OEt)]$ [26]. A similar reaction occurs with the secondary enolate complex $[Re\{CH(Me)CO_2Et\}(CO_5)]$ with EtCN. Kinetic studies of the nitrile insertion reaction revealed a weak linear dependence of the rate constant of the reaction on the concentration of added CH_3CN in benzene; this was attributed to a medium effect.

A two-fold insertion into metal–aryl bonds under mild conditions was observed in the reaction of the dimer $[Fe_2Mes_4]$, having two bridging and two terminal mesityl groups, with PhCN to give the dimer $[\{Fe(Mes)(NCPh)\{\mu\text{-}N{=}C(Ph)Mes\}]_2$, in which the iron atoms are bridged at a distance of 2.860(2) Å [27]:



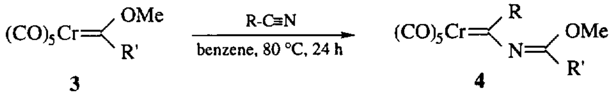
(5)

The reaction is proposed to occur with initial coordination of the nitrile, followed by migration of the bridging mesityl group to the nitrile, while the terminal mesityl does not migrate, as otherwise observed in the analogous reaction with isocyanides.

3.1.2. Metal carbene complexes

The reactions of nitriles with carbene (alkylidene) transition metal complexes proceed differently according to the electrophilicity–nucleophilicity of the carbene (alkylidene) carbon and also to the nature of the R substituent of the nitrile.

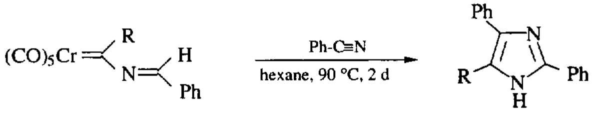
The first examples of the insertion of organonitriles RCN (R = Me, Ph, *i*-Pr, *t*-Bu, CH_2Ph, *p*-$MeOC_6H_4$, 2-furyl) into the metal–carbon bond of heteroatom-stabilized Fischer carbene complexes $[Cr\{C(OMe)R'\}(CO)_5]$ (R′ = Ph, Me) have been reported [28] to give, in moderate to excellent yields, imino (*O*-alkyl imidato) carbene complexes:



3 **4**

(6)

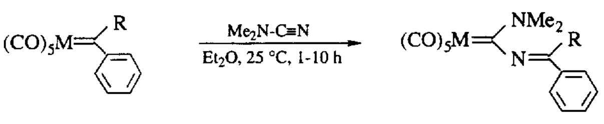
From this study it has also demonstrated that the insertion of the nitrile is reversible in some instances; thus, complex **4** (R = *t*-Bu, R′ = Ph) (Eq. (6)) at 80 °C is in equilibrium with the starting carbene **3** and *t*-BuCN and the equilibrium favours complex **3** by 4.6:1. Type **4** imino carbene complexes are then found to cycloadd nitriles to afford imidazoles in high yield [29]:



R = Me, Ph

(7)

The insertion of the carbon–nitrogen triple bond of dimethyl cyanamide or other diorganyl cyanamides into the carbene–metal bond of some electrophilic Cr and W carbene complexes was previously observed by Fischer and co-workers to give iminocarbene complexes almost quantitatively at room temperature [30]:

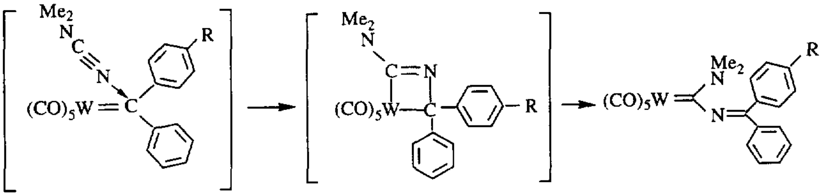


(8)

M = Cr, R = OMe; M = W, R = OMe, Ph, p-tolyl

The kinetics of the insertion of $Me_2N{-}C{\equiv}N$ was studied using the tungsten carbene complexes $[W\{C(p\text{-}C_6H_4R)Ph\}(CO)_5]$ (R = OMe, Me, Ph, Br, CF_3) [30b];

the formation of the imino carbene complexes $[W\{C{=}N(p\text{-}C_6H_4R)Ph(NMe_2)\}(CO)_5]$ follows a second-order rate law, first order to both the starting carbene and the dimethyl cyanamide concentrations. The results of the kinetic investigation suggest an associative stepwise mechanism (Eq. (9)) involving a nucleophilic attack of the negatively polarized CN group of the cyanamide at the δ^+-polarized carbene carbon in the first reaction step, followed by insertion into the M—C(carbene) bond, probably proceeding with the intermediacy of a metallacycle [30b]:



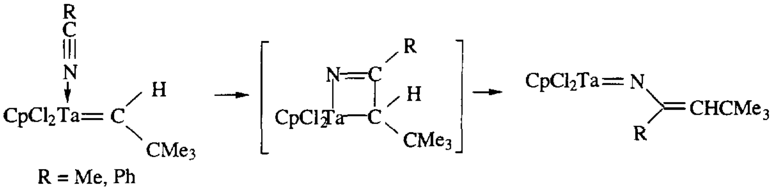
(9)

The reactions of nitriles with electrophilic non-heteroatom-stabilized group 6 carbene complexes proceed differently according to the nature of the R group of the nitrile. Thus, organonitriles RCN ($R{=}p\text{-}C_6H_4NMe_2$, $p\text{-}C_6H_4OMe$, Ph, Me, *t*-Bu) react with $[W({=}CPh_2)(CO)_5]$ to yield a mixture of products including the insertion product $[W\{C(R)N{=}CPh_2\}(CO)_5]$, the mononitrile $[W(CO)_5(N{\equiv}CR)]$ and dinitrile *cis*-$[W(CO)_4(N{\equiv}CR)_2]$ substitution complexes and diphenylketene, $Ph_2C{=}C{=}O$ [31a]. The product distribution depends on the type and the concentration of the organonitrile; at constant temperature the yield of the insertion product and that of the mononitrile substitution product as well as that of diphenyl ketene decrease with increasing concentration of RCN. The reactions of $[W\{C(R')Ph\}(CO)_5]$ ($R'{=}OMe$, Ph) with $N{\equiv}CSiMe_3$ ($R'{=}OMe$) and $N{\equiv}CSn(n\text{-}Bu)_3$ ($R'{=}Ph$) in diethyl ether yield, under different experimental conditions, complexes of the type $[W\{N{\equiv}CC(OMe)(Ph)SiMe_3\}(CO)_5]$ and $[W\{N{\equiv}CC(H)Ph_2\}(CO)_5]$, formally derived by insertion of "N≡C" into the M=C bond and of the "C(R')Ph" moiety into the R—CN bond [31b]; the reaction ultimately leads to the conversion of a carbene to a nitrile.

Tetramethylcyanoguanidine, $N{\equiv}C{-}N{=}C(NMe_2)_2$, reacts with $[Cr\{{=}C(Ph)OMe\}(CO)_5]$ via substitution of the carbene ligand to give $[Cr\{N{\equiv}CN{=}C(NMe_2)_2\}(CO)_5]$, while with the acetoxy(phenyl)carbene complex $[M\{{=}C(Ph)OC(O)Me\}(CO)_5]$ (M = Cr, W) the same reaction yields $[M\{{=}C(Ph){-}N{=}C(NMe_2)_2\}(CO)_5]$, where the acetoxy group of the carbene ligand is exchanged for the $N{=}C(NMe_2)_2$ group of the cyanoguanidine [32]. On the contrary, $[W\{{=}CPh_2\}(CO)_5]$ reacts with diethylamino(dimethyl)acetonitrile, $Me_2(Et_2N)CC{\equiv}N$, to give the isocyanide complex $[W\{C{\equiv}NC(H)Ph_2\}(CO)_5]$ [33].

The synthesis of an (imido)uranium complex of the type $[U\{{=}NC(Me)CHP(Ph)_2Me\}Cp_3]$ results from the reaction of $[U\{{=}C(H)P(Ph)_2Me\}Cp_3]$ with MeCN in equimolar quantities in toluene at 55 °C for 24 h. The insertion product has been structurally characterized; bond distances and angles suggest a delocalized π system of the U—N—C—C moiety and a U—N bond order between 2 and 3 [34].

Nitriles readily react with the nucleophilic alkylidene complexes $[M\{=C(H)CMe_3\}Np_3]$ ($M=Nb$, Ta; $Np=CH_2CMe_3$) [35a] and $[CpTaCl_2\{=C(H)CMe_3\}]$ [35b] to form alkenyl imido complexes:



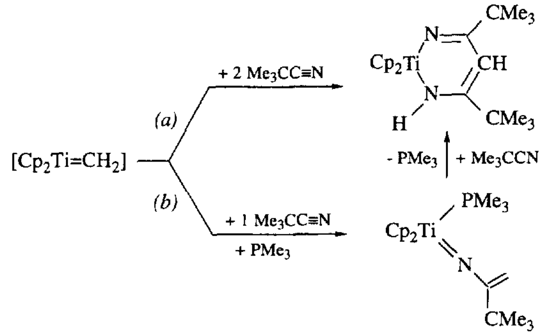
(10)

The suggested mechanism involves initial RCN coordination to the electron-deficient Ta metal centre; subsequent attack of the nucleophilic neopentylidene ligand to the nitrile carbon will form an azametallacyclobutene intermediate, which eventually yields the imido ligand.

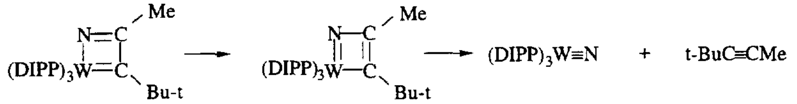
Formation of diazatitanacyclohexadienes and titanocene vinylimido complexes from reactive methylidenetitanocene, $[Cp_2Ti(=CH_2)]$, sources by reaction with nitriles has been reported [36]. The reactions have been suggested [36c,36d] to proceed either (Scheme 2, path (a)) by initial formation of an azametallacyclobutene (as shown above for Ta) followed by direct insertion of RCN into the Ti–C bond or alternatively (path (b)) by initial formation of a vinyilimido complex which could condense directly with the reacting nitrile either through a concerted or stepwise [4+2] cycloaddition reaction.

3.1.3. *Metal alkylidyne complexes*

Some tungsten alkylidyne complexes have been shown to react with nitriles (Wittig-like reaction) as illustrated in Eq. (11) for the reaction of $[W(\equiv C-t\text{-}Bu)(DIPP)_3]$ with CH_3CN to yield, via azatungstenacyclobutadiene species, an insoluble, probably polymeric, air-stable complex that analyses as the nitrido derivative $[W(\equiv N)(DIPP)_3]$ and the alkyne $t\text{-}BuC\equiv CMe$ quantitatively [37]:

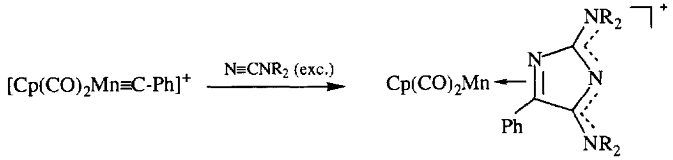


Scheme 2.

 (11)

This type of reaction is very sensitive to the steric bulk of the ligands in the alkylidyne complex as observed for $[W(\equiv C-t\text{-Bu})(O-t\text{-Bu})_3]$ that can be recrystallized from ether–acetonitrile mixtures without forming $[W(\equiv N)(O-t\text{-Bu})_3]_x$ [38]. Furthermore, the W≡C triple bond reacts more rapidly with the C≡C triple bond than it does with the C≡N triple bond as reported, for instance, for the reaction of $[W(CMe)(O-t\text{-Bu})_3]$ with $EtC\equiv CCH_2C\equiv N$ in the presence of pyridine to yield $[W(\equiv CCH_2CN)(O-t\text{-Bu})_3(py)]$ [38].

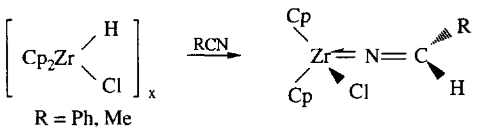
Novel cyclization reactions involving the highly electrophilic carbyne complex $[Cp(CO)_2Mn(\equiv C-Ph)]^+$ and cyanamides $N\equiv CNR_2$ (R = Me, Et, *i*-Pr) have been recently reported [39] by Fischer et al. to give metallacyles, carbocycles or heterocycles, as described for the formation of the imidazolinium derivative, which occurs by initial attack of the cyanamide at the carbyne carbon:

 (12)

3.2. Metal–hydrogen bonds

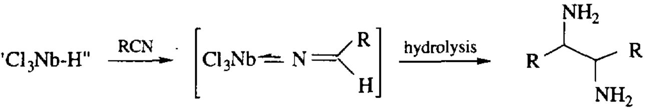
Insertion of RCN into M—H bonds (hydrometallation reaction) has been observed in a few cases with mononuclear transition metal complexes, but more commonly with dinuclear and cluster compounds; this reaction can be viewed as the initial stage of the hydrogenation of the ligand at a metal centre (see reduction of nitriles to amines). The observed insertion products are either the azavinylidene (or azaalkylidene or methyleneamido), —N=C(H)R, or the μ-acimidoyl, μ-N(H)=CR, ligands; while the former is usually observed for mononuclear derivatives, both often result in the hydrometallation of nitriles with di- or polynuclear hydrido complexes.

Erker and co-workers have reported the hydrozirconation reactions of RCN (R = Me, Ph) with $[Cp_2Zr(H)Cl]_x$ (Eq. (13)) or $[Cp'_2Zr(H)Cl]$ to yield $[Cp_2ZrCl\{N=C(H)R\}]$ or $[Cp'_2ZrCl\{N=C(H)R\}]$ respectively [23b,40]. Structural data for R = Ph indicate that the azavinylidene moiety is almost linear with a short M—N bond and with a cis arrangement of the Cl and H(alkylideneamido) atoms as usually observed for hydrozirconation reactions.

 (13)

Scandium and zirconium complexes with terminal hydrides of the type [$ScCp^*_2(H)$] and [$ZrCp^*_2H_2$] react with RCN in a similar manner to that described for the corresponding alkyls to give nitrile insertion into the M—H bond [17]. When the reaction is carried out with an excess of nitrile, the dihydrido complex [$ZrCp^*_2H_2$] slowly yields the double nitrile insertion product [$ZrCp^*_2\{N{=}C(H)R\}_2$]. Similarly, Jordan et al. have reported the insertion of acetonitrile into the Zr—H of $[ZrCp_2(H)(THF)]^+$ to produce $[ZrCp_2\{N{=}C(H)CH_3\}(CH_3CN)]^+$ [22a].

The formation of azavinylidene species of the type [$NbCl_3\{N{=}C(H)R\}$] by insertion of RCN into the Nb—H bond has provided a practical route to vicinal diamines [41]:



(14)

The binuclear tantalum hydride complex [$TaCp''Cl_2H]_2$($Cp''=\eta^5$-C_5Me_4Et) reacts rapidly with 1 equiv of acetonitrile at 25 °C to give the dimeric complex [$Ta_2Cp''_2Cl_3(\mu$-$Cl)(\mu$-$H)\{\mu,\eta^1,\eta^2$-$N{=}C(H)Me\}$], in which the acetonitrile is reduced to N=C(H)Me which bridges two Ta atoms in an η^1-*N*, η^2-*C*,*N* fashion [42].

The yttrium hydrides [$(C_5H_4R')YH(THF)_2]_2$ (R′ = H, Me) react rapidly with RCN (R = Me, *t*-Bu) by 1,2 addition of Y—H to form [$(C_5H_4R')Y\{\mu$-$N{=}C(H)R\}_2]_2$, where the two metal units are connected by asymmetrical alkylideneamido bridges [43].

Reaction of various carbonyls such as $[Fe_2(CO)_8]^{2-}$ in the presence of $[W(CO)_5]^-$, $[HFe_3(CO)_{11}]^-$ or $Fe(CO)_5$ in the presence of NaI with RCN (R = Me, Ph, *n*-Pr) under reflux gives $[Fe_3\{\mu$-N,η^2-C,N-$N(H){=}CR\}(CO)_9]^-$ or $[Fe_3\{\mu$-N,η^2-C,N-$N{=}C(H)R\}(CO)_9]^-$ containing the acimidoyl or alkylideneamido groups [44] respectively, triply bridging the iron triangle as observed in the crystal structures of [$Fe_3(\mu$-$H)\{\mu$-N,η^2-C,N-$N(H){=}CMe\}(CO)_9$] and [$Fe_3(\mu$-$H)\{\mu$-N,η^2-C,N-$N{=}C(H)Me\}(CO)_9$], derived by protonation of the above-mentioned complexes [45].

The reaction of osmium hydrido carbonyls [$H_2Os_3(CO)_9(L)$] (L = CO, PMe_2Ph) [46a,46b] occurs only with the activated nitrile CF_3CN (but not with normal nitriles) to yield complexes similar to those reported for the triiron system, i.e. (μ-H)[$Os_3\{\mu$-N,η^2-C,N-$N(H){=}CCF_3\}(CO)_9(L)$] (L = CO [46a,46b] and (μ-H)[$Os_3\{\mu$-N,η^1-N-$N{=}C(H)CF_3\}(CO)_9(L)$] (L = CO [46a,46b], PMe_2Ph [46b,46c]), containing edge-bridging acimidoyl and azavinylidene ligands.

The mixed Re—Ru unsaturated complex [$(PPh_3)_2(CO)HRe(\mu$-$H)_3RuH(PPh_3)_2$] reacts with MeCN at room temperature to give, on substitution of two hydride ligands by the incoming nitrile, [$(PPh_3)_2(CO)Re(\mu$-$H)_3Ru(MeCN)(PPh_3)_2$], the reaction being reversible under H_2 at atmospheric pressure; with PhCN a substitution reaction occurs as well as a hydrometalation of the nitrile to give the complex [$(PPh_3)_2(CO)Re(\mu$-$H)_2\{\mu$-$NC(H)Ph\}Ru(PhCN)(PPh_3)_2$] containing a benzonitrile and a bridging azavinylidene ligand [47].

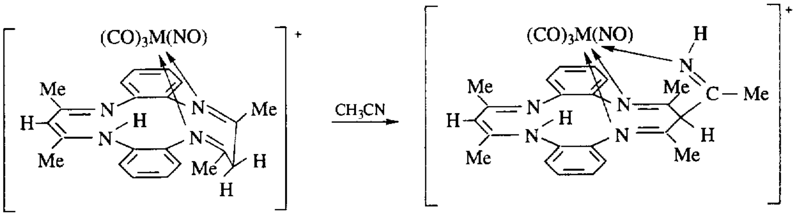
The complexes [$Re_2H(\mu$-$H)(CO)_6(\mu$-$L{-}L)$] (L—L = tedip, dppm) react with acetonitrile under reflux to a major product formulated as

$[Re_2H(CO)_6(\mu\text{-}L{-}L)\{\mu\text{-}NC(H)Me\}]$, containing a bridging azavinylidene group that has been structurally characterized for L—L = dppm; the minor product of the reaction was proposed on the basis of spectroscopic evidence to be $[Re_2H(CO)_6(\mu\text{-}L{-}L)\{\mu\text{-}(H)NCMe\}]$ containing an NC-bonded acetimidoyl ligand [48]. On the contrary, the reactions of equimolecular amounts of RCN with the dihydrido carbonyl complexes $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L{-}L)]$ (L—L = dppm, tedip) proceed under mild conditions either replacing both hydrido ligands or inserting into an Mn—H bond depending on the nature of the nitrile substituent R [8]. Thus, with alkanenitriles RCN (R = Me, Et, *n*-Pr, *t*-Bu) the reaction gives hydride substitution product $[Mn_2(\mu,\eta^1,\eta^2\text{-}NCR)(CO)_6(\mu\text{-}L{-}L)]$, in which the RCN ligand is σ,π bonded, whereas the reaction of nitriles RCN (R = Ph, CH_2Ph, $CH{=}CH_2$), containing electron-withdrawing substituents, gives the insertion methyleneamido derivatives $[Mn_2(\mu\text{-}H)\{\mu\text{-}N{=}C(H)R\}(CO)_6(\mu\text{-}L{-}L)]$. The milder conditions that are observed in the reactions of the dinuclear manganese complexes compared with those of rhenium are probably due to the weakness of the Mn—H in comparison with the Re—H bond.

Reaction of $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][PF_6]$ (R = Me, *i*-Pr) with PhCN in 1,2-dichloroethane under reflux was found to lead to the quantitative formation of the bridging azavinylidene product $[Ru_2\{\mu\text{-}\eta^1\text{-}N{=}C(H)Ph\}(CO)_4\{\mu\text{-}(RO_2)PN(Et)P(OR)_2\}_2][PF_6]$, which has been structurally characterized for R = *i*-Pr [49].

3.3. Miscellaneous

Molybdenum and tungsten complexes of the type $[Mo(CO)_3(NO)(C_{22}H_{24}N_4)]^+$ (M = Mo, W; $C_{22}H_{24}N_4$ = dibenzotetraaza[14]annulene) react with MeCN (Eq. (15)) by a formal insertion on a C—H bond of the annulene, which is eventually converted into a novel tridentate ligand [50a]:



(15)

It is worthwhile noting that the zirconium silyl complex $[CpCp^*Zr(Me)\{Si(SiMe_3)_3\}]$ reacts readily at room temperature with nitriles RCN (R = Me, $CH{=}CH_2$, Ph) to form the azavinylidene derivatives $[CpCp^*Zr(Me)\{N{=}C(R)Si(SiMe_3)_3\}]$ by exclusive insertion of RCN into the Zr—Si bond [50b]. Interestingly, no insertion of MeCN was observed for $[Cp_2Zr(Me)\{Si(SiMe_3)_3\}]$, $[Cp_2Zr(Cl)\{Si(SiMe_3)_3\}]$ or $[CpCp^*Zr(Me)_2]$, although $[CpCp^*Zr(Cl)\{Si(SiMe_3)_3\}]$ appears to react slowly with MeCN over several days to form an insertion product. The observed greater reactivity of $[CpCp^*Zr(Me)\{Si(SiMe_3)_3\}]$ toward nitriles has been explained either by the absence of π donor ligands, which provides a good Lewis acid centre for coordination of the nitrile, or by the weakening of the Zr—Si bond owing to steric repulsions between the bulky Cp* and $Si(SiMe_3)_3$ ligands.

4. Reactions involving metal–metal and metal–X (X = O, S) multiple bonds

4.1. Reactions with metal–metal multiple bonds

The metathesis-like reaction of a W≡W triple bond with RCN constitutes an excellent route to alkylidyne and nitrido complexes. Thus, for instance, the ditungsten hexaalkoxide $[W_2(O{-}t\text{-}Bu_3)_6]$ rapidly reacts with 1 equiv of acetonitrile or benzonitrile [51] according to the following reaction:

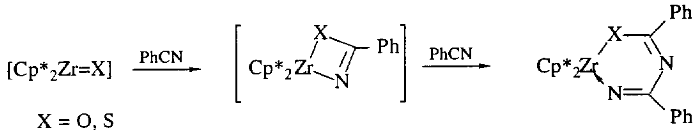
$$[W_2(OCMe_3)_6]+RC{\equiv}N\rightarrow[W({\equiv}CR)(OCMe_3)_3]+[W({\equiv}N)(OCMe_3)_3] \quad (16)$$

Similarly, $[W_2(O{-}t\text{-}Bu)_6]$ reacts with 1 equiv of dimethylcyanamide, Me_2NCN, at room temperature to afford the linear polymer $[W({\equiv}N)(O{-}t\text{-}Bu)_3]_x$ and $[W({\equiv}CNMe_2)(O{-}t\text{-}Bu)_3]$. However, addition of 1 equiv of diethylcyanamide to dimolybdenum hexaalkoxides $[Mo_2(OR)_6]$ (R = t-Bu, i-Pr, $CH_2{-}t$-Bu) under analogous conditions afford 1:1 adducts $[Mo_2(OR)_6(\mu\text{-}NCNMe_2)]$, one of which (R = $CH_2{-}t$-Bu) has been structurally characterized [11a]. In contrast, $[W_2\{OCMe_2(CF_3)\}_6]$ with CH_3CN forms only a labile adduct, $[W_2\{OCMe_2(CF_3)\}_6(CH_3CN)_2]$, instead of $[W(CMe)\{OCMe_2(CF_3)\}_3]$ and $[W(N)\{OCMe_2(CF_3)\}_3]_x$ [52]. On the contrary, alkyne adducts of ditungsten hexaalkoxides $[W_2(O{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2)]$ react at room temperature in hydrocarbon solvents with 1 equiv of nitrile RCN (R = Ph, Me) to give compounds of the type $[W_2(O{-}t\text{-}Bu)_6\{CHCHC(R)N\}]$, containing the metallacyclic ligand $\overline{W{=}CHCH{=}C(R)N{=}W}$, with terminal alkylidene and imido groups, which is formed by coupling of the alkyne and the nitrile [53].

Reduction of nitriles by multiply bonded dirhenium species has been thoroughly investigated by Walton and co-workers [54]. Thus, it was found that the quadruply bonded dirhenium(III) complexes $[(n\text{-}Bu_4N)_2Re_2X_8]$ (X = Cl, Br) react under reflux with alkyl nitriles RCN in the presence of an excess of the bidentate phosphine ligand dppbe and a few drops of concentrated HX to yield the mononuclear Re(V) imido complexes $[Re(NCH_2Et)X_3(dppbe)]$, which have been structurally characterized for X = Cl, Br and R = Et [54b,54c]. The reactions have been suggested to proceed by the formation of the dirhenium(II) complex $\alpha\text{-}[Re_2X_4(dppbe)_2]$, which was found in the case of X = Cl to react with EtCN in the presence of concentrated HCl to give the imido species $[Re(NCH_2Et)Cl_3(dppbe)]$. It is suggested that the key step in the reduction of nitriles by multiply bonded dirhenium species is probably disproportionation of the Re_2^{4+} core to generate a reactive mononuclear Re(I) site that is a potent four-electron reductant.

4.2. Reactions with M—X (X = O, S) multiple bonds

Reactive oxo- and sulphidozirconocene intermediates $[Cp^*_2Zr({=}X)]$ (X = O, S) cycloadd nitriles to form six-membered metallacycles via initial formation of azaoxametallacycle, followed by subsequent insertion of a second nitrile into the Zr—N bond [55]:

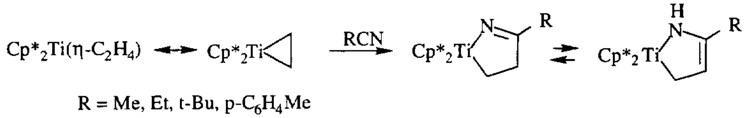


(17)

5. Coupling reactions

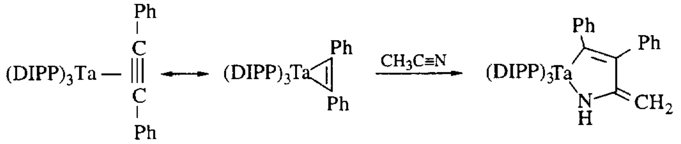
One important aspect of the nitrile reactivity is the coupling (reductive coupling, being accompanied by oxidation of the metal) reaction involving one nitrile and an unsaturated organic molecule (e.g. alkene, alkyne) or two nitrile ligands that lead to the formation of a new carbon–carbon bond. Coupling reactions involving at least one nitrile are promoted by middle-to-low-valent early transition metals and have provided convenient routes to useful organic products such as polyfunctionalized aromatic compounds [56] and related products derived from metallacyclic intermediates [36a,57] and vicinal diamines [41]. These reactions proceed by the initial formation of a metallacyclic imine, which may subsequently rearrange [58] or dimerize [59].

Specifically, the reactions of $[TiCp^*_2(\eta\text{-}C_2H_4)]$ with nitriles (1 equiv) afford a metallacycloimine [58], which is in equilibrium with the metallacycloenamine species $[Cp^*_2Ti\{NHC(R)=CHCH_2\}]$ via an intramolecular pathway:



(18)

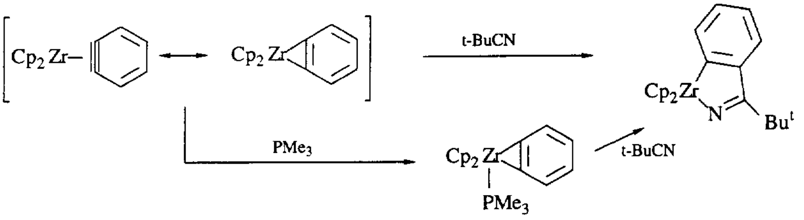
Metallacyclic enamines are slowly formed from tantalum alkyne complexes and nitriles containing α-hydrogen atoms such as CH_3CN and C_2H_5CN at room temperature for a few days [60]:



(19)

Buchwald and co-workers have reported a wide series of nitrile coupling reactions with zirconocene–benzyne [61a], –cyclohexyne [61b], –acyclic alkyne [61c], –naphthalyne [61d], –thioaldehyde [61e] and –imine [57] complexes to form azametallacycles [56,57,59,61] with extremely good regiochemical control.

As shown in Scheme 3 for the zirconocene–benzyne reactions, the coupling reaction with RCN may proceed without isolating the zirconocene–benzyne complex or otherwise with stabilization of the latter by PMe_3. The zirconacycles can be converted, without being isolated, into useful and often otherwise inaccessible organic

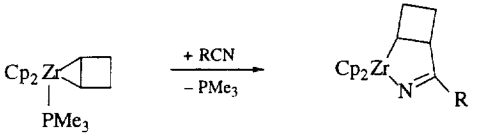


Scheme 3.

products such as aromatic ketones, *o*-iodophenyl ketones and isothiazoles. Notably, a similar reactivity with nitriles is not observed with late transition metal complexes of cycloalkynes and arynes [62].

The reactions of dimethyl- and diethyltitanacyclobutenes with 2 equiv of isobutyronitrile afford a double-insertion product derived by insertion of the nitrile into both the metal–alkyl and –vinyl bonds (Scheme 4, path (a)); in contrast, similar reactions of diphenyltitanacyclobutene with a variety of nitriles yield single-insertion products (path (b)) [63].

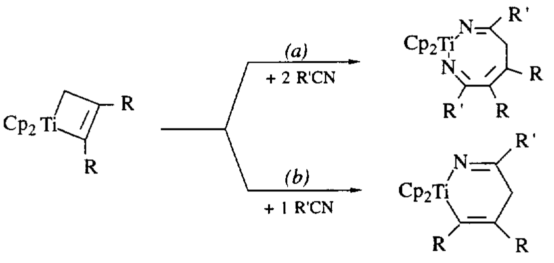
The zirconocene complex of cyclobutene couples with a slight excess of RCN (R = Et, Pr, *i*-Pr) to afford an azametallacycle [64]:



(20)

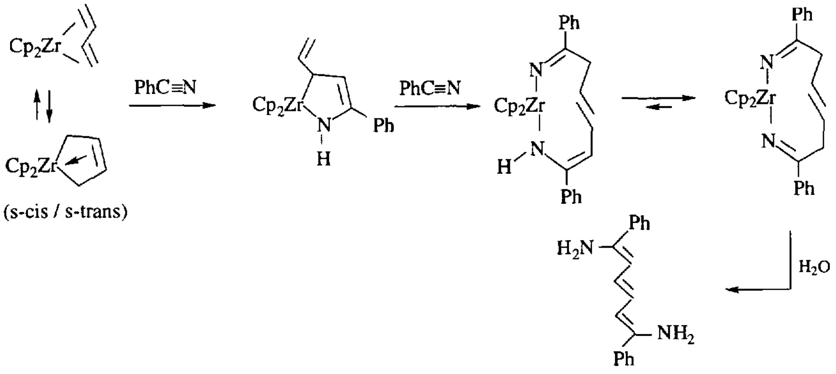
Erker et al. have reported a rather widely applicable synthetic method [65] for the preparation of stable conjugated primary enamines and related systems based on the template-directed coupling of two nitrile functionalities with (butadiene)bis(cyclopentadienyl)zirconium, as reported in Scheme 5.

All the intermediates shown in Scheme 5 were isolated. In similar way, Erker and Pfaff have reported the coupling of difunctional nitriles, such as fumaronitrile or terephtalonitrile, with butadiene at the bis(cyclopentadienyl)zirconium template to give analogously structured nine-membered diazacirconacycles containing free nitrile



(a): R = Me; R' = $(CH_3)_2CH$. (b) R = Ph; R' = alkyl, aryl

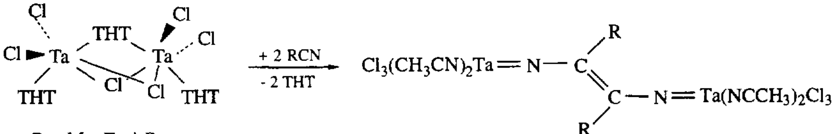
Scheme 4.



Scheme 5.

functionalities; subsequent hydrolysis yields cyano-functionalized conjugated primary enamines [65b]. Coupling of fumaronitrile or terephthalonitrile with (butadiene)bis(cyclopentadienyl)zirconium in a 1:1 stoichiometry gave good yields of organometallic polymers which were hydrolysed to yield conjugated organic (polyacetylene-like) polymers containing $-NH_2$ substituents attached systematically in conjugated positions [65b].

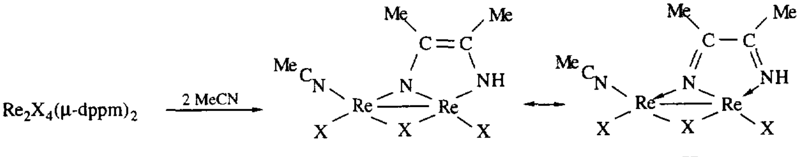
Reductive coupling of two nitriles by Ti(III) [20d] and Ta(III) [66] (Eq. (21)) has been reported to give alkylideneamido ligands bridging two metal centers, while coupling of two nitriles to give azametallaheterocycles has been reported for Sc [17] and Fe [67]:



(21)

R = Me, Et, i-Pr

Coupling of two nitriles at multiply bonded transition metal centres has been reported by Walton and co-workers. The triply bonded dirhenium(II) complexes $[Re_2X_4(\mu\text{-dppm})_2]$ (X = Cl, Br) react with RCN (R = alkyl, aryl) to give reductive coupling of two nitrile ligands with formation of a delocalized, planar, five-membered metallacycle as summarized below (the dppm ligands have been omitted)



(22)

I II

Structural data indicate that the ring system of the resulting nitrile coupled product is best represented as having contributions **I** and **II** [68]. The coupling of two organonitrile molecules by the triply bonded $(\mathrm{Re{\equiv}Re})^{4+}$ core, as is present in

$[Re_2X_4(\mu\text{-dppm})_2]$ and $[ReX_3(\mu\text{-dppm})_2(NCR)_2][PF_6]$, can be represented formally as redox processes that involve oxidation of dirhenium core to Re_2^{5+} or Re_2^{7+}, depending on the description of the resulting $Re_2[\mu\text{-NC(R)C(R)NH}]$ dimetallacycle. It is suggested that the reaction proceeds initially giving the dicationic species $[ReX_3(\mu\text{-}HN_2C_2R_2)(\mu\text{-dppm})_2(NCR)]^{2+}$ (these are formally Re_2^{6+} or Re_2^{8+} derivatives depending on the ligand formulation), which then undergo a one-electron reduction under the reaction conditions to afford the monocation (correspondingly formulated as Re_2^{5+} or Re_2^{7+}). The intramolecular redox process that gives rise to the nitrile coupling is accompanied by the "protonation" (from MeCN) of the terminal nitrogen atom of the coupled ligand.

6. Reduction to amines

Reduction of nitriles to amines with many reducing agents, including molecular hydrogen, alkoxides or hydride reagents, is a known reaction [69a]. Homogeneous catalytic hydrogenation of nitriles is not usually easy; examples of reduction of nitriles to primary amines with pressurized hydrogen have been reported, for instance, using the nickel isocyanide cluster $[Ni_4\{CNC(CH_3)_3\}_7]$ [69b], some anionic ruthenium hydride complexes such as $(K^+)_2[(PPh_3)_3(Ph_2P)Ru_2H_4]^{2-}$ [69c] or ortho metallated Pd(II) complexes [69d]. The rhodium complexes $[RhH(P\text{-i-}Pr_3)_3]$ and $[Rh_2(H_2)(\mu\text{-}N_2)(PCy_3)_4]$ [69e] are active catalysts for the hydrogenation nitriles under ambient conditions producing primary amines selectively, while $CoCl_2$ converts nitriles to primary amines in the presence of $NaBH_4$ [69f]. Studies of the reactions of aluminopolyhydride complexes of tungsten with nitriles [69g] and studies on the mechanism of Co-assisted borohydride reduction of nitriles [69h] have been reported.

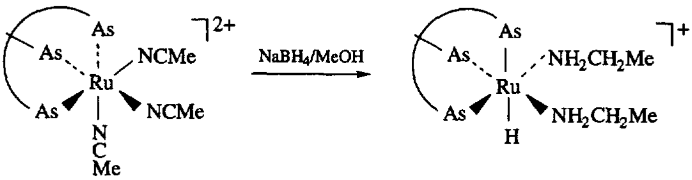
Stepwise stoichiometric reduction of nitriles on poly- and mononuclear transition metal complexes has yielded isolable intermediates (see Section 3.2). In particular, the reduction of an organonitrile by molecular H_2 occurring at a face of a tri-iron carbonyl cluster was studied by Andrews and Kaesz [70] using different iron carbonyl clusters such as the azavinylidene hydrido complex $[(\mu\text{-H})Fe_3\{N{=}C(H)R\}(CO)_9]$ or the acetonitrile complex $[Fe_3(NCMe)(CO_9)]$. In all cases the final product resulted as a triply bridging nitrile complex; other isolated and characterized intermediates are summarized below for the nitrile carbonyl hydrogenation. The crucial step of the displacement of the amine from the dihydronitrene precursor failed, leading to cluster decomposition to metallic iron.

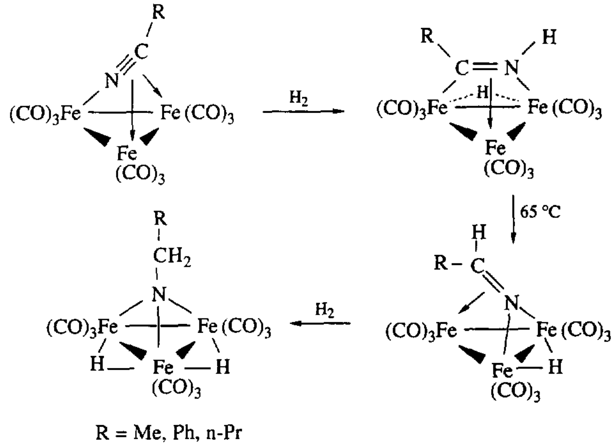
In contrast to the Fe_3–nitrile system, in which the key steps occur on μ_3-bonded, NC-containing ligands, the hydrogenation of other nitriles such as PhCN or CF_3CN on Ru or Os trinuclear clusters respectively has shown that complete hydrogenation of the CN bond is possible with coordination involving only the nitrogen and two metal atoms of the cluster. The $[Ru_3(CO)_{12}]$ benzonitrile reduction with H_2 at atmospheric pressure [71] led to the isolation of the azavinylidene $[(\mu\text{-H})Ru(CO)_{10}\{\mu\text{-N{=}C(H)Ph}\}]$ and nitrene $[(\mu\text{-H})_2Ru(CO)_9\{\mu_3\text{-N}{-}CH_2Ph\}]$ complexes, but not of the benzylamino derivative $[(\mu\text{-H})Ru(CO)_{10}\{\mu\text{-NH}{-}CH_2Ph\}]$, which, however, was formed in low yield in the reaction of PhCN with

$[Ru_3(CO)_{12}]$ under reflux in the presence of acetic acid and structurally characterized [72]. On the contrary, treatment of $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-}N,\eta^1\text{-}N\text{-}N{=}C(H)CH_3\}]$, derived from insertion of CF_3CN on Os—H of $[H_2Os_3(CO)_{10}]$ [46a, 46b], with molecular hydrogen (49 atm, 140 °C, 16 h) leads to the formation of three complexes $[(\mu\text{-H})Os_3(CO)_{10}\{\mu_2\text{-N(H)CH}_2CF_3\}]$, $[(\mu\text{-H})_2Os_3(CO)_9\{\mu_3\text{-NCH}_2CF_3\}]$ and $[H(\mu\text{-H})_2Os_3(CO)_8\{\mu_3\text{-NCH}_2CF_3\}]$, in approximately equal yields and structurally characterized [73]. Also, the acimidoyl ligand in $[(\mu\text{-H})Os_3(CO)_{10}$ $\{\mu\text{-}N,\eta^2\text{-}C,N\text{-N(H)}{=}CCF_3\}]$ is reduced by H_2 to give the nitrene complex $[(\mu\text{-H})_2Os_3(CO)_9\{\mu_3\text{-NCH}_2CF_3\}]$ in ≈80% yield [73]. However, in no case has the free amine been obtained from either the Ru or Os cluster, thus parallelling the behaviour of the Fe_3 system.

Stepwise reduction of the carbon–nitrogen triple bond of simple nitriles at two metal centres has been also reported [8,74]. Nitriles RCN (R = CH_3, Ph, o-tolyl) react smoothly with electron-rich dinuclear rhodium hydride derivatives of the type $[Rh(\mu\text{-H})(L{-}L)]_2$ (L—L = chelating diphosphine ligand) to afford in high yield the azavinylidene derivatives $[\{Rh(L{-}L)\}_2(\mu\text{-H})\{\mu\text{-N}{=}C(H)R\}]$ apparently by insertion of the nitrile into a bridging hydride bond [74a]. Further reduction occurs by addition of H_2 (1 atm.) to generate the corresponding amide hydride derivatives $[\{Rh(L{-}L)\}_2(\mu\text{-H})\{\mu\text{-N(H)CH}_2R\}]$ [74a]. Stepwise reduction of the C≡N triple bond occurring at two different metal centres has been attempted [74b] with the bimetallic azavinylidene complex $[(CO)(PPh_3)_2Re(\mu\text{-H}_2\{\mu\text{-H}{=}C(H)Ph\}Ru(PPh_3)_2(PhCN)]$, obtained by insertion of PhCN into a metal–hydrogen bond (see Section 3.2) [47], upon reaction with $HBF_4 \cdot Me_2O$ to generate $[(CO)(PPh_3)_2Re(\mu\text{-H})_2\{\mu\text{-}\eta^1,\eta^2\text{-N(H)}{=}C(H)Ph\}Ru(PPh_3)_2(PhCN)][BF_4]$, containing an imine ligand, which is σ-bonded to the Re atom and π-bonded to Ru [74b]. Attempted reduction of the imine ligand by a nucleophile (H^- or CN^-) failed, regenerating the starting azavinylidene complex; under pressure of H_2 (50 atm.), the imine complex slowly converts into $[(CO)(PPh_3)_2HRe(\mu\text{-H})_3Ru(PPh_3)_2(PhCN)][BF_4]$, liberating benzylamine [74b].

Characterization of intermediates in the —C≡N nitrile reduction promoted by metal monomers remains rare. The reduction of t-BuCN by the amido complex $[Cp^*_2Sc\{NHCH_2Bu\text{-}t\}]$, derived by initial insertion of t-BuCN into the Sc—H bond of $[Cp^*_2ScH]$ and subsequent treatment with H_2 [17], in the presence of molecular hydrogen (4 atm), proceeds at 80 °C for a few turnovers to liberate $t\text{-BuCH}_2NH_2$. The formation of the amine is accounted for by a stepwise addition of dihydrogen across the Sc—N bond. The conversion of acetonitrile to ethylamine results when $[Ru(NCMe)_3(triars)]^{2+}$ (triars = $MeC(CH_2AsPh_2)_3$) is treated with $NaBH_4$ in MeOH as $[RuH(NH_2CH_2Me)_2(triars)]^+$ forms [75]:





Scheme 6.

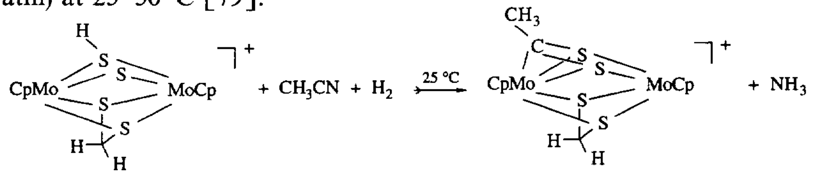
The formation of the amine is accounted for by an initial nucleophilic attack of H^- to the nitrile carbon atom, which is activated by coordination of the nitrile to the electron-withdrawing metal centre; then repetitive addition of a hydride to the β-carbon atom and then a proton to the nitrogen atom would yield the observed product. It is interesting to note that $[RuCl(MeCN)_3(dppb)]^+$ was found to be catalytically active in the homogenous hydrogenation, under base-assisted conditions, of MeCN to ethylamine under relatively mild conditions [76].

An unusual reduction of CH_3CN to an imido ligand has been found to occur on addition of $Ba(CF_3SO_3)_2$ to the coordinated acetonitrile in *trans*-[CrCl(NCMe)(dmpe)$_2$][BPh$_4$], which yields *trans*-[CrCl(=NEt)(dmpe)$_2$][CF$_3$SO$_3$], whose structure has been confirmed by X-ray crystallography [77]. A mechanism for this conversion has been proposed to involve oxidative addition of MeOH to afford a hydrido–methoxo complex; hydride transfer to an intermediate η^2-CH_3CN species affords initially {Cr—N=C(H)Me}, which gives {Cr≡N—CH$_2$CH$_3$} by a second hydride transfer from the methyl group of the coordinated methoxide with elimination of formaldehyde. A similar reduction by MeOH has been reported for *trans*-[MoCl(η^2-NCMe)(dmpe)$_2$]$^+$ to give *trans*-[MoCl(NEt)(dmpe)$_2$]$^+$ [5].

In an elegant study, Feng and Templeton have reported the stereoselective stepwise reduction of acetonitrile using chiral [Tp′(CO)(RC≡CR)W]$^+$ (R = Ph, Me) templates [78]. The stepwise reduction [78b] of the nitrile has been accomplished by sequential addition of nucleophiles and electrophiles to the C≡N triple bond as summarized in Scheme 7.

The intermediate azavinylidene, imine, amido and amine metal complexes have all been isolated and characterized. Notably, addition of a second nucleophile (e.g. CN^-), at the imine stage, is highly stereoselective, as the nucleophile attacks from only one face of the imine ligand. Acidification of the amine ligand in acetonitrile in the last step frees the ammonium salt and regenerates the acetonitrile adduct.

It is also interesting to note that the reductive cleavage of the carbon–nitrogen triple bond in nitriles (and isonitriles) to give ammonia has been achieved by a sulphido-bridged dinuclear molybdenum complex in the presence of hydrogen (1–2 atm) at 25–50 °C [79]:



(24)

This reaction, which is of possible significance for the mechanism of nitrogenase enzymes in the reductive cleavage of the carbon–nitrogen triple bond in nitriles and isonitriles, appears to proceed by initial nitrile insertion into the S—H bond.

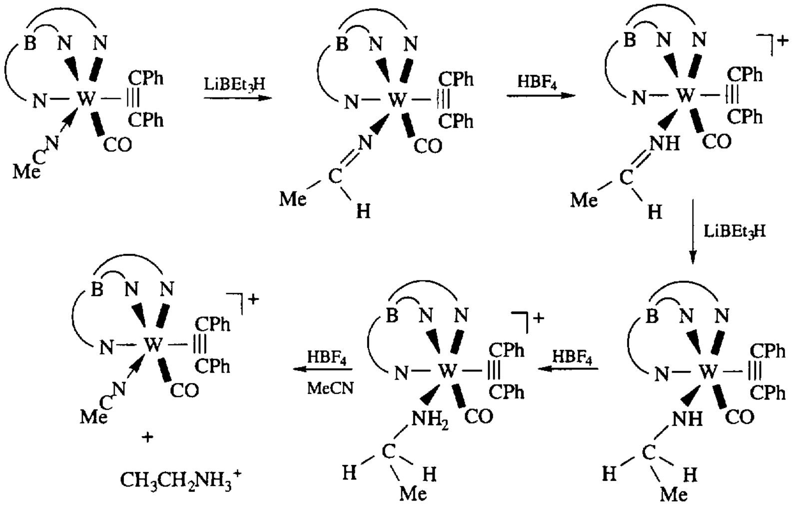
7. Nucleophilic attack

Coordination of nitriles to electron-withdrawing transition metal ions results in an enhanced electrophilicity of the nitrile carbon, thus making it susceptible to nucleophilic attack. Although reactions of metal nitriles with protic nucleophiles such as water, alcohols and amines to generate the corresponding amidates, imido esters and amidines respectively (Scheme 8) have been exploited and broadly established [1b], herein further development of this chemistry will be described.

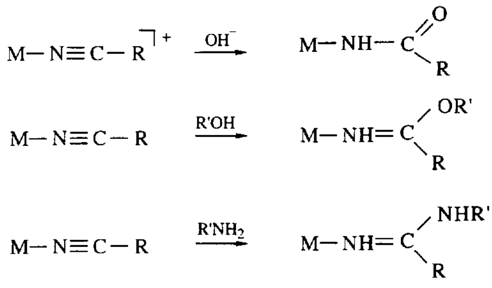
7.1. Reactions with protic nucleophiles

7.1.1. Water–hydroxide

The kinetics and mechanism of the base-catalysed hydrolysis of pentaammine nitrile complexes of the type $[M(NH_3)_5(NCR)]^{3+}$ (M = Rh, Ir, Co, Ru) to give the



Scheme 7.



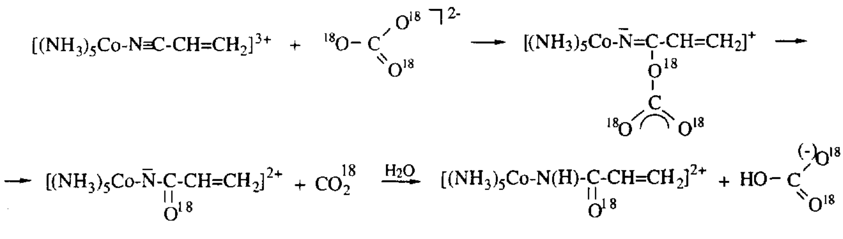
Scheme 8.

corresponding amidate complexes have been extensively investigated [80]:

$$[M(NH_3)_5(NCR)]^{3+} + OH^- \rightarrow [M(NH_3)_5\{N(H)C(=O)R)\}]^{2+} \qquad (25)$$

As a general feature, the hydrolysis of nitriles by OH^- in aqueous solution is greatly enhanced by coordination of RCN as demonstrated by the 10^6–10^8-fold increase in the rate of the hydrolysis compared to the uncoordinated ligand. The base hydrolysis (Eq. (25)) is generally thought to proceed by initial external OH^- attack to the electrophilic nitrile carbon atom, as indicated by the first-order dependence on OH^- concentration of the rate law; electron-releasing substituents on the nitrile group can retard this reaction. The acid hydrolysis of organonitriles proceeds much more slowly [81] but with a similar mechanism, except that H_2O is the attacking nucleophile. Similar direct attack of nucleophiles occurs also in the hydrolysis of the CN group of acrylonitrile in $[Co(NH_3)_5(N{\equiv}C{-}CH{=}CH_2)]^{3+}$ in carbonate buffer medium ($k_{obs} = k_1[OH^-] + k_2[CO_3^{2-}]$, with $k_1 = 35k_2$ at 25 °C). ^{18}O tracer studies [80a] indicate that the mechanism of hydrolysis by carbonate ion involves direct nucleophilic attack at the nitrile group by CO_3^{2-} with subsequent elimination of CO_2 (Scheme 9).

Deviation from a first-order rate equation has been reported [80b] for the base hydrolysis of $[Ir(NH_3)_5(NCMe)]^{3+}$; the second-order term in the rate equation $k_{obs} = k_1[OH^-] + k_2[OH^-]^2$ is attributed to the partial formation of the amido complex $[Ir(NH_3)_4(NH_2)(NCMe)]^{2+}$ as a result of attack of OH^- to a coordinate NH_3 molecule. Significant departures from expected rates have also been reported to occur for a number of pentaammine functionalized nitrile complexes of Co(III) [80c,80d], as a consequence of cyclization following the hydrolysis of phthalonitrile [80c,80d] and *ortho* group participation of 2-carboxamidobenzonitrile [80c].

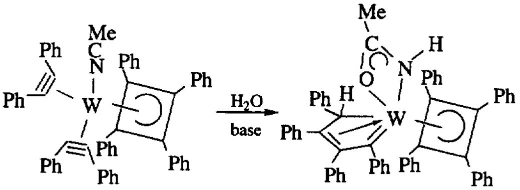


Scheme 9.

The factors that influence the N- vs. O-bonding mode of amides in pentaamminecobalt(III) complexes and the kinetics and mechanism of rearrangement have been reported [80f].

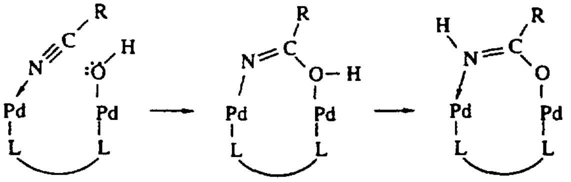
The hydrolysis of organonitriles to amidates has been described in several different studies, but the structural characterization of the resulting products has been achieved in a limited number of cases. The hydrolysis of acetonitrile in *cis*-[$PtCl_2(NCMe)(DMSO)$] gave green crystals of [$PtCl_2(\mu$-$NHCOMe)(DMSO)]_2$, containing bridging acetamido ligands, which was structurally characterized and is believed to be an analogue of "platinblau" [82]. The hydrolysis of Pt(II)-coordinated nitriles to give terminal amidates has been reported by Natile and co-workers [83]. The reactions of mono- and bis-nitrile complexes (K)[$PtCl_3(NCR)$] and *cis*- and *trans*-[$PtCl_2(NCR)_2$] (R = Me, Ph, Bu-*t*) with stoichiometric amounts of KOH(aq) or with an excess of KOH in dichloromethane respectively gave the amidate complexes (K_3)[$PtCl_3\{HN{=}C(O)R\}$] and (K_2)[$PtCl_2\{HN{=}C(O)R\}_2$] respectively, which are converted to the amide derivatives by treatment with aqueous HCl [83b]. The amide ligands generally adopt the enol form, HN=C(OH)R. The presence of two amides cis to one another plays a critical role in favouring the association of platinum units in dimers, as shown in the X-ray structure of *cis*-[$PtCl_2\{HN{=}C(OH)Bu$-$t\}_2$], which comprises two monomeric units, placed face to face, with a weak Pt—Pt distance of 3.165(1) Å and four interplanar N—H···Cl hydrogen bonds [83b].

In the case of the cyclobutane complex [$W(\eta^4$-$C_4Ph_4)(C_2Ph_2)_2(CH_3CN)$] the hydrolysis in alkaline solution leads to not only hydration of the acetonitrile ligand but also alkyne–alkyne coupling to generate a metallacyclic complex [$W(\eta^4$-$C_4Ph_4)(\eta^4$-$C_4Ph_4H)(\eta^2$-$CH_3C(O)NH)$] (Eq. (26)), which was structurally characterized and showed to contain the acetamido ligand η^2 coordinated to W [84].



(26)

Formation of amidate complexes has been obtained also by OH^- or H_2O addition in other nitrile complexes such as *cis*-[$Pt(C_6X_5)_2(NCPh)_2$] (X = F, Cl) [85], *cis*-[$Pd(o$-$CH_2C_6H_4CN)L_2][BF_4]_2$ (L = 2PPh$_3$, diphosphine) [86] or Ni(II) complexes with cyanopyridine [87]. The nitrile ligands in these complexes have been also shown to react with alcohols [85–87], amines [86] and thiols [86]. The hydration of nitriles has been reported to be facilitated in the complex [$LPd_2(OH)]_{3-4}$ (L = binucleating ligand) [88], which reacts with nitriles at room temperature to give the corresponding amidate bound at the dipalladium site. It is proposed that the nitrile hydration proceeds via an intermediate in which the nitrile is bound to one palladium centre and the nucleophilic hydroxide is held in close proximity, bound to the second palladium, thus facilitating the C—O bond formation.



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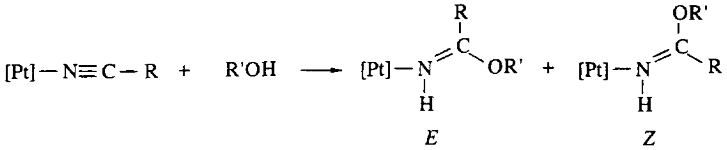
7.1.2. Alcohols

A wide series of reactions with hydroxide [83], alcohols, amines and aprotic nucleophiles have been carried out using the bis(nitrile) Pt(II) complexes *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = various alkyls and aryls), which have been prepared by either treating an aqueous solution of K_2PtCl_4 with an excess of RCN or heating solid $PtCl_2$ in neat RCN [89]. Both procedures give rise to a mixture of cis and trans isomers in different ratios depending on the experimental conditions such as the reaction temperature and the reaction time; the cis isomer is favoured at lower temperature and shorter reaction times. The separation of the stereoisomers can be achieved by fractional crystallization [89b,89c] by taking advantage of the generally higher solubility of the trans species in non-polar solvents [89c], but complete separation can be accomplished by chromatography [89b]. The IR [89b,89c], ^1H NMR [89b,89c] and ^{13}C NMR [89c] data have been reported; the IR data exhibit positive values of $\Delta\nu = \nu(C{\equiv}N)_{coord} - \nu(C{\equiv}N)_{free} = \approx 50\ cm^{-1}$, indicating the susceptibility of the nitrile carbon to nucleophilic attack. The number of the Pt—Cl stretchings are not always diagnostic of the stereochemistry of these complexes [89b,89c]. However, the stereoisomers display different values of $^2J_{PtC}$ in their ^{13}C NMR spectra [89c]; the cis isomers have lower values (218–234 Hz) than the corresponding trans species (273–298 Hz) in agreement with the higher trans influence of chloride compared with the nitrile ligand.

The reactions of *cis*- and *trans*-$[PtCl_2(NCPh)_2]$ with MeOH occur at ambient temperature in the presence of a catalytic amount of KOH and proceed stepwise to give the mono and bis imido ester derivatives *cis*- and *trans*-$[PtCl_2(NCPh)\{HN{=}C(OMe)Ph\}]$ and *cis*- and *trans*-$[PtCl_2\{HN{=}C(OMe)Ph\}_2]$ respectively [90]. The imido ester ligand is present in *E* and *Z* conformations, corresponding to cis and trans addition of the alcohol to the C≡N triple bond.



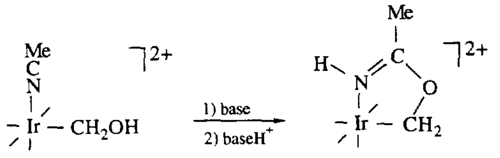
$$[Pt]{-}N{\equiv}C{-}R + R'OH \longrightarrow \underset{E}{[Pt]{-}\underset{H}{N}{=}\overset{R}{C}{-}OR'} + \underset{Z}{[Pt]{-}\underset{H}{N}{=}\overset{OR'}{C}{-}R} \qquad (28)$$

The rate of interconversion of the isomers is slow under normal conditions, but it becomes faster in the presence of a catalytic amount of ^-OMe, which adds reversibly to the azomethine residue of the imido ester group [90].

A wide series of reactions of alcohols and amines have been reported [91] with the Ni(II) nitrile complexes $[NiL(NCR)][ClO_4]$ (L = an *S*,*N*,*N* tridentate anion;

R = Me, Ph, Et). The complexes react under reflux with dry alcohols R′OH (R′ = Me, Et, *n*-Pr) to give the corresponding imido ester complexes [NiL{NH=C(OR′)R}][ClO$_4$] [91a] and the kinetics and mechanism of these reactions have been investigated [91b]. If the alcohol used is wet, the product is an amido complex [NiL(NH$_2$COR)][ClO$_4$], which results on attack of water on the amidate ligand rather than direct attack on the nitrile carbon. Secondary amines react to form the amidine complexes [NiL{NH=C(NR′$_2$)R}][ClO$_4$] [91a], but with primary amines both addition to and substitution of the nitrile take place; with other nucleophiles such as H_2O, NH_3, pyridine, PPh_3, $Ph_2PCH_2CH_2PPh_2$ and some anions (N_3^-, CN^-, NCO^-) only the displacement of the nitrile occurs.

The hydroxymethyl complex $[Ir(CH_2OH)(MeCN)(PMe_3)_4]^{2+}$ undergoes base-catalysed intramolecular attack by the oxygen atom of the hydroxymethyl group to form a metallacyclic complex, which has been structurally characterized [92]:



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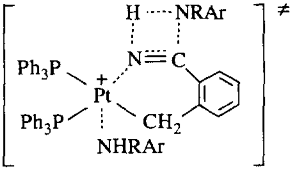
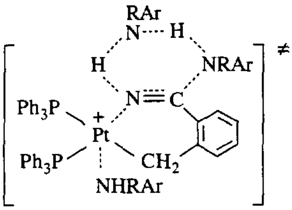
7.1.3. Amines

The kinetics and mechanism of nucleophilic attack of amines on coordinated nitriles have been investigated in a limited number of cases and, specifically, with the dimeric *o*-cyanobenzyl Pt(II) complex [Pt(μ-*o*-$CH_2C_6H_4CN$)(PPh_3)$_2$]$_2$[BF$_4$]$_2$ (**5**) [93] and the bis(nitrile) complexes *cis*-[PtCl$_2$(NCAr)]$_2$ (**6**) (Ar = Ph [94a]; Ar = *o*-, *m*- or *p*-$CH_3C_6H_4$ [94b]).

The reaction of the dimeric *o*-cyanobenzyl complex **5** with primary anilines ArNH$_2$ (Ar = Ph, *p*-MeC$_6$H$_4$, *p*-OMeC$_6$H$_4$) to form monomeric amidino complexes *cis*-[Pt{*o*-$CH_2C_6H_4$C(=NH)(NHAr)}(PPh$_3$)$_2$][BF$_4$] in 1,2-dichloroethane is a two-stage process [93a]. The first, rapid stage involves displacement of the nitrile group by the entering amine leading to a labile mononuclear amino complex bearing a dangling —CN group. This intermediate reacts with the amine in the second slower stage via external nucleophilic attack of the amine nitrogen atom on the nitrile carbon atom in a cyclic four-centre transition state $I^{\neq}$ to yield the final Pt(II)–amidino species: this mechanism is consistent with the rate expression of the second step which is of the type rate = k_2[complex][amine].



$I^{\neq}$

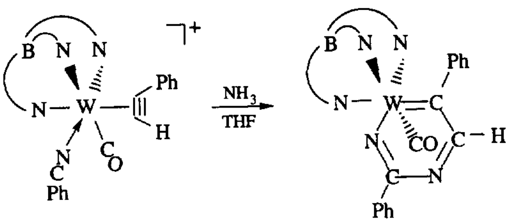


$II^{\neq}$

Similar reactions carried out for **5** with secondary anilines [93b] Ar(R)NH (Ar = *p*-MeC_6H_4, *p*-$OMeC_6H_4$; R = Me, Et) involve the same first stage, but the second step is found to obey a two-term rate expression of the form rate = k_2[complex][NHRAr] + k_3[complex]$[NHRAr]^2$. While the first-order dependence in the rate law has been explained by the same mechanism suggested previously for the reactions of primary anilines, the second-order term in amine concentration has been explained on the basis of rapid pre-equilibrium formation of an aniline dimer which adds to the nitrile via a six-membered cyclic activated complex $\mathbf{II}^{\neq}$. This mechanism has been also proposed for the reactions of primary amines RNH_2 (R = *n*-Pr, *n*-Bu) with type **6** complexes. Two reaction steps are observed: the product of the first reaction is the amidine complex *trans*-$[PtCl(NH_2R)\{NH{=}C(Ar)(NHR)\}_2]^+$ which, in the second reaction, undergoes replacement of coordinated Cl^- by amine. The kinetics of these reactions were studied in chloroform using *n*-butylamine as reacting nucleophile. For the first reaction the observed rate law is of the form rate = k_3[complex]$[RNH_2]^2$, while the second reaction follows the expected second-order kinetic behaviour. The second-order dependence on amine concentration in the first reaction has been accounted for by a rate-determining step similar to that mentioned above for the *o*-cyanoalkyl reactions [93b], which involves attack by amine dimer on the carbon atom of one of the nitrile ligands. Subsequent rapid steps involving addition of amine to the second nitrile, replacement of Cl^- (trans to the amidine ligand) by amine and isomerization lead to the product of this first reaction. Electronic and steric effects influence the reactions of amines on Pt(II)-coordinated nitriles [94b] as shown in the kinetic investigation of coordinated tolunitriles with *n*-butylamine; the observed order of reactivity is PhCN > *p*-MeC_6H_4CN > *m*-$CH_3C_6H_4CN$ > *o*-C_6H_4CN. The reduced reactivity of *p*-tolunitrile relative to benzonitrile may be attributed to a positive inductive effect of this group which would reduce the partial positive charge of the nitrile carbon, making it less susceptible to nucleophilic attack. For the *m*- and *o*-tolunitrile derivatives, steric hindrance of the methyl group causes a further reduction in the observed rate constant.

The reactions of bidentate amines with coordinated nitriles have been reported. Nucleophilic attack of one end of the diamine on the coordinated nitrile precedes coordination of the second amino group to the metal as observed, for instance, in the reactions of the trans and cis isomers of $[PtCl_2(NCPh)_2]$ with *N,N′*-di-*tert*-butylethylenediamine(*t*-Bu_2en) to give under normal conditions the cationic [Pt{NH=C(Ph)N(*t*-Bu)CH_2CH_2NH(*t*-Bu)}Cl(NCPh)][Cl] and neutral *cis*-[$PtCl_2${NH=C(Ph)N(*t*-Bu)CH_2CH_2NH(*t*-Bu)}(NCPh)] complexes respectively, the latter having been structurally characterized [83a]. In both cases one end of the diamine adds to benzonitrile yielding an amino–amidine ligand which is chelated in the first complex giving rise to a seven-membered metallacycle and monocoordinated in the second complex. The residual benzonitrile in the cationic complex reacts with OH^- to give a benzamidate species [Pt{NH=C(Ph)N(*t*-Bu)CH_2CH_2NH(*t*-Bu)}Cl(NHCOPh)], which has been structurally characterized, while the neutral derivative exhibits in solution isomerization about the azomethine double bond ($\Delta G^{\neq} = 10.8 \pm 0.3$ kcal mol^{-1}) and slowly undergoes an internal rearrangement with substitution of the residual benzonitrile by the uncoordinated end of the diamine and formation of [Pt{NH=C(Ph)N(*t*-Bu)CH_2CH_2NH(*t*-Bu)}Cl_2]. Seven-membered amino–amidine chelating ligands have also been prepared by reaction of the diruthenium(III) complex $[Ru_2O(O_2CAr)_2(MeCN)_4(PPh_3)_2][ClO_4]_2$ [95] with 1,2-diaminoethane in MeOH, where two facial MeCN ligands undergo nucleophilic attack yielding the complex $[Ru_2O(O_2CAr)_2\{NH_2CH_2CH_2NHC(Me)NH\}_2(PPh_3)_2][ClO_4]_2$, containing two seven-membered amino–amidine chelating ligands, which has been structurally characterized.

Cationic amidine complexes of the type $[Tp'(CO)(PhC{\equiv}CR'')W\{NH{=}C(R)NHR'\}][BF_4]$ (R = Me; R′ = H, Ph; R″ = Me, H) are formed by reaction of $[Tp'(CO)(PhC{\equiv}CR'')W(N{\equiv}CR)][BF_4]$ with amines NH_2R' [96]. These reactions reflect net addition of H—NHR′ across the nitrile triple bond in contrast with the stepwise nucleophile–electrophile sequence reported previously for the reduction of a coordinated nitrile to amine [78b]. The solid state structure of $[Tp'(CO)(PhC{\equiv}CH)W\{NH{=}C(Me)NH_2\}][BF_4]$ shows that trans $H{-}NH_2$ addition across the carbon–nitrogen triple bond has occurred. The alkyne ligand in the nitrile or the amidine complexes is subject to intramolecular nucleophilic attack to form metallacyclic–carbene–imine complexes as found, for instance, in the reaction the benzonitrile derivative with NH_3 in THF:



The reaction is likely to proceed with the initial formation of the amidine derivative $W{-}NH{=}(Me)NH_2$; subsequent deprotonation at NH_2, attack of a nitrogen lone pair to couple with the alkyne terminal site and net H_2 loss would lead to the formation of the observed product.

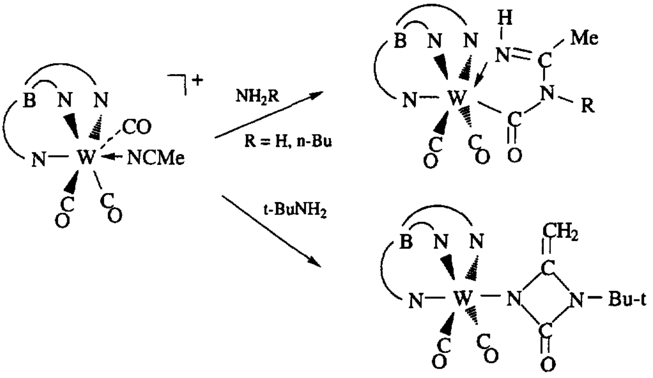
An amine-induced coupling of carbonyl and nitrile ligands to give heteroatom metallacycle complexes was shown [97] to occur on treatment of the W(II) complex $[Tp'(CO)_3W(NCMe)][BF_4]$ with ammonia or *n*-butylamine; however, the analogous reaction with the bulky *t*-butylamine leads to the formation of an unusual four-membered cyclic amido ligand (Scheme 10).

Finally, it is worthwhile to mention the formation of amidines and guanidines from the reactions of NH_3 with nitrile and (substituted)cyanamide complexes of Co(III) of the type $[Co(NH_3)_5(NCR)]^{3+}$; the acid–base properties and solution structures of such complexes have been reported [98].

7.2. Catalytic hydration

Intensive research efforts have been devoted to developing metal catalysts for the hydration of nitriles to amides and for the regioselective hydration of α-unsaturated nitriles, particularly the hydration of acrylonitrile to acrylamide [99].

$$R{-}C{\equiv}N + H_2O \xrightarrow{cat.} RCONH_2 \qquad (31)$$



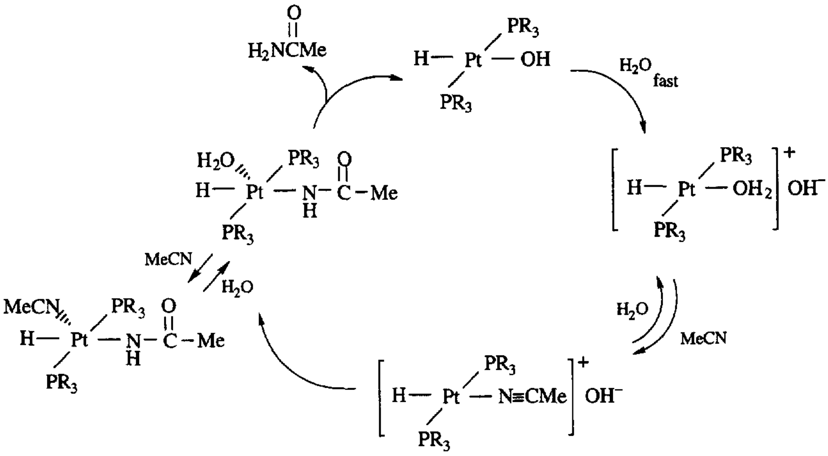
Scheme 10.

Of relevance are some Pt(II) complexes such as the hydrido species *trans*-[$PtHCl(PR_3)_2$] (R = Me, Et) [99], the hydroxo *trans*-[$PtR(OH)L_2$] and acetamido *trans*-[$PtR(NHCOR')L_2$] (R = Me, Ph; L = various tertiary alkyl and/or aryl phosphine) complexes [100] and some Pt(0) complexes such as [$Pt(PCy_3)_2$] and [$Pt(P-i\text{-}Pr)_3)_3$] [101], which have been investigated in the homogeneous catalytic conversion of nitriles to acetamides. Other homogeneous systems, which have been shown to be active catalysts for this process, are, for instance, the complexes [$Rh(OH)(CO)(PPh_3)_2$] [102a], [$PdCl(OH)(bipy)(H_2O)$] [102b] and $K_2PdCl_4(bipy)NaOH$ [102b].

A detailed study on the kinetics and mechanism of the catalytic hydration of acetonitrile to acetamide has been reported by Jensen and Trogler [99] using *trans*-[$PtHCl(PR_3)_2$] (R = Me, Et) in the presence of 1 equiv of NaOH; metathesis in 50–50 CH_3CN–H_2O solutions yields a catalyst, namely *trans*-[$PtH(H_2O)(PR_3)_2$][OH], for the hydration of acetonitrile to acetamide with a rate higher than that of any other previously known catalytic systems at 80 °C [100–102]. The catalytic cycle [99] is summarized in Scheme 11 and the catalytic intermediates [$PtH(H_2O)(PEt_3)_2$]$^+$, [$PtH(N{\equiv}CCH_3)(PEt_3)_2$]$^+$ and [$PtH\{NHC(O)Me\}(PEt_3)_2$] have been spectroscopically detected and characterized and their interconversions demonstrated.

Rates of catalysis were independent of [OH^-] at a pH greater than 10 and proton transfer from solvating water to coordinated *N*-carboxamido, rather than nucleophilic attack of hydroxide on coordinated nitrile, limits the rate; at pH ≈ 8.5, a linear dependence of the catalytic rate on [OH]$^-$ was found, which is consistent with a nucleophilic attack of hydroxide on the coordinate nitrile. The calculated rate constants for the nucleophilic attack by OH^- are greater (11–7000) than those found in studies of the rate of stoichiometric base hydrolysis of Ru-, Rh- and Co-coordinated nitriles [103] and this may be attributed to higher temperatures (80 vs. 25 °C) as well as to decreased steric barriers in the unhindered Pt(II) complexes.

These catalysts remain active for days and exhibit appreciable catalytic activity even at 25 °C; the catalytic activity of the PMe_3 derivative is higher than the



Scheme 11.

corresponding PEt_3 species. This latter feature parallels the behaviour observed for some alkyl [100,101], aryl [100] and hydrido [101] hydroxo bis(phosphino) complexes of Pt(II) for which the catalytic activities in the nitrile hydration increase with decreased steric bulk of the phosphine ligands and increased electron-donating ability of the group trans to hydroxide, i.e. hydride > alkyl, aryl. The $[PtH(H_2O)(PMe_3)_2]^+$ derivative [99] catalyses the hydration of acrylonitrile but exhibits low regioselectivity between the olefin and the nitrile functionalities at 80 °C, while at 25 °C displays a regioselectivity of 97% in the hydration of acrylonitrile to acrylamide. The hydration of the nitrile group of acrylonitrile is likely to proceed [99] by the same mechanism as for acetonitrile, while studies on the catalytic hydration of the olefinic group indicate that it proceeds through a Pt(II)-coordinated olefin intermediate, and OH^- attack to form a σ-bonded $Pt-CH(CN)CH_2OH$ ligand, followed by reductive elimination of the hydride and $-CH(CN)CH_2OH$ groups with formation of 2-cyanoethanol and a Pt(0) species, which is then converted to $[PtH(OH)(PMe_3)_2]$ by oxidative addition of water, a known process for Pt(0) complexes [101].

As previously mentioned, the acetamido $[PtR(NHCOMe)(PR_3)_2]$ [100], the hydroxo complexes $[PtR(OH)(PR_3)_2]$ [100] (R = Me, Ph) and, particularly, the Pt(0) complexes $Pt(P-i\text{-}Pr_3)_3$ and $Pt(PCy_3)_2$ [101] are also active catalysts for the conversion of nitriles, including acrylonitrile, to the corresponding amides and the mechanisms of the corresponding catalytic cycles have been proposed; in all cases, the formation of a carboxamido, Pt—NHCOR, by attack of OH^- on the coordinated nitrile is considered.

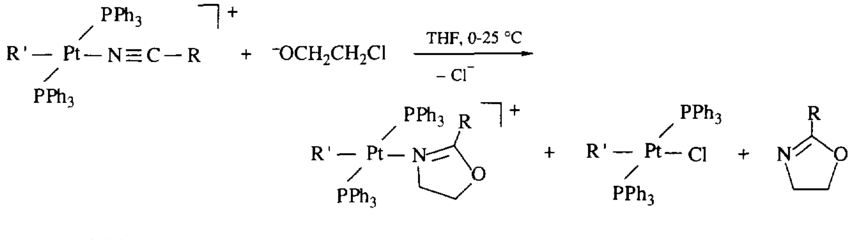
7.3. Synthesis of heterocycles

Following previous studies on CNR [104] and CO [104] ligands in transition metal isocyanide and carbonyl complexes, a detailed investigation on the cyclization reactions of nitrile ligands in Pt(II) complexes by haloalcohols $HO-(CH_2)_n-Cl$ ($n = 2$, 3) and the three-membered heterocycles $\overline{YCH_2CH_2}$ (Y = O, NH) to afford

N-heterocycles has been recently reported. It was found that both nitrile ligands in the complexes *cis*- and *trans*-$[\mathrm{PtCl_2(NCR)_2}]$ react under mild conditions with 2 equiv of $^{-}\mathrm{OCH_2CH_2Cl}$ to produce in good yield five-membered 2-oxazoline derivatives *cis*- and *trans*-$[\mathrm{PtCl_2}\{\overline{\mathrm{N{=}C(R)OCH_2C}}\mathrm{H_2}\}_2]$ [105]. Scheme 12 describes the proposed mechanism for these reactions. The attacking haloalkoxide ion can be generated by reaction of 2-chloroethanol with a base (usually *n*-BuLi) (route (a)) or by ring opening of oxirane on reaction with $\mathrm{Cl^-}$ ions (route (b)).

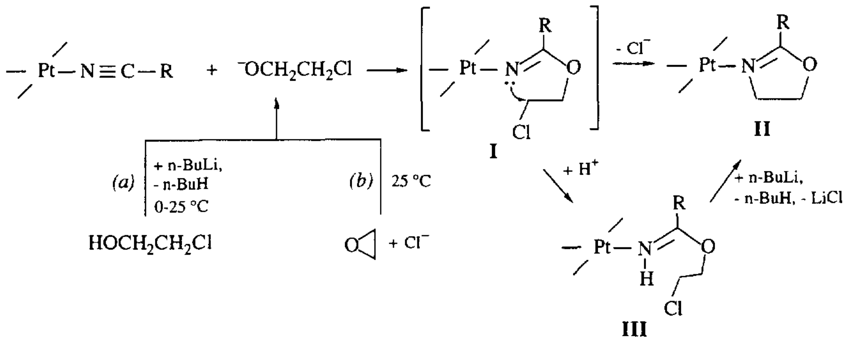
Further steps involve nucleophilic attack of the haloalkoxide ion to the nitrile carbon atom to give intermediate **I**, which rearranges to the 2-oxazoline product **II** by intramolecular cyclization or it undergoes proton addition (from 2-chloroethanol solvent) to afford the imido ester **III**, which is then converted to **II** on treatment with a base. The species **III** could be isolated when the reaction was performed in the presence of a low alkoxide concentration (Pt:alkoxide < 1:0.2) and the conversion of **III** to **II** was proved. The bis(oxazoline) complex *cis*-$[\mathrm{PtCl_2}\{\overline{\mathrm{N{=}C(Ph)OCH_2C}}\mathrm{H_2}\}_2]$ was structurally characterized and showed that the two oxazolines are almost planar with an extensive electron delocalization within the N—C(Ph)—O ring system. The generality of the reaction chemistry illustrated in Scheme 12 has been also explored in the reaction of $\mathrm{HOCH_2CH_2Cl}$ under basic conditions with *cis*- and *trans*-$[\mathrm{PtCl_2(NCR)_2}]$ complexes (R = various alkyls and aryls) in which the steric and electronic properties of the R groups of the nitriles have been varied over a wide range to afford 2-oxazoline complexes [106]. It is generally found that the nitrile to 2-oxazoline conversion proceeds without isomerization at the metal centre and no difference has been found in the reactivity of an alkyl compared with an aryl nitrile ligand since the corresponding oxazolines are obtained in comparable yields and reaction times [106].

The reactions of $^{-}\mathrm{OCH_2CH_2Cl}$ with the cationic nitrile complexes *trans*-$[\mathrm{Pt(R')(NCR)(PPh_3)_2}][\mathrm{BF_4}]$ ($\mathrm{R' = H, CH_3, CF_3}$; R = alkyl, aryl) proceed similarly to those already described for the neutral complexes, but with some significant differences [107] as shown in



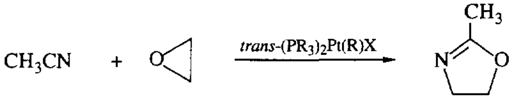
(32)

The nucleophilic attack of $^{-}\mathrm{OCH_2CH_2Cl}$ at the nitrile carbon atom affords the coordinated oxazoline, by a mechanism that has been illustrated in Scheme 12, with liberation of a $\mathrm{Cl^-}$ ion. The oxazoline is then replaced by $\mathrm{Cl^-}$, probably by an associative pathway as is common in reactions of square planar Pt(II) complexes, with the formation of the neutral halide complex *trans*-$[\mathrm{PtCl(R')(PPh_3)_2}]$. This last process was also independently confirmed by reacting the isolated oxazoline compounds with chloride ions to yield quantitatively the chloro derivatives and the corresponding free oxazolines [107].



Scheme 12.

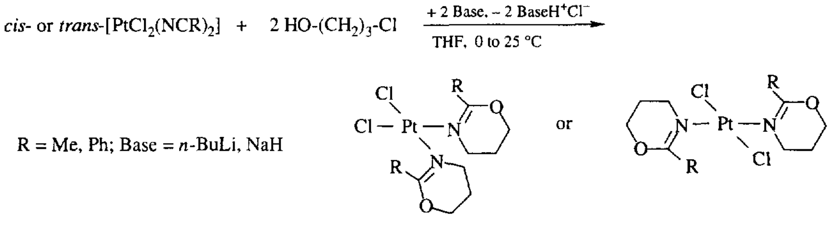
The stoichiometric synthesis of 2-oxazolines from cationic Pt(II) nitrile complexes described in Eq. (32) has suggested [107] that these heterocycles might be also formed catalytically using Pt(II) species according to the general reaction



(33)

where the metal has a bifunctional role of nitrile activator and also source of X^- ion, this latter being necessary for the ring opening of oxirane. The formation of 2-(methyl)oxazoline from acetonitrile in the presence of oxirane and LiBr was observed using Pt(II) complexes such as *trans*-$[PtBr(CH_3)(PEt_3)_2]$ and *trans*-$[PtBr(CF_3)(PMe_2Ph)_2]$ with a complex:CH_3CN:$\overline{OCH_2CH_2}$ molar ratio of 1:500:200 at 75 °C for 120 h and 36 h respectively, but the conversion of MeCN to oxazoline was not found to be catalytic, the oxazoline being formed in an almost stoichiometric amount with respect to the complex [107]. These poor results were explained either by an unfavourable equilibrium $\overline{OCH_2CH_2}+Br^- \rightleftharpoons {}^-OCH_2CH_2Br$ or by this reaction being very slow; furthermore, the low observed conversion is probably affected by a possible competitive nucleophilic attack of ${}^-OCH_2CH_2Br$ on the metal centre with subsequent reductive elimination processes, which are known to occur for Pt(II)–alkoxo systems [108].

The nitrile ligands in the neutral complexes *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (cis, R = Me, Et, *t*-Bu, Ph; trans, R = Me, Ph) can be also converted to the corresponding 1,3-oxazine derivatives *cis*- and *trans*-$[PtCl_2\{\overline{N{=}C(R)OCH_2CH_2CH_2}\}_2]$, by reaction with 2 equiv of ${}^-OCH_2CH_2CH_2Cl$ generated by deprotonation of 3-chloro-1-propanol with a base [109]:

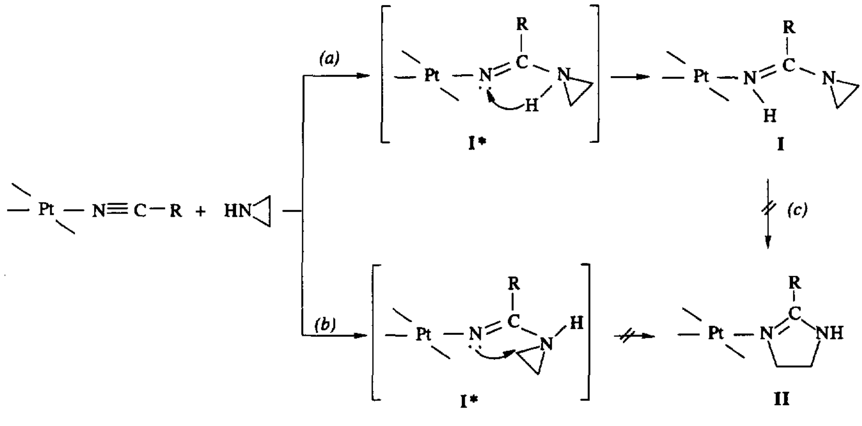


(34)

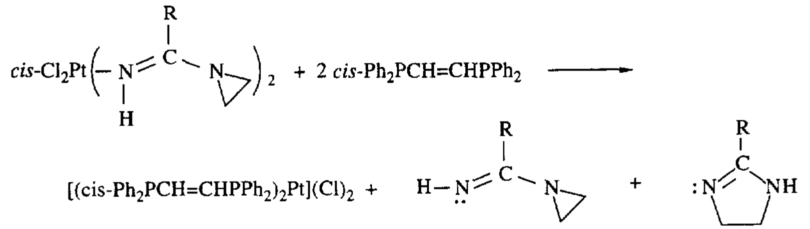
When the cationic nitrile complexes *trans*-$[Pt(CF_3)(NCR)(PPh_3)_2][BF_4]$ (R = Me, Ph) are reacted with 1 equiv of $^{-}OCH_2CH_2CH_2Cl$ a mixture of products, including the corresponding oxazine derivatives *trans*-$[Pt(CF_3)\{\overline{N{=}C(R)OCH_2CH_2C}H_2\}(PPh_3)_2][BF_4]$, the chloro complex *trans*-$[PtCl(CF_3)(PPh_3)_2]$ and the free oxazine $\overline{N{=}C(R)OCH_2CH_2C}H_2$ are formed in a similar way to that described for the analogous oxazoline reactions (Eq. (32)). The complex *trans*-$[Pt(CF_3)\{\overline{N{=}C(Ph)OCH_2CH_2C}H_2\}(PPh_3)_2][BF_4]$, which is an intermediate in the formation of the free 1,3-oxazine, was also structurally characterized [109].

In contrast with the reactions of Pt(II)—CNR and —CO complexes with aziridine, $H\overline{NCH_2C}H_2$, which have been reported to afford five-membered cyclic carbene complexes [104d,104e], similar reactions with Pt(II) nitriles *cis*- and *trans*-$[PtCl_2(NCR)_2]$ afford the amidine complexes *cis*- and *trans*-$[PtCl_2\{NH{=}C(R)\overline{NCH_2C}H_2\}_2]$ (R = Me, Ph) [110]. An X-ray investigation carried out for *trans*-$[PtCl_2\{NH{=}C(Ph)\overline{NCH_2C}H_2\}_2]$ showed that the crystal consists of "dimers" $[Pt_2Cl_4L_4]$ (L = amidine ligand) formed by two $[PtCl_2L_2]$ units intermolecularly associated through four N—H···Cl hydrogen bond interactions involving the chlorine atoms and the amidinic proton. On the basis of previous mechanistic studies reported for the reactions of primary and secondary amines with Pt(II) nitriles complexes, these reactions are likely to proceed by nucleophilic attack of the amine on the nitrile carbon atom followed by hydrogen transfer to the nitrile amino nitrogen atom to yield the amidine derivative according to Scheme 13.

Of the two possible pathways, i.e. (a) (hydrogen transfer of the aziridine nitrogen to the imino ligand) or (b) (intramolecular ring closure by imino nitrogen attack to the aziridine ring), only the former occurs and this may be explained by the low nucleophilicity of the imino N atom being linked to a good electron-withdrawing Pt(II) ion. While the formation of 2-imidazolines by treatment of coordinated amidines with bases (path (c)) is not observed, these are, however, produced by reaction of the bis(amidine) dichloro Pt(II) complexes with a diphosphine such as *cis*-$Ph_2PCH{=}CHPPh_2$ [110]:



Scheme 13.

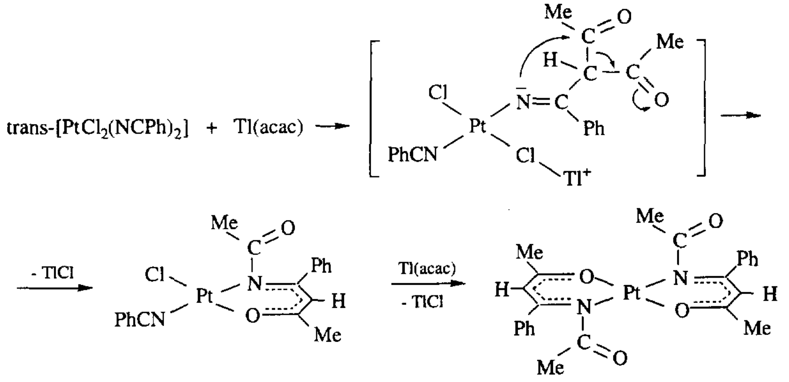


(35)

The formation of the heterocyclic ligand only on displacement of the coordinated amidine may be reasonably explained, as mentioned earlier, by the fact that in this process the electron-withdrawing Pt(II) fragment is being removed, thus making the amidino nitrogen atom sufficiently basic to attack intramolecularly the aziridine ring.

7.4. Reactions with aprotic nucleophiles

The reactions of coordinated nitriles with carbanions and azide ion have shown to produce metallacyclic and heterocyclic derivatives by initial attack at the nitrile carbon atom. Nakamura and co-workers [111] have found that *cis*- and *trans*-$[PtCl_2(NCPh)_2]$ react with 2 equiv of thallium(I) acetylacetonate in dichloromethane at room temperature to afford mainly β-ketoamine chelates:

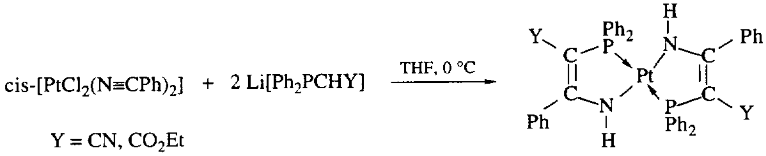


(36)

The suggested mechanism involves initial nucleophilic attack of the β-diketonate carbanion on the coordinated nitrile carbon atom, migration of the acetyl group to the bound nitrogen atom and then coordination of the residual carbonyl group to the metal to form the N,O-chelate ring, the last process being favoured by Cl^- abstraction by Tl^+. $[PtCl_2(NCPh)_2]$ is unreactive with acetylacetone, even at reflux, while these reactions with $[PdCl_2(NCPh)_2]$ take a different course, but do not involve attack at the nitriles [111c].

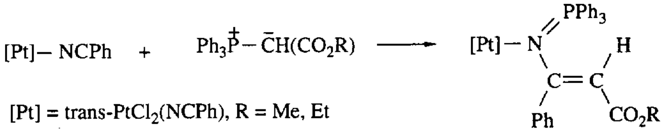
It is worthwhile noting that recently the reactions of β-dicarbonyls with nitriles leading to carbon–carbon bond formation based on the use of metal(II) centres as homogeneous catalysts has been recently reviewed [112].

The α-phosphino carbanions $Li[Ph_2PCHY]$ ($Y = CO_2Et$, CN) react with the coordinated nitrile ligands of *cis*-$[PtCl_2(PhCN)_2]$ to give the new bis-chelate (P,N) platinum complexes (Eq. (37)) via attack of the carbanion on the coordinated nitrile and cyclization through P coordination to the metal [113]; the structure of one of them ($Y=CO_2Et$) has been determined by X-ray diffraction [113b].



(37)

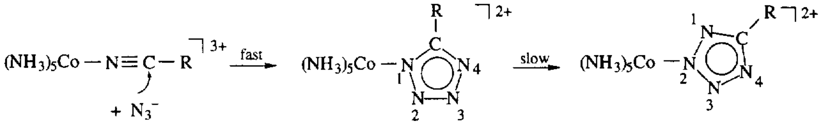
Although the reactions of ylids with transition metal nitrile complexes do not usually involve attack on the nitrile ligand [114], in one case it has been reported that the ylids $Ph_3P{=}CHCO_2R$ (R = Et, Me) react with *trans*-$[PtCl_2(NCPh)_2]$ in acetone at room temperature for 14 h to give in good yield the iminophosphorane complexes *trans*-$[PtCl_2\{E\text{-}N({=}PPh_3)C(Ph){=}C(H)CO_2R\}(NCPh)]$ (Eq. (38)); a stepwise mechanism, where attack of the ylidic carbon to the nitrile carbon is also involved, has been proposed for their formation [115].



(38)

Attack of cyanide ion on coordinated acetonitrile in the trinuclear cluster $[Os_3H(CO)_{10}(MeCN)(PMe_2Ph)][PF_6]$ has been reported to give $[Os_3H\{\mu\text{-}N{=}C(Me)CN\}(CO)_9(PMe_2Ph)]$ [116].

The conversion of organonitriles to tetrazolates has been exploited in several studies using different transition metal complexes and it occurs by a 1,3-dipolar cycloaddition either via nucleophilic attack of azide ion to a coordinated nitrile (Eq. (39)) [1b,117a] or from the reactions of azido complexes with RCN [117c].



(39)

The formation of tetrazolates in certain Co(III) and Ni(II) complexes is favoured with electron-deficient nitriles compared with electron-rich nitriles; for $[Co(NH_3)_5(NCR)]^{3+}$ (R = Ph, Me) it is found that benzonitrile is much more reactive than acetonitrile. As a general feature, in all these reactions the N-1 bonded tetrazole complex is initially formed, but it slowly isomerizes to the more stable N-2 bonded isomer. A study, using ^{15}N NMR as a mechanistic probe, of the linkage isomerization reaction of a tetrazole coordinated to pentaaaminecobalt(III) complexes has been recently reported [118a].

Templeton et al. have recently reported an interesting conversion of nitriles to nitrenes via azavinylidenes in low-valent tungsten carbonyl complexes [118b]. The neutral azavinylidene complexes of the type $[Tp'(CO)_2W\{N{=}C(Nu)R\}]$ (R = Me; Nu = H, Et, OMe) are formed by reaction of the corresponding cationic nitriles $[Tp'(CO)_3(N{\equiv}CMe)][BF_4]$ with the nucleophiles $LiBH_4$, EtMgBr or NaOMe, respectively. The W{N=C(H)R} azavinylidene complexes are also obtained by photolysis of [Tp′(CO)$_3$WH] with the appropriate nitrile in THF via insertion of the nitrile triple bond into the W—H bond as reported for other alkyl- hydrido-transition metal complexes (see Section 3). Protonation of the azavinylidene complexes [Tp′(CO)$_2$W{N=C(R)(R′)}] with HBF$_4$ occurs at the ligand carbon atom to oxidize the metal to W(IV) and and form cationic nitrene complexes [Tp′(CO)$_2${NCH(R)(R′)][BF$_4$]; similar nitrene products are obtained using [Ph$_3$C][PF$_6$], i.e. [Tp′(CO)$_2$W{NCH(R)CPh$_3$}][PF$_6$].

8. Electrophilic attack

Wilkinson and co-workers have reported that protonation of the Mo(II) complex [MoCp$_2$(MeCN)], where the nitrile is η^2 bonded, with HBF$_4$·Et$_2$O in MeCN results in the doubly protonated Mo(IV) imine complex [MoCp$_2$(NCMe)(NH=CHMe)][BF$_4$]$_2$, which has been structurally characterized [119]. The interaction of the related CF$_3$CN complex [MoCp$_2$(η^2-CF$_3$CN)] with gaseous HCl gives rise to an iminium salt [MoCp$_2${C(CF$_3$)=NH$_2$}][Cl] [120], the structure of which was proposed on the basis of spectroscopic data. The mechanism of the reduction of η^2-MeCN ligand by a proton acid [119] probably involves protonation at the metal followed by hydrogen shift to the —N≡C triple bond; the net result is reduction of the acetonitrile to the imine as molybdenum is oxidized from Mo(II) to Mo(IV). The reaction of [Mo(CO)$_3$(MeCN)$_3$] with HBF$_4$·Et$_2$O under H$_2$ affords [Mo(CO)$_2$(MeCN)$_3$(η^3-CH$_2$CHNH$_2$)][BF$_4$], containing the aza-allylic species η^3-CH$_2$CHNH$_2^+$, which has also been structurally characterized [119].

The coordination chemistry of organonitriles and cyanamide at electron-rich rhenium(I) centres has been recently reviewed by Pombeiro [121] and therefore it will be only briefly summarized herein. Neutral, [ReCl(NCR)(dppe)$_2$], and cationic, [Re(NCR)$_2$(dppe)$_2$][BF$_4$] and [Re(N$_2$)(NCR)(dppe)$_2$][BF$_4$], nitrile complexes (R = various alkyls, aryls or NH$_2$) have been prepared by displacement of N$_2$ and/or the chloride ligand (in the presence of TlBF$_4$) respectively from [ReCl(N$_2$)(dppe)$_2$]. The neutral mononitrile complexes present ν(NC) in their IR spectra considerably below those observed for the free ligands (ca. 140–20 cm^{-1}) in agreement with a strong π electron releasing ability of the Re(I) centre to the NC π^* orbitals of the coordinated nitrile. This feature has been also confirmed by an X-ray structure analysis of [ReCl(NCR)(dppe)$_2$] [122], which indicates an unusually short Re—N bond (1.978(5) Å). As a result of the strong π electron releasing ability of the {ReCl(dppe)$_2$} site, the [ReCl(NCR)(dppe)$_2$] complexes (R = aryl) undergo protonation at the nitrile carbon to yield azavinylidene derivatives [123]], i.e.

$$[\mathrm{ReCl(NCR)(dppe)_2}] + \mathrm{HBF_4(Et_2O)} \rightarrow [\mathrm{ReCl\{N{=}C(H)R\}(dppe)_2}]\mathrm{BF_4} \quad (40)$$

although the metal centre is also susceptible to protic attack to afford hydrido derivatives [ReHCl(NCR)(dppe)$_2$]$^+$. Kinetic studies of the protonation by HCl of the nitrile ligand vs. protonation of rhenium at *cis*- or *trans*-[ReCl(NCC$_6$H$_4$R-4)(dppe)$_2$] (R = Cl, F, Me, MeO) have been recently reported

[124] and indicate that proton addition occurs firstly at the nitrile ligand, the hydride complexes, when formed, being derived from methylene intermediates by proton migration to the metal. Possibly related proton addition at the nitrile carbon also occurs in the formation of [Re(NCH$_2$Et)Cl$_3$(dppbe)] in the reaction of [(*n*-Bu$_4$N)Re$_2$Cl$_8$] with alkyl nitriles EtCN in the presence of an excess of the bidentate phosphine ligand dppbe and a few drops of concentrated HCl [54a,54c].

While the nitrile ligands in [ReCl(NCR)(dppe)$_2$] undergo a single protonation and no further protic attack is observed, treatment of *cis*-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$], having an electron-rich metal centre with labile ligands, with an alkyl or an aromatic nitrile results in replacement of dinitrogen or phosphine by this substrate and the products undergo protonation by HBF$_4$(Et$_2$O) in methanol to afford, albeit generally in low yields, amines, ammonia and hydrocarbons [121] conceivably via azavinylidene intermediates.

Cyanamide ($N{\equiv}C{-}NH_2$), which has been recognized [125] as a substrate of nitrogenase being reduced to methylamine and ammonia (six-electron pathway) or to methane and ammonia (eight-electron pathway), reacts with *trans*-[M(N$_2$)$_2$(dppe)$_2$] (M = Mo, W) to afford *trans*-[M(NCN)$_2$(dppe)$_2$], which contain two cyanoimido(2−) ligands, as also confirmed by X-ray crystallography [121,126], probably derived by dehydrogenation of cyanamide by the metal centres. In contrast, the reaction of cyanamide with the isocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$] (R = Me, *t*-Bu) in the presence of TlBF$_4$ affords the η^1-coordinated cyanamide derivatives *trans*-[Re(CNR)($N{\equiv}C{-}NH_2$)(dppe)$_2$]$^+$, which undergo reversible deprotonation to give the hydrogen cyanamide compounds *trans*-[Re(CNR)(NCNH)(dppe)$_2$] [121,127].

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