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Addition of HO-nucleophiles to free and coordinated nitriles

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Abstract. The review surveys data on the addition of HO-nucleophiles (water, oximes, hydroxylamines, hydroxamic acids, alcohols) to nitriles. Main methods for C≡N bond activation in nucleophilic addition reactions are discussed. Particular attention is given to activation of nitriles through coordination to metal centres. The bibliography includes 191 references.

I. Introduction

Nitriles are widely used in preparative chemistry due to their ability to be involved in nucleophilic and electrophilic addition and [2 + 3]-cycloaddition reactions. In particular, these reactions are used to synthesise amides and carboxylic acids [for example, acrylamide, nicotinamide and *S*-(+)-ibuprofen], which are of considerable practical importance, and a wide range of heterocyclic compounds containing one or more nitrogen atoms. The addition of various nucleophiles at C≡N bonds giving rise to compounds containing new C–N, C–O, C–S, C–C or C–P bonds is most generally employed in nitrile chemistry.

Nitriles containing activating electron-withdrawing groups, for example, perfluoroalkyl groups, can react with various nucleophiles without additional C≡N bond activation, whereas the addition reactions to nitriles containing electron-donating or weak electron-withdrawing groups require that the electrophilicity of the carbon atom in the RCN molecule be additionally enhanced. In organic chemistry, activation of nitriles and nucleophilic addition reactions are often carried out with the use of acid catalysis (Pinner reaction;[1] see also Refs 2–10) or alkylation giving rise to nitrilium salts.[11–13] Another efficient method for activation is based on coordination of RC≡N to the metal centre. Nowadays, numerous reactions involving the activated C≡N bond are known: metal-mediated and metal-catalysed hydrolysis and alcoholysis of nitriles,† nucleophilic addition reactions of amines, imines and sulfimides and addition reactions of halo- and aminoalcohols.[14–24] Coordination to metal can not only activate the C≡N bond but also promote reactions accompanied by α-C–H and C–C bond cleavage in nitriles.[25–28]

The body of literature on metal-mediated reactions of nitriles published in recent years is too large to be reviewed here. Hence, this review covers the reactions of nitriles with one particular group of nucleophiles, *viz*., HO-nucleophiles, accompanied by their addition at the C≡N bond to form imidoates HN=C(R)O–. HO-Nucleophiles include a wide range of compounds of various classes, which differ in reactivity.

In the last few years, data on reactions of nitriles with particular classes of HO-nucleophiles have been summarised in several publications (for example, hydrolysis of RCN involving various metals was considered in the rewiews,[19,29–38] reactions with nitrile hydratases and mimetic complexes of these enzymes were surveyed in publications[33–48]). However, in none of these publications were the addition reactions of different classes of HO-nucleophiles with nitriles compared. Moreover, abundant new data on the reactions of nitriles with such HON-nucleophiles as oximes, hydroxylamines and hydroxamic acids have been reported in the very recent past.

The aim of the present review is to survey the available data and perform comparative analysis of the data on interactions of the C≡N group of free and coordinated nitriles with HO-nucleophiles. The review provides an overview of recent studies of the reactions of nitriles with water and alcohols in the presence of metal centres and reveals the main factors responsible for these reactions. Considerable attention is given to reactions with poorly known nucleophiles (in particular, with HON-nucleophiles), which have been investigated rather recently. It should be noted that the present review is a continuation of a series of articles published in this journal[12,13,49–52] and devoted to reactions of nitriles in organic and coordination chemistry.

II. Metal-mediated and metal-catalysed hydrolysis of nitriles

Hydrolysis of nitriles proceeds in two steps to form carboxamide, which is then transformed into acid. In most cases, the rate of the second step of hydrolysis is higher than that of the first step.[53]

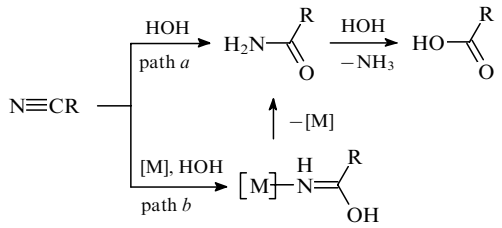
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† Hydrolysis and alcoholysis of nitriles with stoichiometric (metal-mediated) or catalytic (metal-catalysed) amounts of metal complexes.

Hence, the reaction affords carboxylic acid as the major transformation product (Scheme 1, path *a*).[53, 54]

Scheme 1



A specific feature of metal-mediated hydrolysis is that, as a rule, the reaction stops at coordinated amide [M]–NH=C(OH)R (Scheme 1, path *b*). This reaction pathway is favoured by mild reaction conditions, under which the resulting free or coordinated amide is not subjected to the transformation into RCO_2H.

Metal-mediated and metal-catalysed transformations of nitriles into amides were examined in numerous experimental studies, which have been surveyed in sufficient detail in several reviews.[11–24, 32] Hence, here we consider only the main factors responsible for hydrolysis and give selected examples of unusual hydrolytic transformations of coordinated nitriles, which have been reported in the last few years.

The intra/intermolecular character of the reaction. The rate of hydrolysis of metal-coordinated nitriles by an intramolecular mechanism (unlike hydrolysis proceeding by an intermolecular mechanism) was found[55–70] to be substantially higher than that of uncoordinated nitriles. In this case, the reaction can be accelerated by a factor of 10^{18} (the rate of reactions proceeding by the intermolecular mechanism increases by a factor of 10^6–10^9).[55–70] Apparently, the efficiency of the reaction proceeding by the intramolecular mechanism is achieved mainly due to an increase in the 'local' concentration of an H_2O/OH^- nucleophile in the vicinity of coordinated nitrile.

The nature of the metal. The position of the metal in the Periodic table influences substantially the reaction rate and is also responsible for the either catalytic or stoichiometric character of the process. Analysis of the reactivities of related complexes with metals varying within a single subgroup allows one to compare adequately the results of investigations and reveal the corresponding correlations. For example, the rate of hydrolysis of coordinated benzonitrile in the $[M(NH_3)_5(NCPh)]^{3+}$ complexes (M = Co, Rh, Ir) increases with decreasing ionic radius in the series Co(III) > Rh(III) > Ir(III).[65] The same tendency is observed for hydrolysis of nitriles in Pt(II) and Pd(II) complexes [Pd(II) > Pt(II)].[71] If the metal has several oxidation states a higher rate of hydrolysis is observed in complexes, in which the central atom exists in a higher oxidation state. For example, hydrolysis of acetonitrile coordinated to the $Ru^{III}(NH_3)_5$ group proceeds 10^8 times more rapidly than hydrolysis of uncoordinated nitrile, whereas coordination to $Ru^{II}(NH_3)_5$ has virtually no effect on the reaction rate.[66]

In most cases, metal-mediated hydrolysis of nitriles affords stoichiometric amounts of amide complexes, whereas examples of catalytic reactions are scarce.[18, 19, 32, 54, 72–106] Systems based on platinum(II) phosphinite complexes (see Section VI)[32, 54, 72, 73] and zinc(II) salt–oxime systems (see Section III)[74] proved to be most efficient in metal-catalysed hydrolysis. In both cases,[32, 54, 72–74] hydrolysis involves nitrile activation in one of the initial steps followed by the intramolecular reaction with HOP-[32, 54, 72, 73] or HON-nucleophiles.[74] Among other catalytic systems used in hydrolysis of nitriles, let us mention Ni(II) and Cu(II) complexes with ethylenediamine,[75, 76] Co(III) sulfenate complexes,[77, 78] Hg(II) salts in acidic solutions,[79, 80] low-valent ruthenium[27, 81–84] and iridium[26, 27] hydride complexes, systems based on $[Rh(\mu\text{-}Cl)(cod)]_3$ and $P(C_6H_4SO_3Na\text{-}m)_3$,[85] Ir(I) phosphine complexes,[86] mixtures of Rh(III) or Ir(III) halides with $(PhO)_3P$ or Ph_3P and their derivatives,[87–89] mixtures of $RuCl_3$ with phenanthroline or $Na_2[PdCl_4]$ with 2,2′-bipyridyl,[90] Pd(II) aqua and hydroxo complexes,[91–97] Pd(II) thiolate complexes,[98, 99] Pt(0) and Pt(II) phosphine complexes[100–104] and clusters with a Pt_4 core.[105, 106]

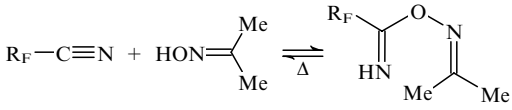
It should be noted that hydrolysis of nitriles in the coordination sphere of the metal affords not only amides but also other products of hydrolytic transformations, for example, the metallacycles $[RuCl(CO)\{\underline{N}H=C(p\text{-}MeC_6H_4)N=C(p\text{-}MeC_6H_4)\underline{O}\}.(PPh_3)_2]$,[107] $[PtCl\{\underline{O}=\overline{C}(CCl_3)NC(CCl_3)=\underline{O}\}(Me_2SO)]$[108] and $[PtCl_4\{\underline{N}H=C(NR_2)OC(NR_2)=\underline{N}H\}]$ (R = Me, Et; R_2 = C_5H_{10}, $\overline{C_4H_8O}$)[109] (hereinafter, atoms bound to metals are underlined). These complexes are generated in multistep processes involving hydrolysis of one of the nitrile molecules in the coordination sphere of the metal followed by the reaction of the hydrolysis product with another nitrile. The formation of amidines and coordinated imidoyl amidines is considered in Section III. It is believed that these transformations also involve hydrolysis of nitrile in the coordination sphere of the complex as one of the initial steps.

Therefore, the use of metal complexes in reactions of nitriles with water leads to a substantial increase in the rate of the first step of hydrolysis (due to electrophilic activation of the nitrile through its coordination) and provides the possibility of stopping hydrolysis selectively at the formation of amide (due to its stabilisation as a result of coordination and milder reaction conditions).

III. Reactions of oximes with free and coordinated nitriles

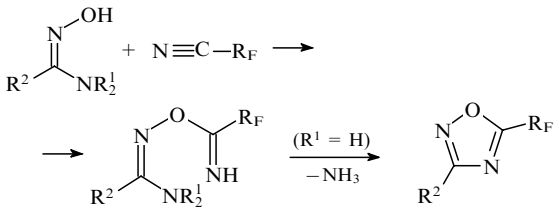
1. Nucleophilic addition of oximes to free nitriles and nitrilium salts

In organic chemistry, only a few examples of the nucleophilic addition of oximes to nitriles are known. These reactions proceed exclusively with activated nitriles, for example, with those containing a perfluoroalkyl group.[110, 111] The reactions of perfluorocarbonitriles with acetone oxime were investigated.[110]



R_F = CF_3, C_3F_7.

These reactions are reversible: *O*-imidoyl oxime that formed in good yield is unstable and decomposes on heating to give the starting compounds.[110] Kabakchi *et al.*[111] prepared 1,2,4-oxadiazoles by the reaction of perfluorocarbonitriles [R_F = C_6F_{13}, $CF_3O(CF_2CF_2O)_4CF_2$, $(\overline{O(CF_2)_3CF})CF_2$] with aromatic amidoximes HON=$C(NR^1_2)R^2$ (benzamidoxime, substituted and unsubstituted terephthalamidoximes).

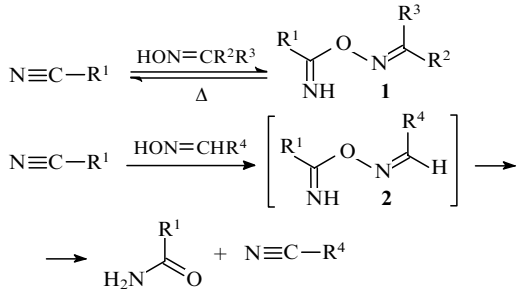


R^1 = H: R^2 = Ph, *p*-$HON(NH_2)CC_6H_4$;
NR^1_2 = $N(CH_2)_4$, $N(CH_2)_5$, R^2 = *p*-$HON(NH_2)CC_6H_4$.

The first step of the synthesis of 1,2,4-oxadiazoles also involves the formation of *O*-imidoyl oximes. In the study,[111] the authors noted that, although the addition of unsubstituted amidoximes to nitriles could, in principle, occur in two different ways, *viz*., the addition of either the amide or oxime group could take place, exclusively the latter situation was experimentally observed. It should be noted that *O*-imidoyl oximes were prepared

under mild conditions in good yields. In the reactions with perfluorocarboxylic acid fluorides, *O*-imidoyl oximes are transformed into 1,2,4-oxadiazoles with elimination of ammonia.

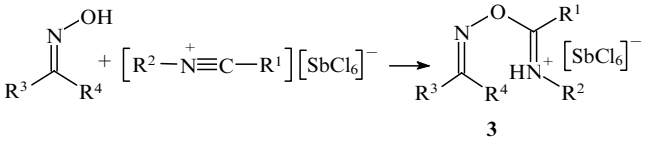
Activation of nitriles with electron-withdrawing groups, such as CCl_3 and CCl_2CN, is also sufficient for them to react with oximes. For example, $Cl_3CC{\equiv}N$ and $(N{\equiv}C)Cl_2CC{\equiv}N$ readily react with oximes to give unstable *O*-imidoyl oximes.[112, 113] Imines **1** produced by the reactions with ketoximes $R^2R^3C{=}NOH$ can be isolated, whereas unstable *O*-imidoyl oximes **2** formed in the reactions with aldoximes $R^4CH{=}NOH$ are rearranged to give halogenated carboxamide and nitrile R^4CN as a dehydration product of the corresponding aldoxime.[113]



$R^1 = CCl_3, CCl_2CN$; R^2 = Me: R^3 = Me, Ph, 4-HOC_6H_4; $R^2 = R^3$ = Ph; R^4 = 2-C_4H_7O, Pr^n, Pr^i, Ph, 4-MeC_6H_4, 3,4-$(MeO)_2C_6H_3$, 1-naphthyl, PhCH=CH.

In the study,[112] dehydration of aldoximes with trichloroacetonitrile was proposed for use for the preparation of aromatic nitriles, which are difficult to synthesise (dehydration of aldoximes with coordinated nitriles is considered in Section III.3).

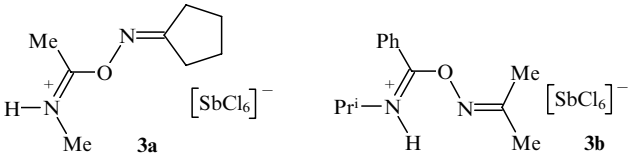
Nitriles can be activated also by alkylation of the nitrogen atom of the nitrile group to form nitrilium salts.[114, 115] For example, $[R^1C{\equiv}N^+R^2][SbCl_6]^-$ salts can be involved in the addition reactions to oximes $R^3R^4C{=}NOH$. The initiating role of nitrilium salts in the Beckmann rearrangement in anhydrous aprotic solvents was examined in the studies.[114, 115] The reactions of the $[R^1C{\equiv}N^+R^2][SbCl_6]^-$ salts with oximes were demonstrated to afford imidoyl compounds as unstable intermediates.



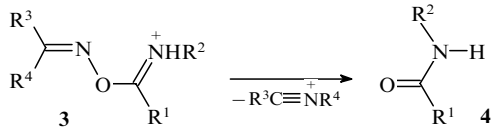
3

R^1 = Me, Pr^i, Ph; R^2 = Pr^i; $R^1{-}R^2 = Me_2, (CH_2)_5$; $R^3{-}R^4 = Me_2, (CH_2)_n$ (n = 4–7, 12), Ph_2.

Addition products **3** exist in solution as mixtures of *E* and *Z* isomers. Compounds with $R^1 = R^2$ = Me, $R^3{-}R^4 = (CH_2)_4$ (**3a**) and R^1 = Ph, $R^2 = Pr^i$, $R^3 = R^4$ = Me (**3b**) were characterised by X-ray diffraction. It was established that compounds **3a** and **3b** have *Z* and *E* configurations, respectively.



Iminium salts **3** can be subjected to the Beckmann rearrangement to form the corresponding carboxamides **4**.[114, 115]



Hence, for the nucleophilic addition of oximes to nitriles to occur, it is necessary either to use nitriles RCN containing strong electron-withdrawing R groups or to activate nitriles by alkylation of the nitrogen atom of the nitrile group. A considerable drawback of the first method is that the field of its application is limited to a relatively small set of perfluorocarbonitriles and some other nitriles containing the chlorine atoms and/or a pseudohalide group in the activating fragment. This method can be used to prepare only derivatives containing electron-withdrawing groups at the carbon atom. The second method can be employed to synthesise nitrile derivatives containing electron-donating groups at the carbon atom (in this case, acylation of oximes affords salts). It was noted[110–115] that imidoyl compounds formed upon addition of nitrilium salts to oximes are unstable. In some cases, they were characterised only in a reaction mixture and were not isolated as individual products.

2. Reactions of 'simple' oximes with coordinated nitriles

The nucleophilic addition of 'simple'‡ oximes to coordinated nitriles was investigated in much more detail. The reaction of oxime with nitrile in the presence of a metal centre giving rise to a stable imino complex was described for the first time in 1990.[116] In this study, the authors performed the reaction of the palladium complex $[PdCl_2(PhCN)_2]$ with $HON{=}CMeBu^t$ to prepare the $[PdCl_2\{\underline{N}H{=}C(Ph)O\underline{N}{=}CMeBu^t\}]$ complex as one of products and characterised the latter. More than ten studies devoted to the addition of oximes to nitriles in the presence of V(IV), Re(IV), Rh(III), Ni(II), Pt(II) and Pt(IV) complexes were published by the mid-1990s.[117–132] In all these studies (see below), the reactions of oximes with nitriles proceed under mild conditions to give coordinated imines $HN{=}C(R^1)ON{=}CR^2R^3$. It was reported that even nitriles containing electron-donating substituents, such as MeCN and EtCN, which do not react with oximes in the free state, are involved in nucleophilic addition to oximes in the presence of metal complexes (see Section III.1).[117–126] Evidently, the metal centre plays a decisive role in these reactions. The metal centre not only activates nitrile but also stabilises the resulting imino ligand.

In spite of the diversity of the starting compounds and reaction conditions, there are several factors influencing the nucleophilic addition of oximes to nitriles in the presence of metal.

a. Effect of the central metal atom on the reactivity of nitrile

The nature of the central atom. In accordance with the logic of the discussion, let us first consider the role of the central metal atom in activation of nitrile followed by consideration of the role of the metal centre in stabilisation of coordinated imines $HN{=}C(R^1)ON{=}CR^2R^3$.

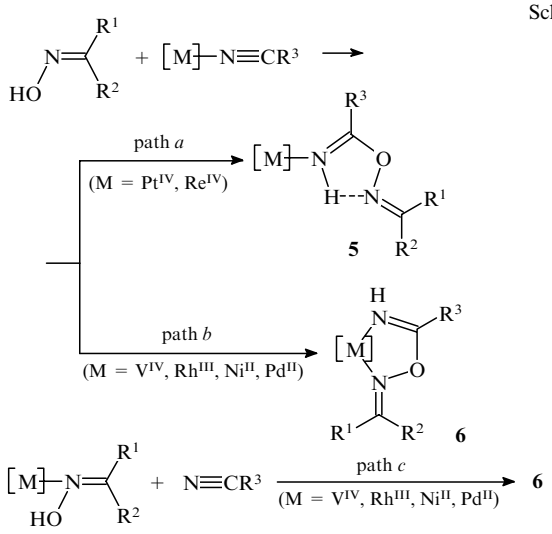
The way of performing the reaction and the character of the reaction products depend on the nature of the central atom. For example, the reactions of oximes $R^1R^2C{=}NOH$ with nitrile complexes of platinum(IV)[117–119] and rhenium(IV),[120] *viz.*, *trans*-$[PtCl_4(R^3CN)_2]$, $[PtCl_5(EtCN)]^-$ and *cis*-$[ReCl_4(MeCN)_2]$, respectively, proceed under mild conditions to give complexes **5** with monodentate imino ligands in nearly quantitative yields (Scheme 2, path *a*). These complexes exist in the *E* form stabilised by hydrogen bonding between the hydrogen atom of imine and the nitrogen atom of oxime.

It was demonstrated[117–120] that free nitrile is not involved in these reactions even under more drastic conditions (on refluxing and/or in the presence of a large excess of R^3CN).

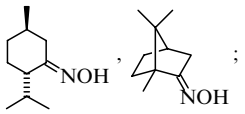
Another way of performing metal-mediated reactions of nitriles with oximes is based on the use of relatively labile V(IV), Rh(III), Ni(II) and Pd(II) complexes (Scheme 2, paths *b* and *c*). Imines $\underline{N}H{=}C(R^3)O\underline{N}{=}CR^1R^2$ formed in the course of the reaction are coordinated to the metal atom in a bidentate fashion

‡ By 'simple' oximes is meant compounds containing only one functional (oxime) group.

Scheme 2



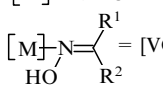
(*a*) R^1 = H: R^2 = Ph, *o*-HOC_6H_4; R^1 = R^2 = Me, R^1-R^2 = $(CH_2)_4$,

$(CH_2)_5$, $R^1R^2C{=}NOH$ = 

$[M{-}N{\equiv}CR^3]$ = *trans*-$[PtCl_4(R^3CN)]$ (R^3 = Me, Ph, Bn);
$[PtCl_5(EtCN)]^-$, *cis*-$[ReCl_4(MeCN)_2]$.

(*b*) R^1 = R^2 = Me, R^1-R^2 = $(CH_2)_4$,

$[M{-}N{\equiv}CR^3]$ = *mer*-$[RhCl_3(R^3CN)_3]$ (R^3 = Me, Ph);

(*c*)  = $[VOL_2]$ (L is salicylaldoxime or analogous ketoxime, salicylamidoxime);

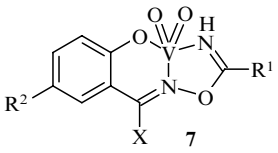
$[RhCl_3(HON{=}CR^1R^2)_3]$ (R^1 = R^2 = Me, R^1-R^2 = $(CH_2)_4$);

$[PdCl_2(HON{=}CR^1R^2)_2]$ (R^1 = R^2 = Me, R^1 = Me, R^2 = Et, R^1-R^2 = $(CH_2)_5$);

R^3 = Me, Et, Ph.

through two nitrogen atoms. In the presence of 'labile' metal complexes,§ the addition of oximes to nitriles can occur by two mechanisms, *viz*., either as the addition of the nitrile complex to free oxime (path *b*) or as the addition of the oxime complex to free nitrile (path *c*) ¶ giving rise to the same product **6**. It is believed that the first step of the reaction of an oxime complex with nitrile involves coordination of nitrile at the *cis* position with respect to complexed oxime followed by the reaction of the adjacent oxime and nitrile ligands, the latter being activated as a result of its coordination.

Dissolution of the oxovanadium oximate complexes $[VOL_2]$ (L is salicylaldoxime or analogous ketoxime and salicylamidoxime) by heating in nitriles [121, 122] affords complexes **7** with the tridentate imino ligand.



X = H, Me, Et; R^1 = Me, Ph, $C_6H_4NO_2$-*p*, C_6H_4Me-*p*, $MeC(O)CH_2$; R^2 = H, Cl, Bu^t;

X = NH_2, R^1 = Me, R^2 = H.

§ The metal centre is labile with respect to substitution reactions.

¶ It should be noted that the reaction does not occur in the presence of Pt(IV) or Re(IV) complexes.[117, 118]

In both studies,[121, 122] the authors noted that the imino ligand cannot be prepared by the direct reaction of oximes with nitrile and, consequently, the reaction is promoted by metal. It was suggested [121] that the reaction mechanism involves coordination of nitrile to V(IV) as the initial step followed by nucleophilic addition of oxime to the nitrile to form a tridentate ligand. In addition, the reaction is accompanied by oxidation of the central atom to V(V). It was hypothesised that one of the inner-sphere oximes in the starting complex serves as the oxidiser.[121] The structure of complex **7** (X = NH_2, R^1 = Me, R^2 = H) is shown in Fig. 1.

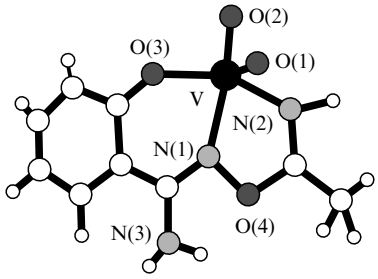
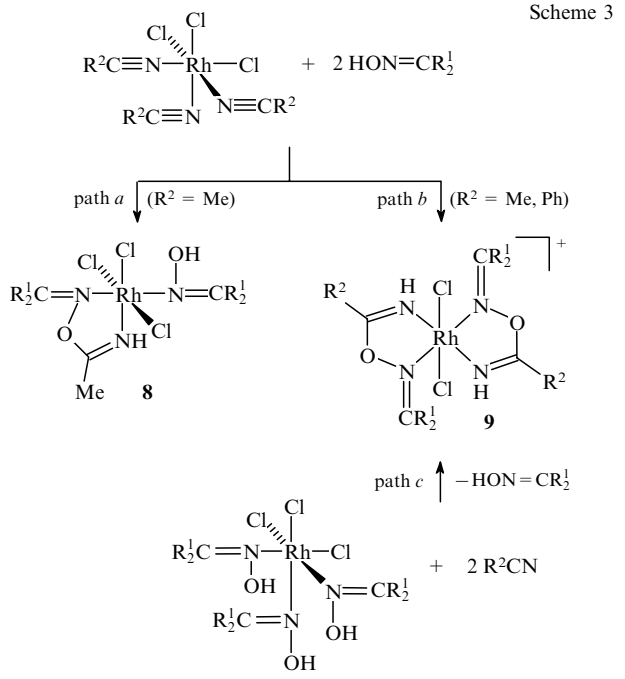


Figure 1. Molecular structure of complex **7** (X = NH_2, R^1 = Me, R^2 = H).

In the studies of the reactions of $R^1_2C{=}NOH$ with the rhodium(III) nitrile complexes *mer*-$[RhCl_3(R^2CN)_3]$ (R^2 = Me, Ph) (Scheme 3, paths *a* and *b*), several imino complexes were isolated and characterised: $[RhCl_3\{\underline{NH}{=}C(R^2)O\underline{N}{=}CR^1_2\}.\{HON{=}CR^1_2\}]$ (**8**, R^2 = Me) and $[RhCl_2\{\underline{NH}{=}C(R^2).O\underline{N}{=}CR^1_2\}_2]Cl$ (**9**, R^2 = Me, Ph).[123, 124]

Scheme 3



R^1_2 = Me_2, $(CH_2)_4$; R^2 = Me, Ph.

In the resulting compounds **8** and **9**, the imino ligand is coordinated to Rh(III) through two nitrogen atoms. The rhodium complexes $[RhCl_2\{\underline{NH}{=}C(R^2)O\underline{N}{=}CR^1_2\}_2]Cl$ [**9**, R^1_2 = Me_2, $(CH_2)_4$; R^2 = Me] were also prepared by independent synthesis by the reaction of the rhodium oxime complexes $[RhCl_3\{HO\underline{N}{=}CR^1_2\}_3]$ with acetonitrile (Scheme 3, path *c*).[123] It was suggested that the reaction proceeds in two steps and involves the initial coordination of MeCN and its activation followed by

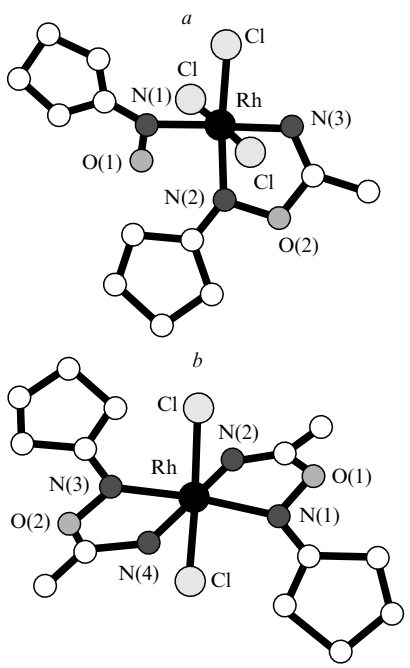
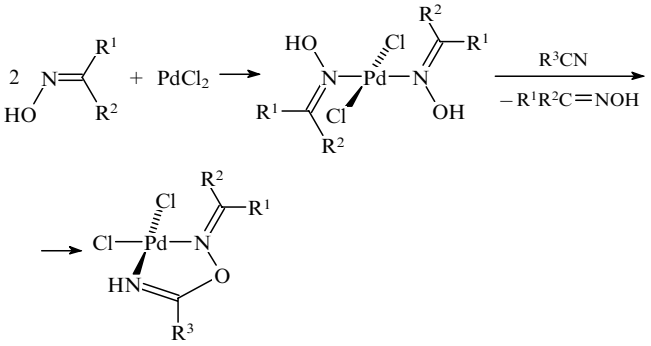


Figure 2. Molecular structures of complexes **8** (*a*) and **9** (*b*) [$R^1_2 = (CH_2)_4$ and $R^2 = Me$].

nucleophilic addition of oxime to nitrile. The molecular structures of complexes **8** and **9** are shown in Fig. 2.

Nickel(II) complexes promote the addition of sulfur-containing dioxime $HON=C(Me)CH_2S(CH_2)_2SCH_2C(Me)=NOH$ to nitriles (see Section III.3).[125,126] In the absence of metal the oxime does not react with nitriles.

It was found [127] that $PdCl_2$ (which is consistent with the results of the study [116]) promotes nucleophilic addition of oximes $R^1R^2C=NOH$ to nitriles R^3CN on heating in a solution of the corresponding nitrile to form the $[PdCl_2\{\underline{NH}=C(R^3)O\underline{N}CR^1R^2\}]$ complex. The reaction proceeds through the formation of the oxime complex $[PdCl_2\{HON=CR^1R^2\}_2]$, whose heating in a solution of nitrile affords an imino complex. Garnovskii *et al.*[127] demonstrated that the reaction is accelerated under microwave irradiation.



$R^1 = R^2 = Me$: R^3 = Me, Et, Ph; R^3 = Me: R^1 = Me, R^2 = Me, Et; $R^1-R^2 = (CH_2)_5$.

The above data show that the nature of the imidoylation product of oxime (which can be coordinated to [M] in either monodentate or bidentate fashion), as well as the possibility of the independent synthesis of an imino compound by the reaction of an oxime complex with nitrile proceeding in the presence of labile metal complexes, depends on the nature of the central metal atom.

The oxidation state of the central atom has a substantial effect on nitrile activation, which is clearly demonstrated by comparing the reactivities of the related platinum(II and IV) nitrile complexes $[PtCl_n(RCN)_2]$ (n = 2, 4). Nitriles in the platinum(IV) complexes easily react with oximes at room temperature to give addition products. By contrast, for the platinum(II) complexes, the addition products were neither isolated nor detected in the reaction mixtures even in attempting to perform the reaction under much more drastic conditions (prolonged heating) or under microwave irradiation.[117,118] The reaction of oximes with the dialkylcyanamide complex $[Pt(PPh_3)_2(NCNR_2)_2](BF_4)_2$ is the only example of the addition of oximes to nitriles involved in a Pt(II) complex.[128] However, this reaction also proceeds due to additional activation of the ligand with yet another Lewis acid.

The charge of a complex. The effect of the charge of the complex on the addition of oximes to nitriles was examined in the study of the reactions of the neutral and anionic Pt(IV) complexes, *viz*., $[PtCl_4(MeCN)_2]$ and $[Ph_3PCH_2Ph][PtCl_5(EtCN)]$, respectively, with oximes $R^1R^2C=NOH$ (R^1 = H: R^2 = Ph, *o*-HOC_6H_4; $R^1 = R^2$ = Me; $R^1-R^2 = (CH_2)_4$, $(CH_2)_5$). No substantial difference in the reaction rate for these compounds was revealed. Apparently, this provides evidence that activation of nitrile through coordination to Pt(IV) was sufficiently strong for the reaction to proceed in both cases.[117–119] For compounds of other metals, an analogous comparison was not performed, although it has been *a priori* assumed that the charge of a complex can also affect the rate of nucleophilic addition of oximes to coordinated nitriles.

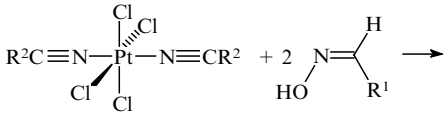
b. Electron-withdrawing properties of R in RCN

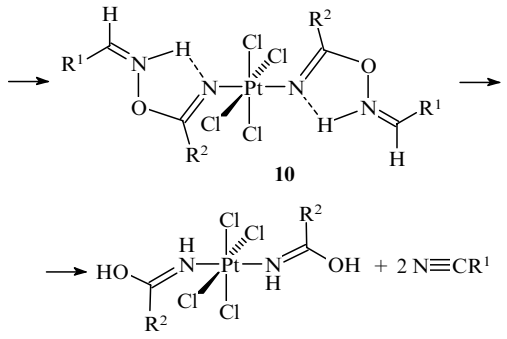
As mentioned above (see Section III.1), the rate of the reaction of oximes with free nitriles depends substantially on the nature of the R group in RCN. This phenomenon is also observed for coordinated nitriles. Nitriles containing electron-withdrawing groups R are more active in addition reactions with oximes. It was demonstrated [122] that compound **7** is more easily formed by the reaction with the use of PhCN than with the use of MeCN (the yield of the product was estimated after 48 h at 20–25 °C). By contrast, the reactivity of nitriles in the platinum(IV) complexes $[PtCl_4(RCN)_2]$ depends only slightly on the character of the R group (electron-donating Me, Et, Bn or electron-withdrawing Ph).[117,118] Apparently, this is associated with the fact that stronger activation by the central atom masks the less significant effect of the R group in RCN.

c. Nature of oxime

Variations in the nature of the R and X groups in the $RXC=NOH$ molecule can change the rate of nucleophilic addition and determine both stability of the reaction product and the probability of occurrence of side reactions. For example, the reactions of imidoyl chlorides $ArC(Cl)=NOH$ with nitriles in the $[PtCl_4(MeCN)_2]$ complex are substantially more difficult to perform than the reactions of alkyl(aryl)- or dialkyl oximes,[129] whereas the reactivity of methyl *N*-hydroxyimidoate $Me_3C_6H_2C(OMe)=NOH$ in the addition reactions to coordinated nitrile is higher than the reactivities of ketoximes containing alkyl, aryl and electron-withdrawing groups.[130]

Aldoximes $R^1(H)C=NOH$, like ketoximes, readily react with coordinated nitriles in the platinum(IV) complexes $[PtCl_4(R^2CN)_2]$, but the resulting imino complexes **10** are unstable and undergo further transformations to give the carboximide complex $[PtCl_4\{NH=C(OH)R^2\}_2]$ and nitrile R^1CN. The latter is formed as a result of dehydration of aldoxime.





10

R^1 = Me, Ph, PhC(O); R^2 = Alk, Ar.

The molecular structure of the product obtained upon the addition of aldoxime PhC(O)CH=NOH to nitrile EtC≡N in the $[PtCl_4(NCEt)_2]$ complex is shown in Fig. 3.

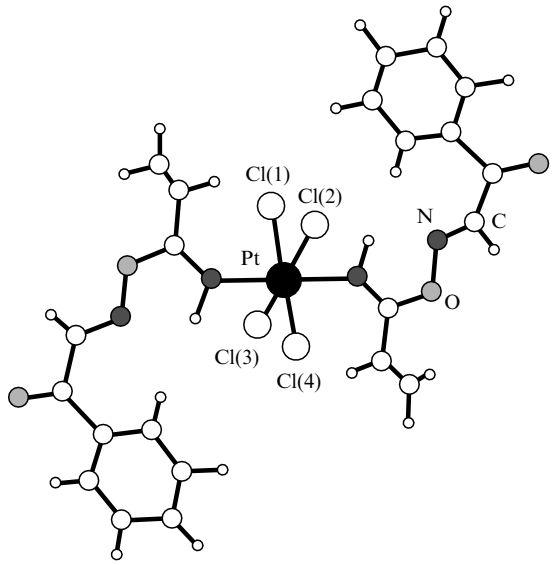
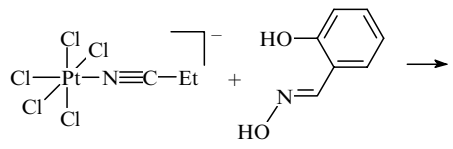


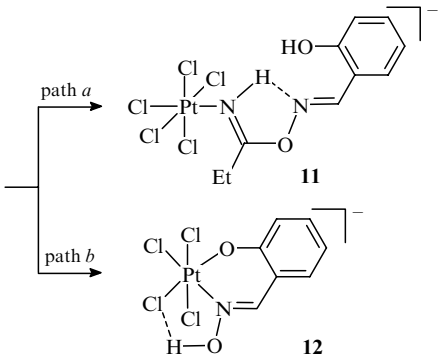
Figure 3. Molecular structure of complex **10** [R^1 = PhC(O), R^2 = Et].

This transformation is the first example of dehydration of aldoximes with coordinated nitriles.[131] Derivatives of aliphatic aldoximes were found to be more reactive than derivatives of aromatic aldoximes, particularly if the aryl group contains bulky substituents.[131]

d. Concentration of reagents

In the study of the reaction of salicylaldoxime *o*-HO.C_6H_4C=NOH with the anionic platinum(IV) complex $[Ph_3PCH_2Ph][PtCl_5(EtCN)]$,[132] the addition of oximes to coordinated nitriles was demonstrated to depend on the concentrations of the reagents. The addition of oxime to coordinated nitrile was found to compete with the replacement of nitrile with salicylaldoxime. In dilute solutions, one of these reactions becomes the major process. If the concentration of the $[Ph_3PCH_2Ph][PtCl_5(EtCN)]$ complex in CH_2Cl_2 is 0.36 mmol ml^{-1}, the reaction follows the path *a* to form imino complex **11**.





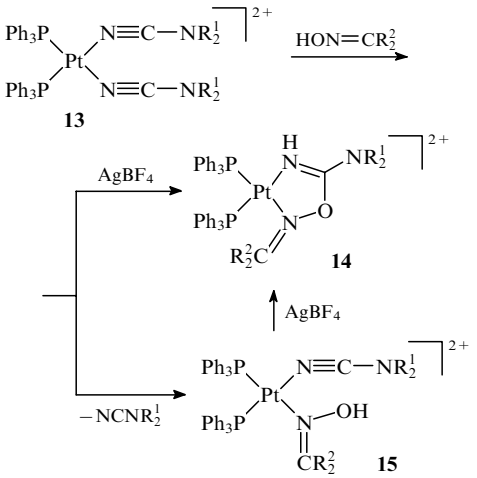
11 **12**

The reaction in a 50-fold diluted solution in wet CH_2Cl_2 affords substitution product **12** (path *b*) and the $[Ph_3PCH_2Ph]_2[PtCl_6]$ complex. The addition of a small amount of EtCN to a dilute reaction mixture suppresses the formation of product **12** and facilitates the formation of compound **11**. The 'switching' of the reaction from the addition (path *a*) to substitution (path *b*) by dilution of the reaction mixture was explained by an increase in dissociation of the EtCN ligand in a dilute solution and, correspondingly, by promotion of the replacement of nitrile.[132]

e. Activation of two donor centres in dialkylcyanamide

To understand the mechanism of the nucleophilic addition of oximes to nitriles, let us consider the reaction of oxime with dialkylcyanamide $NCNR_2^1$ involved in platinum(II) complex **13** (Scheme 4).

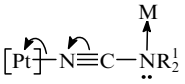
Scheme 4



13 **14** **15**

R^1 = Me, Et; R^2 = Me, R_2^2 = $(CH_2)_4$.

The dialkylcyanamide complexes $[Pt(NCNR_2^1)_2(PPh_3)_2].(BF_4)_2$ (**13**) were found to react with oximes in the presence of a catalytic (10%) or stoichiometric amount of $AgBF_4$ to form chelate **14**.[128] The reaction of the dialkylcyanamide complex with oxime in the absence of Ag^+ affords complex **15**, in which the nitrile and oxime ligands do not interact with each other. Therefore, the presence of a silver salt is necessary for the reaction of coordinated dialkylcyanamide with oxime to proceed. A catalytic amount of $Cu(OAc)_2$ can be used instead of $AgBF_4$. It is believed that in this case metal additionally activates the nitrile group due to coordination of Lewis acid (Ag^+ or Cu^{2+}) to amide nitrogen resulting in an increase in electrophilicity of the carbon atom of the nitrile group.



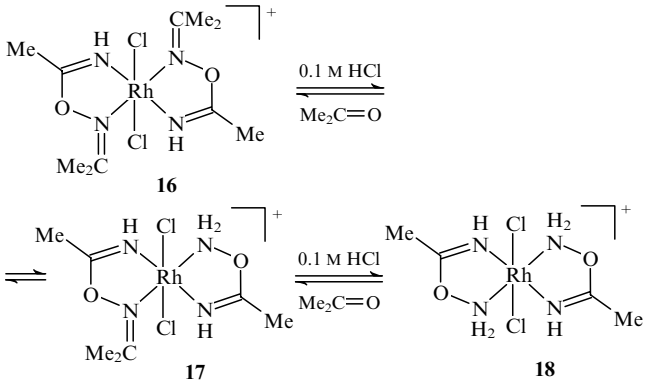
M = Ag^+, Cu^{2+}.

All attempts to perform the addition of oximes to nitriles in analogous platinum complexes with alkano- and arenonitrile

ligands instead of dialkylcyanamide {$[Pt(RCN)_2(PPh_3)_2](BF_4)_2$; R = Et, C_6H_4OMe-*p*} and in complexes of another type {$[PtCl_2(RCN)_2]$; R = Me, Ph} with nitrile ligands in the presence or absence of an Ag^+ catalyst failed.[117,128] This fact suggests that nitrile is insufficiently activated by platinum(II) for the nucleophilic addition of oxime to occur (addition at the C≡N bond becomes possible only for dialkylcyanamide complexes in the presence of Lewis acids, which additionally activate the nitrile group).

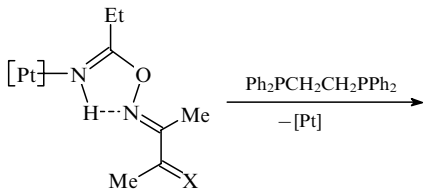
f. Role of the central atom in stabilisation of imino ligands

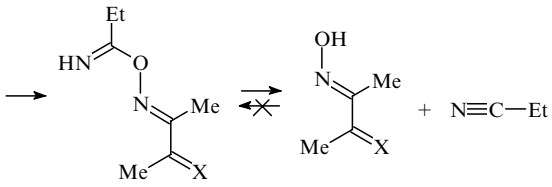
In most studies of nucleophilic addition of oximes to nitriles, it was noted that coordinated imines produced in these reactions are resistant to hydrolysis.[117–120,123,124,128] For example, platinum(II and IV) and rhodium(III) imino complexes,[117–119,123,124] which were prepared by the reactions in wet solvents, can be stored for a long period of time without changes. Storage of the rhodium imino complex $[RhCl_2\{\underline{NH}=C(Me)O\underline{N}=CMe_2\}_2]Cl$ (**16**) in 0.1 M HCl at 80 °C for several days was demonstrated to lead to hydrolysis of the C=N bond of oxime giving rise to products **17** and **18**, while the imine C=N bond remains intact.



It is also known that the C=N bond in oximes is rather stable, whereas the C=N bond in imines is readily hydrolysed. In this case, coordination to metal stabilises the imino group and destabilises the oxime group resulting in selective hydrolysis of the latter. This procedure was used to prepare the *O*-imidoylated hydroxylamine complex, whereas the reaction of free hydroxylamine with coordinated nitrile afforded a mixture of unidentified products.[124]

Stabilisation of a ligand through coordination is also evident from the fact that known free imidoylated oximes are rather unstable (see Section III.1). Liberation of imines, which are generated through metal-mediated addition of oxime to nitrile, from metal complexes gave the decomposition products $HN=C(R^3)ON=CR^1R^2$.[117,118] The imino ligand was liberated in the free state from the $[PtCl_2\{\underline{NH}=C(Et)ON=C(Me)-C(Me)=X\}_2]$ complex (X = O, NNH_2) in the presence of 1,2-bis(diphenylphosphino)ethane in a $CDCl_3$ solution.[133,134] Although such imines can exist as ligands of platinum complexes during a long period of time even in wet solvents, free imines decompose in solution within a few hours to form the starting oxime and nitrile.[133,134]



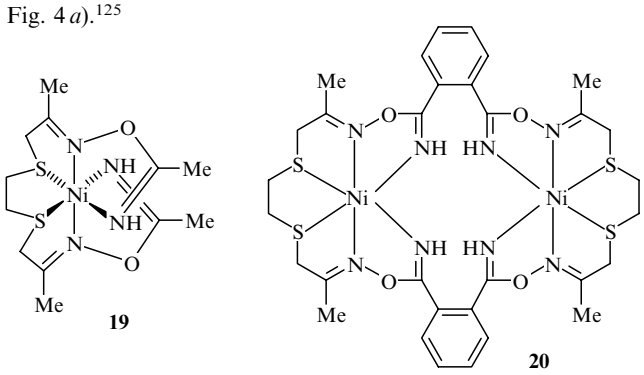


X = O, NNH_2.

Therefore, the central metal atom stabilises the resulting coordinated imine $HN=C(R^3)ON=CR^1R^2$, whereas the free imine is either unstable or does not exist at all. Coordination of nitriles favours C≡N triple bond activation in addition reactions of oximes, the reaction pathway and the character of the product being dependent on numerous factors, among which the nature of the metal and its oxidation state are of most importance. Coordination also provides stabilisation of the addition product of oxime.

3. Reactions of functionalised oximes

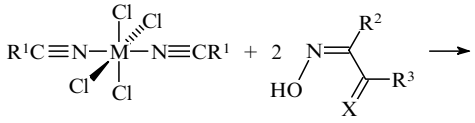
Functionalised oximes (with sulfide groups,[125,126] *vic*-dioximes,[118,120] ketoximes,[133] hydrazone oximes[134]), like 'simple' oximes, are involved in nucleophilic addition to metal-activated nitriles. For example, treatment of sulfur-containing dioxime $HON=C(Me)CH_2S(CH_2)_2SCH_2C(Me)=NOH$ ($DtoxH_2$) with nickel perchlorate in acetonitrile afforded two compounds, *viz*., the trinuclear complex $[Ni_3(Dtox)(DtoxH)_2](ClO_4)_2 \cdot MeCN$ and the imino complex $[Ni\{NH=C(Me)ON=C(Me).CH_2S(CH_2)_2SCH_2C(Me)=NO-C(Me)=NH\}](ClO_4)_2$ (**19**, Fig. 4 *a*).[125]



In the absence of a metal centre, dioxime $DtoxH_2$ does not react with MeCN. Hence, it was suggested[125] that, on the one hand, the reaction is determined by activation of nitrile though coordination to Ni(II) and, on the other hand, the reaction of oxime with nitrile is facilitated by the close arrangement of the reacting molecules upon coordination (the reaction product is stabilised through chelation).

More recently, unusual dinuclear complex **20** with a macrocyclic ligand (Fig. 4 *b*) was prepared by the reaction of the dioxime complex $[Ni(DtoxH_2)(H_2O)_2](ClO_4)_2$ with *o*-phthalonitrile $C_6H_4(CN)_2$.[126] The presence of additional functional (sulfide) groups in the oxime molecule is favourable for stabilisation of the macrocyclic ligand, which forms a stable complex with nickel.

The extremely reactive nitrile ligands in the rhenium(IV) and platinum(IV) complexes $[MCl_4(R^1CN)_2]$ react with *vic*-dioximes $HON=C(R^2)C(R^3)=NOH$,[118,120] ketoximes $HON=C(R^2).C(O)R^3$ (see Ref. 133) and hydrazone oximes $HON=C(R^2).C(R^3)=NNH_2$ (see Ref. 134) to give imino complexes **21**.



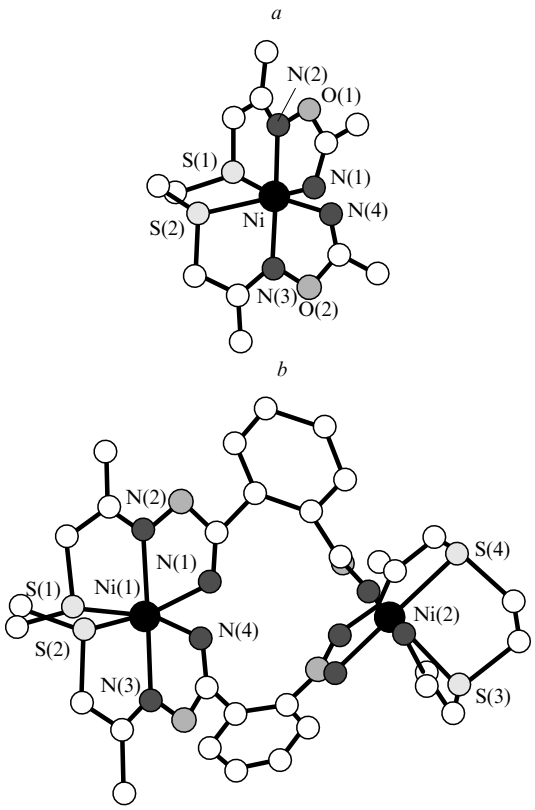
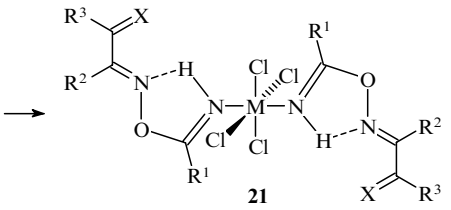
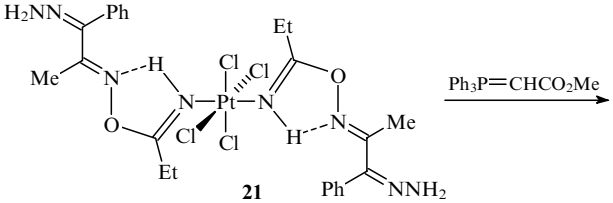


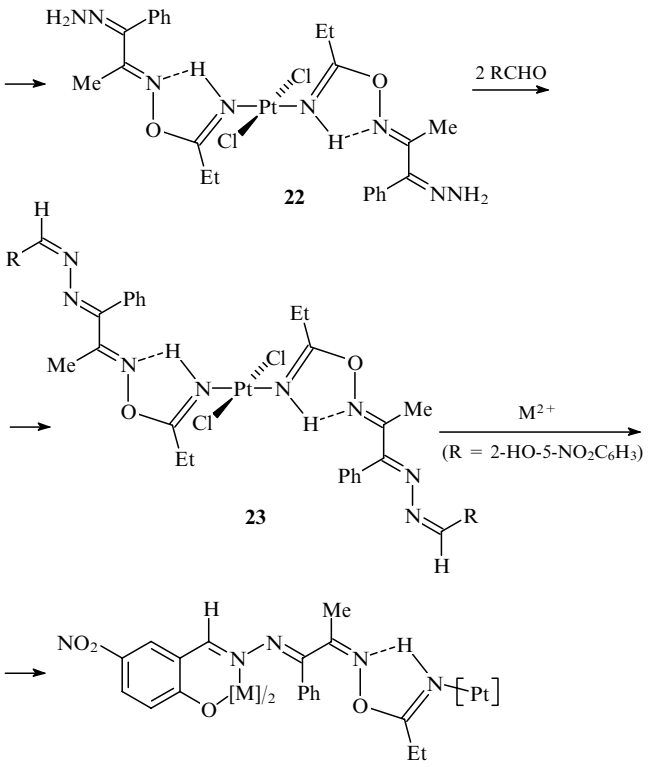
Figure 4. Structures of imino complex **19** (*a*) and dinuclear complex **20** with a macrocyclic ligand (*b*).



X = NOH: M = Re, Pt; R^1 = Me; R^2 = R^3 = Me,
R^2–R^3 = $(CH_2)_n$ (n = 4–6);
X = O: M = Pt; R^1 = Me, Et; R^2 = Me; R^3 = Me, Ph, C_6H_4F;
X = NNH_2: M = Pt; R^1 = Me, Et; R^2 = Me; R^3 = Me, Ph.

Imino complexes **21** are of interest because the ligand formed upon nucleophilic addition of oxime to nitrile contains a remote free functional group, which can be involved in further reactions.[134] For example, reduction of imino complex **21** (M = Pt, X = NNH_2, R^1 = Et, R^2 = Me, R^3 = Ph) with phosphorus ylide $Ph_3P{=}CHCO_2Me$ afforded the corresponding platinum(II) complex **22** containing peripheral NH_2 groups, which undergo Schiff condensation with aromatic aldehydes RCHO (R = 2-HO-5-$NO_2C_6H_3$ and 4-$NO_2C_6H_4$) to give complexes **23** containing the newly formed free remote functionalised groups. Compound **23** with R = 2-HO-5-$NO_2C_6H_3$ was used as a metal-containing ligand for subsequent complexation with Cu^{2+} and Co^{2+}.[134]





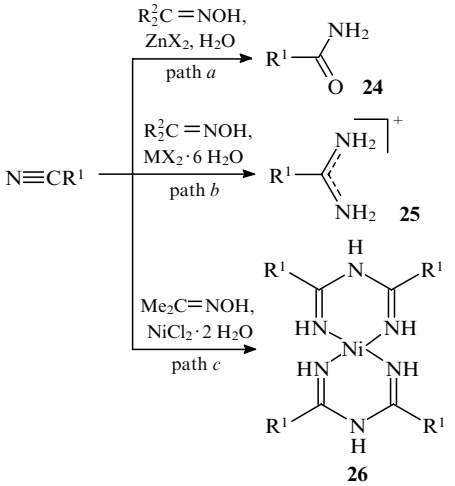
R = 2-HO-5-$NO_2C_6H_3$, 4-$NO_2C_6H_4$; M = Cu^{2+}, Co^{2+}.

To summarise, a new type of reactivity of *vic*-dioximes, dione monooximes and hydrazone oximes with respect to nitriles was revealed in the studies of nucleophilic addition reactions.[118, 120]

4. Transformations of nitriles promoted by 3d-metal – oxime systems

Reactions of nitriles with 'simple' oximes in the presence of complexes and salts of labile 3d metals afford products (free carboxamides **24**, amidinium salts **25** and coordinated imidoyl amidines **26**) different from those described in Sections III.2 and III.3. For example, catalytic hydrolysis of a series of nitriles R^1CN in the presence of the ZnX_2–$R^2_2C{=}NOH$ system produces the corresponding carboxamides $R^1C(O)NH_2$ (Scheme 5, path *a*).[74]

Scheme 5



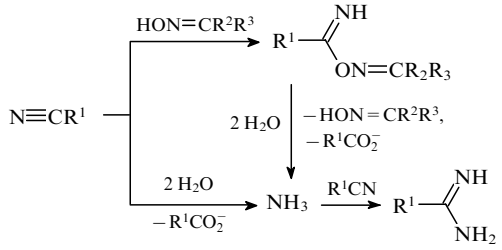
R^1 = Me, CH_2Cl, Et, Pr^n, Pr^i, Bu^n, Bu^t, *p*-$MeOC_6H_4CH_2$, Ph;
R^2_2 = Me_2, $(CH_2)_4$, $(CH_2)_5$; M = Co, Ni; X = Cl, NO_3.

This system containing the zinc salt and oxime in a molar ratio of 1 : 4 (which is optimal for hydrolysis of RCN) allows one to transform nitriles into carboxamides under mild conditions with a

catalyst turnover number of about 100 for the majority of nitriles and up to 1000 for the conversion of *p*-$MeOC_6H_4CH_2CN$ into *p*-$MeOC_6H_4CH_2C(O)NH_2$. It should be noted that, taken separately, the zinc salt and oxime do not exhibit catalytic activity. The intermediate $[ZnX_2(R^2_2C=NOH)_2]$ was isolated and its catalytic activity in hydrolysis was experimentally confirmed, which provide evidence that this complex is directly involved in the catalytic cycle.[74] It is believed [74] that one step of the process involves the reaction of the $[ZnX_2(R^2_2C=NOH)_2]$ complex with R^1CN, resulting in its electrophilic activation followed by the formation of the imino complex. The $ZnX_2-R^2_2C=NOH$ reagent system is the most readily accessible and inexpensive catalytic system for the transformation of R^1CN into the corresponding carboxamides $R^1C(O)NH_2$.[135]

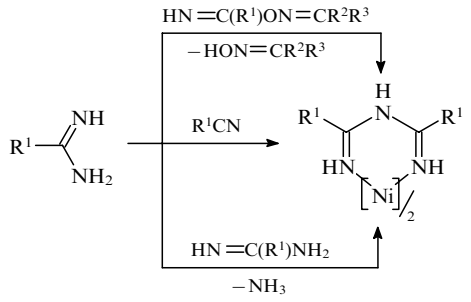
In the presence of salts $MX_2\cdot 6H_2O$ (M = Co, Ni) and an excess of oxime $R^2_2C=NOH$, sterically unhindered nitriles are quantitatively transformed into amidinium salts $R^1C(NH)NH_2\cdot HNO_3$ (Scheme 5, path *b*).[136,137] The optimal conditions for the formation of $R^1C(NH)NH_2\cdot HNO_3$ are those where salt $M(NO_3)_2\cdot 6H_2O$ and oxime $R^2_2C=NOH$ are used in a molar ratio of 1 : 4. A change in the ratio to 1 : 2 leads to a substantial decrease in the yield of the target product and an increase in the reaction time. The results of investigation of the reaction products and intermediates suggested [136,137] the following mechanism: initial metal-mediated hydrolysis of nitrile giving rise to R^1CO_2H and ammonia followed by the reaction of the latter with metal-activated nitrile to produce amidine (Scheme 6). It is believed that all steps of the process yielding amidines require the involvement of a metal centre, and some steps are additionally catalysed by oxime.

Scheme 6

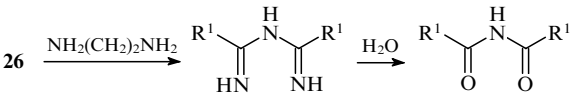


The reaction of nitriles with oximes in the presence of nickel salt $NiCl_2\cdot 2H_2O$, which is less hydrated than $M(NO_3)_2\cdot 6H_2O$ (M = Ni, Co), follows a different pathway.[137] For example, the reaction of R^1CN with a $NiCl_2\cdot 2H_2O-Me_2C=NOH$ mixture affords the imidoyl amidine complexes $[Ni\{\underline{N}H=C(R^1).NHC(R^1)=\underline{N}H\}_2]^{2+}$ (Scheme 5, path *c*).

Although the mechanism of this process is not entirely understood, it was hypothesised [137] that the initial step affords coordinated amidines according to Scheme 6, which are then involved in transformations to give chelating imidoyl amidine.



The resulting imidoylamidine ligand was isolated in the free state by the reaction with ethylenediamine or as a salt by the reaction of $HBF_4\cdot Et_2O$ with a solution of complex **26** in MeCN.[137] The reaction of ethylenediamine with complex **26** in an aqueous methanolic solution produced acylamides $R^1C(O)NHC(O)R^1$ through hydrolysis of intermediate imidoyl amidines **27**. This is a new procedure for the preparation of imidoyl amidines **27**, which are used in the synthesis of triazines and triazine-containing polymers.



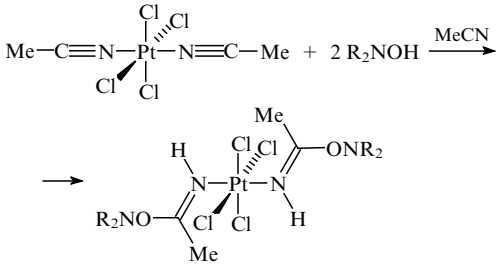
27

Therefore, 3d-metal salt – oxime systems can be employed to activate nitriles in the reactions giving rise to carboxamides, amidines, imidoyl amidines and acylamides, which are of great commercial and/or preparative importance. It should be noted that variation of the metal salts in the activating system allows one to prepare selectively and in good yield different products from the same starting nitriles.

IV. Reactions of hydroxylamines and hydroxamic acids

Other HON-nucleophiles (along with oximes), such as substituted hydroxylamines and hydroxamic acids, can be used in addition reactions to coordinated nitriles. Although hydroxamic acids are formally hydroxylamine derivatives, the nitrogen atoms in these compounds are in different hybridisation states and, consequently, act as nucleophiles of different types.

Unsubstituted hydroxylamine, being an ambidentate N,O-nucleophile, can be involved in the addition to free nitriles at both centres. In most cases, the addition occurs at the nitrogen atom. These reactions produce amidoximes.[11] The addition of unsubstituted hydroxylamine NH_2OH to complexed nitriles has not been documented. Several studies were devoted to reactions of alkylated hydroxylamines R_2NOH with coordinated nitriles.[138–140] For instance, N-addition of alkylated hydroxylamines to Mo and W nitrile complexes was described.[138,139] Only one example of addition of hydroxylamines R_2NOH to coordinated nitrile in *trans*-$[PtCl_4(MeCN)_2]$ involving the OH group is known.[140]



R = Me, Et, Bn.

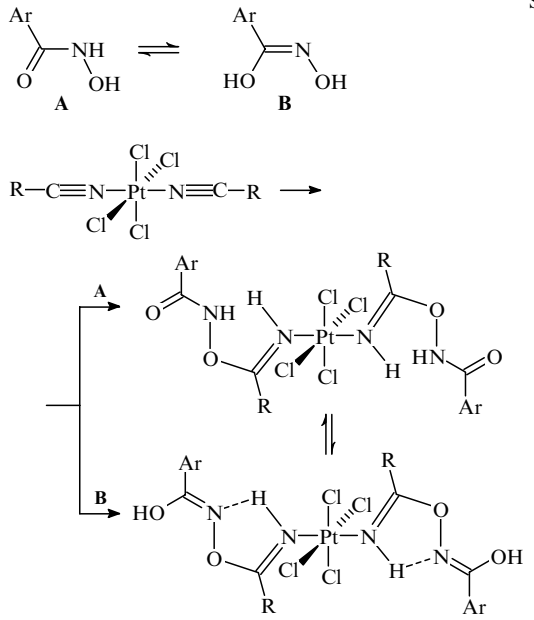
Hydroxamic acids ArC(O)NHOH also show unusual reactivity with respect to the nitrile complex *trans*-$[PtCl_4(EtCN)_2]$.[141] In this case, hydroxamic acids, which are known in chemistry primarily due to chelation reactions giving rise to stable five-membered metallacycles, act as nucleophiles and react with a coordinated nitrile.

Hydroxamic acids exist as two tautomeric forms **A** and **B**. Both forms can potentially act as HO-nucleophiles (Scheme 7).

Their contribution to the addition reactions was elucidated in the study of the reactions of *trans*-$[PtCl_4(EtCN)_2]$ with hydroxamic acid PhC(O)N(Me)OH (corresponds to the form **A** in Scheme 7) and methyl *N*-hydroxyimidoate $Me_3C_6H_2.C(OMe)=NOH$ (corresponds to the form **B** in Scheme 7), which are 'frozen' through N- or O-alkylation.[130]

The reaction of the platinum(IV) nitrile complex with methyl *N*-hydroxyimidoate is completed at room temperature in a few minutes, whereas the reaction with hydroxamic acid requires more drastic conditions (heating to 50 °C) and longer reaction time (2–3 h), which is indicative of the difference in the reactivity of

Scheme 7



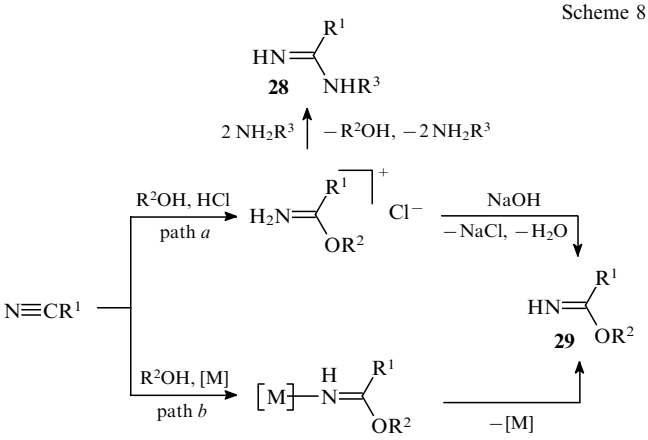
R = Alk, Ar; Ar = Ph, *o*-HOC_6H_4, *p*-ClC_6H_4, *p*-MeC_6H_4, *p*-$MeOC_6H_4$.

these forms. This suggests that the form **B** makes a greater contribution to the nucleophilic addition of unsubstituted hydroxamic acids to coordinated nitriles.

V. Reactions of alcohols with coordinated nitriles

The reaction of free nitriles with alcohols is involved in the two-step Pinner synthesis used for the preparation of amidines **28**. In the first step, the reaction of nitrile R^1CN with alcohol R^2OH in the presence of an excess of dry HCl (Scheme 8, path *a*) affords the salt $[R^1C(OR^2)=NH_2]Cl$, which (in the second step) reacts with two moles of amines to form amidines **28** and with alkali to give imidoates **29**.

Scheme 8

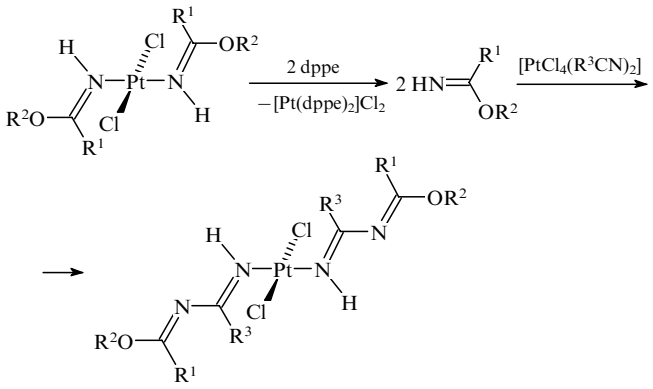


In this process, nitrile is activated through protonation. The main drawback of the Pinner synthesis of amidines is that it requires a large excess of HCl.

The reactions of alcohols with coordinated nitriles proceed analogously to the Pinner reaction with the difference that the metal centre serves as an activator (Scheme 8, path *b*). The nucleophilic addition of alcohols to nitriles affords imidoates, which are stabilised through coordination to the metal and, in the coordinated state, are resistant to hydrolysis. Since the nucleophilic addition of alcohols to nitriles has been surveyed in the reviews,[17,18] we do not consider this reaction in detail. Table 1 gives examples of these reactions.[93,102,142–188]

In summary, it should be noted that the conditions of the reactions of alcohols with nitriles depend substantially on the oxidation state of the metal. The addition of R^2OH to R^1CN present in low-oxidation-state metal complexes [Pt(II),[102,143–146] Pd(II),[158] Ni(II),[165] Ir(III),[171] Cu(II)[177]] requires that the nucleophilicity of R^2OH be additionally increased by adding alkali or another base (for example, NR_3; see Refs 158 and 165) in a catalytic or stoichiometric amount. Nitrile ligands in high-oxidation-state complexes [Pt(IV), Re(IV)][157,174] can react with alcohols in a neutral medium under rather mild conditions. The reaction is influenced by the nature of the R^1 group in the R^1CN molecule, and the reactions with nitriles containing electron-withdrawing groups (for example, R^1 = Ph) proceed more readily.[165,167,168] The addition of alcohols to nitriles also depends substantially on the steric parameters of the R^2 group in the alcohol molecules. Alcohols containing unhindered groups (R^2 = Me, Et) react more readily, whereas sterically hindered alcohols or phenols (R^2 = Ph, Bu^t) do not react at all.[102,142,165,167,168]

Imidoate complexes are of interest because they contain imine in the 'frozen' coordinated form, which provides stability of imidoates $R^1C(OR^2)=NH$. In the free state, the latter are generally easily subjected to hydrolysis. Imines can be isolated by decoordination under anhydrous conditions and used in subsequent reactions. An example of the use of this methodology was given in the study,[189] where imidoates were involved in subsequent reactions with nitriles included in platinum(IV) complexes in non-aqueous solutions.



Imidoates are better ligands than nitriles and they are more tightly held in the inner sphere of the metal, which, in most cases, excludes the possibility of a catalytic process. Nevertheless, several examples of catalytic alcoholysis of nitriles in the presence of Pd(II),[93] Re(III)[175] and Ir(III)[171] complexes have been documented. Unfortunately, the available data on the catalytic transformations of RCN into imidoates are insufficient for an understanding of the general features of this process.

VI. Reactions of other HO-nucleophiles

Examples of the addition of HOP-nucleophiles to coordinated nitriles are scarce. For instance, heating of complex **30** with nitrile *p*-MeC_6H_4CN for two days afforded compound **31** containing a new five-membered ring formed through nucleophilic attack of the oxygen atom of the P—OH group on the coordinated nitrile.[190]

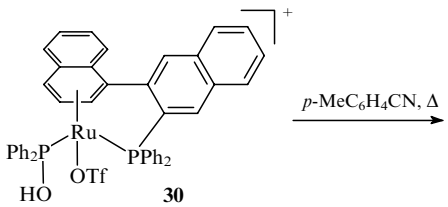


Table 1. Examples of nucleophilic addition of alcohols to coordinated nitriles.

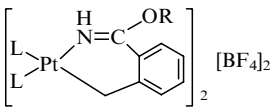
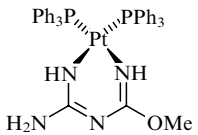
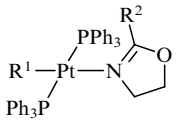
Starting reagents	Reaction conditions	Reaction products	Comments	Ref.
$[PtR^1XL_2]$ + $C_6F_4(CN)_2$-*p* + R^2OH R^1 = Me: X = Cl, L = PMe_2Ph, $AsMe_3$; R^1 = CF_3: X = I, L = PMe_2Ph; R^2 = Me, Et, Pr^n, Pr^i, CH_2CH_2OMe, $(CF_3)_2CH$	in the presence of Ag^+ salts	$[L_2MePt\{\underline{NH}=C(OMe)C_6F_4C(OMe)=\underline{NH}\}PtL_2Me]$, $[L_2MePt\{\underline{N}\equiv CC_6F_4C(OR^2)=\underline{NH}\}PtL_2Me]$ for R^1 = Me	a complex with bis-imidoate is formed only by the reaction with MeOH, whereas the reaction with R^2OH (R^2 = Et, Pr^n, CH_2CH_2OMe) affords monoaddition products; Pr^iOH and $(CF_3)_2CHOH$ are not involved in addition reactions. If R^1 = CF_3, the reaction proceeds more rapidly than that involving compounds with R^1 = Me	142
$[PtCl_2(MeCN)_2]$ + ROH R = Me, Et, Pr^i	1 equiv. of KOH or 3 equiv. of KOPh, room temperature	$[PtCl_2\{\underline{NH}=C(OR)Me\}_2]$	yield of the product is 50% – 70%	143
$K[PtCl_3(R^1CN)]$ + R^2OH R^1 = Me, Et, Ph, Bu^t; R^2 = Me, Et, Ph	catalytic amount of KOH	$K[PtCl_3\{\underline{NH}=C(OR^2)R^1\}]$	the reaction was demonstrated to produce initially the $[PtCl_3\{(Z)\text{-}NH=C(OR^2)R^1\}]^-$ complex followed by either complete isomerisation to $[PtCl_3\{(E)\text{-}NH=C(OR^2)R^1\}]^-$, if R^2 = Me or Et, or the formation of an equilibrium mixture of *E* and *Z* isomers, if R^2 = Ph	144, 145
cis(*trans*)-$[PtCl_2(R^1CN)_2]$ + R^2OH R^1 = Me, Et, Ph, Bu^t; R^2 = Me, Et, Ph	the same	$[PtCl_2\{NH=C(OR^2)R^1\}_2]$		144, 145
$[Pt(EtCN)_4][CF_3SO_3]_2$ + EtOH	2 equiv. of KOH	$[Pt\{(E)\text{-}NH=C(OEt)Et\}_4][CF_3SO_3]_2$	the *E* configuration of the ligand was confirmed by X-ray diffraction	146
$[Pt(\mu_2\text{-}C,N\text{-}CH_2C_6H_4C\equiv N)L_2]_2[BF_4]_2$ + ROH L = Ph_3P, L_2 = $Ph_2P(CH_2)_2PPh_2$ (dppe); R = Me, Et, Pr^i, Bn, Bu^t, Ph	–		the effect of steric hindrance of the R group of alcohol on the reaction rate was studied: the reaction does not occur for compounds with R = Bu^t	102
cis-$[Pt\{NCN=C(NH_2)_2\}_2(PPh_3)_2][BPh_4]_2$ + + MeOH	–		addition of a methanol molecule at the triple bond of one of the ligands, decoordination of another ligand and the metallacycle formation	147, 148
$[PtCl_2(RCN)_2]$ + $HO(CH_2)_2Cl$ R = Alk, Ar	BuLi or NEt_3	$[PtCl_2\{\overline{N=C(R)OCH_2CH_2}\}_2]$	in the reaction in the presence of NEt_3, the formation of $[PtCl_2\{NH=C(R)OCH_2CH_2Cl\}_2]$ as an intermediate was detected. The reaction of dppe with complexes afforded Δ^2-oxazolines	149, 150
$[Pt(R^1)(NCR^2)(PPh_3)_2]^+$ + $HO(CH_2)_2Cl$ R^1 = H, Me, CF_3; R^2 = Alk, Ar	Bu^nLi		the reaction of an excess of Cl^- with the $[Pt(CF_3)\{\overline{N=C(R)OCH_2CH_2}\}_2(PPh_3)_2]^+$ complex produced free Δ^2-oxazoline	151, 152
$[PtCl_2(NCR)_2]$ + $HOCH_2C^*(H)(Cl)Me$ R = Alk, Ar	Bu^nLi	$[PtCl_2\{\overline{N=C(R)OCH_2CH(Me)}\}_2]$	the absolute configuration of the chiral carbon atom in the Δ^2-oxazoline ligand is retained	153

Table 1 (continued).

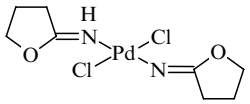
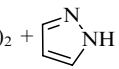
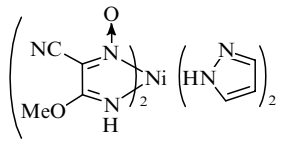
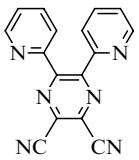
Starting reagents	Reaction conditions	Reaction products	Comments	Ref.
$[PtCl_2(NCR)_2]$ + $HO(CH_2)_3Cl$ R = Alk, Ar	Bu^nLi	$[PtCl_2\{\overline{N=C(R)OCH_2CH_2CH_2}\}_2]$	the reaction of dppe with the complex afforded 1,3-oxazine	154
$[Pt(CF_3)(NCR)(PPh_3)_2]^+$ + $HO(CH_2)_3Cl$ R = Alk, Ar	Bu^nLi	$[Pt(CF_3)\{\overline{N=C(R)OCH_2CH_2CH_2}\}(PPh_3)_2]^+$	the reaction of $[(PPh_3)_2N]Cl$ with the complex produced 1,3-oxazine	154
$[PtMe_2I_2(PMe_2Ph)_2]$ + C_6F_5CN + MeOH	$AgPF_6$	$[PtMe_2\{NH=C(OMe)C_6F_5\}_2(PMe_2Ph)_2]$	it was suggested that the reaction proceeds through the formation of the solvated complex $[PtMe_2(MeOH)_2(PMe_2Ph)_2]^{2+}$, which then reacts with nitrile	155, 156
$[PtCl_4(NCR^1)_2]$ + R^2OH R^1 = Me, Et, Bn, Ph; R^2 = Me, Et, Pr^n, Pr^i, Bu^n	40 °C in the absence of a base	$[PtCl_4\{NH=C(OR^2)R^1\}_2]$		157
cis-$[Pd(\mu_2\text{-}C,N\text{-}CH_2C_6H_4CN)L_2]_2[BF_4]_2$ + MeOH L = PPh_3, L_2 = $Ph_2P(CH_2)_2PPh_2$	NEt_3	$[Pd\{\mu_2\text{-}C,N\text{-}CH_2C_6H_4C(OMe)=NH\}L_2]^+$		158
$Na_2[PdCl_4]$ + $HO(CH_2)_3CN$	–		in the absence of the palladium complex, nitrile $HO(CH_2)_3CN$ is not subjected to intramolecular cyclisation	159
$[Pd_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ + R^1CN + R^2OH R^1 = Me, Ph, $NC(CH_2)_n$ (n = 1, 2), 2-NC_5H_4; R^2 = Me, Et	–	$[Pd(C_6F_5)_2\{NH=C(OR^2)R^1\}_2]$ (for R^1 = Me, Ph), $[Pd(C_6F_5)_2\{NH=C(OR^2)(CH_2)_nC(OR^2)=NH\}]$ (for R^1 = $NC(CH_2)_n$) and $[Pd(C_5F_5)_2\{NC_5H_4C(OR^2)=NH\}_2]$ (for R^1 = NC_5H_4)	in solution, imidoate complexes exist as equilibrium mixtures of *E*,*E*, *E*,*Z* and *Z*,*Z* isomers	160 – 164
$[Pd(solv)_2\{HO(CH_2)_2S(CH_2)_2S(CH_2)_2OH\}]^{2+}$ + + MeOH + Cl_2CHCN solv = D_2O, $(CD_3)_2CO$, CD_3OD	–	$Cl_2CHC(OMe)=NH$	the $[Pd(solv)_2\{HO(CH_2)_2S(CH_2)_2S(CH_2)_2OH\}]^{2+}$ complex catalyses methanolysis of nitrile Cl_2CHCN. The reaction is accelerated by a factor of 10^6 compared to the uncatalysed reaction. An intermolecular mechanism of the reaction of coordinated nitrile with free alcohol was established	93
$[Ni(C_6Cl_5)(NCR^1)L_2][ClO_4]$ + R^2OH R^1 = Me, Ph; L = PPh_2Me, $PPhMe_2$; R^2 = Me, Et	catalytic amount of NEt_3	$[Ni(C_6Cl_5)\{NH=C(OR^2)R^1\}L_2][ClO_4]$	the formation of the product is determined by steric hindrance of phosphine and/or R^2OH and the electron-withdrawing properties of the R^1 group in R^1CN	165
$Ni(NO_3)_2$ +  + $NaON=C(CN)_2$ + + MeOH	–		the complex was characterised by X-ray diffraction	160, 166
Ni^{2+} +  + ROH (R = Me, Et)	–	the complex with the imidoate ligand	the complex was characterised by X-ray diffraction	161, 162

Table 1 (continued).

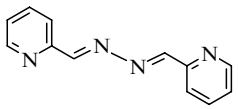
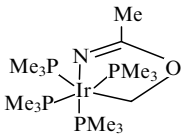
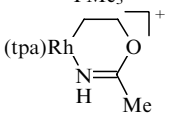
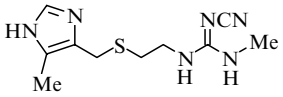
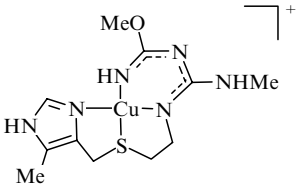
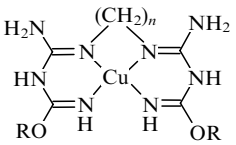
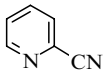
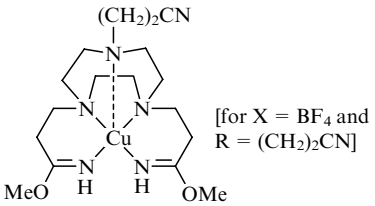
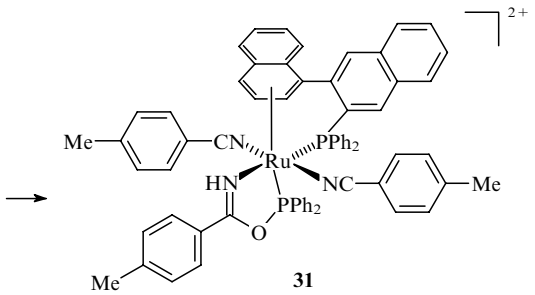
Starting reagents	Reaction conditions	Reaction products	Comments	Ref.
$[NiL(NCR^1)][ClO_4]$ + R^2OH L is an *S*,*N*,*N*-tridentate ligand; R^1 = Me, Et, Ph; R^2 = Me, Et, Pr^n	reflux in the presence of an excess of R^1CN		the reaction rate is determined by the steric properties of the R^1 and R^2 groups and can be increased by four orders of magnitude with the use of catalytic amounts of $NaOR^2$. The reaction in wet alcohol produces $[NiL\{NH_2COR^1\}][ClO_4]$ due to hydrolysis of the imidoate ligand	167, 168
$[IrL(NO)(PPh_3)_2][PF_6]_2$ + RCN + EtOH R = Me, Ph Bn; L = 	CH_2Cl_2, room temperature, 30–40 days	$[Ir\{(2\text{-}C_5H_4N)CH{=}N{-}N{=}C(NOH)(NC_5H_4\text{-}2)\}.\{NH{=}C(OEt)R\}(PPh_3)_2][PF_6]_2$		169
$[IrMeClI(CO)L_2]$ + NCC_6F_5 + MeOH L = PMe_2Ph, $PMePh_2$	$AgPF_6$	$[IrMeCl(CO)\{NH{=}C(OMe)C_6F_5\}L_2]^+$	Ag^+ is used for binding iodide to form AgI, the reaction proceeds through the formation of the $[IrMeCl(MeOH)(CO)L_2]^+$ intermediate, which reacts with nitrile	170
$[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(NCMe)]^+$ + ROH Cp^* = $\eta^5\text{-}C_5Me_5$, R = Me, Et, Pr^i	–	$[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)\{NH{=}C(OR)Me\}]^+$	the initially formed mixture of *E* and *Z* isomers of the imidoate ligand (R = Me, Et) is transformed into the *Z* isomer in the presence of the corresponding alcohol. For Pr^iOH, only the *Z* isomer was isolated. Imidoate NH=C(OR)Me was isolated from the $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)\{NH = C(OR)Me\}]^+$ complex by replacement with PPh_3	171
$[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(NCPh)][SO_3CF_3]$ + + PhCN + MeOH	catalysis, Na_2CO_3, 70 °C	free NH=C(OMe)Ph		171
$[Ir(CH_2OH)(MeCN)(PMe_3)_4]^{2+}$	catalysis by Py or PMe_3		in the absence of a catalyst, the reaction proceeds more slowly and is suppressed upon the addition of $HBF_4 \cdot Et_2O$	172
$[Rh(tpa)\{\underline{C}H_2CH_2\underline{O}\}]^+$ + MeCN tpa is *N*,*N*,*N*-tris(2-pyridylmethyl)amine	NH_4PF_6		the reaction proceeds through the formation of the $[Rh(tpa)(CH_2CH_2OH)(MeCN)]^{2+}$ intermediate	173
$[ReCl_4(MeCN)_2]$ + ROH R = Me, Et	–	$[ReCl_4\{NH{=}C(OR)Me\}_2]$	free imidoate was isolated from the complex upon the addition of PPh_3	174
$[Re_6(\mu_3\text{-}Se)_8]^{2+}$ + MeCN + ROH R = Me, Et	UV irradiation, catalysis by a Re cluster	NH=C(OR)Me		175
$AuCl_3$ + R^1CN + R^2OH R^1 = Me, Et; R^2 = Me, Et	–	$[R^1C(OR^2)NH_2][AuCl_4]$	the $[EtC(OEt)NH_2][AuCl_4]$ complex was characterised by X-ray diffraction	176

Table 1 (continued).

Starting reagents	Reaction conditions	Reaction products	Comments	Ref.
$Cu(ClO_4)_2$ +  + MeOH	KOH, 60 °C		the complex was characterised by X-ray diffraction	177
$CuSO_4$ + $NCNC(NH_2)NH(CH_2)_nNHC(NH_2)NCN$ + + ROH R = Me, Et; n = 2, 3	reflux, 8 – 12 h		–	178
$Cu(NO_3)_2$ + $KN(CN)_2$ + MeOH	Py	[Cu{NH = C(OMe)NC(OMe) = NH}$_2$]	the reaction affords a product isoelectronic to the β-diketonate complexes [M(acac)$_2$]	179, 180
$[Cu(bipy)]^{2+}$ + $[ONC(CN)_2]^-$ + MeOH	–	the complex with the chelate ligand N(O)C(C ≡ N)C(OMe) = NH	the compound was characterised by X-ray diffraction	181, 182
CuX_2 +  + ROH X = Cl, Br, NCS, ClO_4; R = Me, Et, Bu^n	–	complexes with chelated pyridinecarboximidoate NH = C(OMe)C_5H_4N	the reactions of Na_2(EDTA) with the [$CuCl_2(H_2O)_2${NH = C(OR)C_5H_4N}$_2$] and [$CuCl_2${NH = C(OR)C_5H_4N}] complexes gave imidoate, which underwent rapid hydrolysis to form O = C(OR)C_5H_4N. In the absence of a metal salt, 2-cyanopyridine does not react with methanol. Analogous complexes with imidoates were prepared starting from Co(II), Ni(II) and Fe(II) salts	183 – 185
CuX_2 + ArCH = NNHC(O)CH_2CN + EtOH X = Cl, Br, 0.5 SO_4	–	the complex with the imidoate ligand ArCH = NNHC(O)CH_2C(OEt) = NH	the ligand is coordinated in a tridentate fashion	186
[CuCl(NHR^{1}R^2){NH = C(OMe)C_5H_4N}]Cl + + $NC_5H_3R^3R^4$ + MeOH R^1 = H, R^2 = Bn; R^1 – R^2 = $(CH_2)_5$; R^3 = 2-CN: R^4 = H, 4-CN, 6-CN	in the presence of Cu salts	free NH = C(OMe)C_5H_4N, 2-{NH = C(OMe)}-4-NCC_5H_3N and 2,6-{NH = C(OMe)}$_2C_5H_3N$	copper salt catalysed the formation of imidoates, the reactivity of alcohols decreases with increasing steric hindrance of amine	187
CuX_2 + 1,4,7-tris-(R)-triazacyclononane + MeOH X = Cl, BF_4; 1,4,7-tris-(R)- is 1,4,7-tris(cyanomethyl)-, 1,4,7-tris(2-cyanoethyl)-, 1,4-bis(2-cyanoethyl)-7-methyl	reflux	 [for X = BF_4 and R = $(CH_2)_2$CN]	only copper-coordinated nitrile groups of the macrocycle are subjected to methanolysis. If X = Cl, only one nitrile group is involved in the reaction with methanol	188

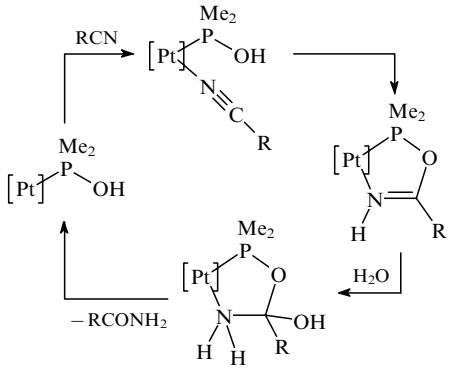


31

OTf = O_3SCF_3.

The structure of compound **31** was confirmed by elemental analysis, ^{1}H, ^{13}C, ^{31}P, ^{19}F and $^{15}N-^{1}H$ COSY NMR spectroscopy and FAB mass spectrometry.[190]

Several of the most efficient systems for catalytic hydrolysis of nitriles giving rise to amides are based on the platinum phosphinite complexes $[PtX(R_2PO\cdots H\cdots OPR_2)(PR_2OH)]$ (X = H, Hal; R = Alk, Ar).[32] It was hypothesised that the initial step involves dissociation of the complex to form the $[Pt(R_2PO\cdots H\cdots OPR_2).(PR_2OH)]^+$ cation followed by coordination of nitrile.[32] Hydrolysis of coordinated nitrile involves the intramolecular attack of the oxygen atom of hydroxy phosphine on RCN to give an intermediate analogous to that described in the study.[190]



Systems based on the $[PtX(R_2PO\cdots H\cdots OPR_2)(PR_2OH)]$ complexes allow one to perform efficient transformations of various nitriles into amides, including the synthesis of acrylamide, which is of great commercial importance.[32, 73]

The platinum phosphinite complexes $[PtH(R_2PO\cdots H\cdots OPR_2)(PR_2OH)]$ catalyse the formation of *N*-substituted amidines from nitriles and primary (or secondary) amines. Presumably,[191] the mechanism of this reaction is analogous to the mechanism of hydrolysis of nitriles involving these complexes.

VII. Conclusion

The present review surveys recent data on the addition of HO-nucleophiles to nitriles. In most cases, additional electrophilic activation of the C≡N group is required for these reactions to occur. Analysis of the published data shows that coordination to a metal centre is one of the most efficient ways of activating nitriles. Since the nucleophilic addition to nitriles provides the basis for the synthesis of a series of compounds of commercial value, the determination of optimal conditions for these reactions is an important problem in preparative chemistry.

Coordination of nitriles leads to a substantial increase in electrophilicity of the C≡N group, which substantially influences their reactivity. A comparative evaluation of the rates of hydrolysis of free and coordinated nitriles shows that the reaction constant increases by 6–8 orders of magnitude in metal-mediated processes. Nitrile ligands in high-oxidation-state metal complexes can bind nucleophiles. These reactions with free nitriles do not occur even under drastic conditions. In some cases, the resulting imino ligands can be isolated.

Metals not only increase the reactivity of the C≡N group but also influence the course of the reaction of nitriles with HO-nucleophiles. For instance, metal-mediated hydrolysis of nitriles, unlike hydrolysis of free RCN, generally stops at the formation of carboxamides, which do not undergo transformations into carboxylic acids. The latter fact is associated with a change in the ratio of the rate constants of the first and second steps of hydrolysis and stabilisation of the product formed in the first step (carboxamide) through coordination. In the presence of metal complexes, the reactions of nitriles with HO-nucleophiles proceed by mechanisms distinct from those observed in the absence of metal complexes (for example, nitriles are hydrolysed in the presence of nickel and cobalt salts to amidinium salts and imidoyl imidates).

In the addition of HO-nucleophiles to nitriles, metal often serves as a stabiliser of the reaction product. In most cases, metal-mediated reactions of HO-nucleophiles with nitriles produce coordinated imino compounds, which are generally unstable in the free state or do not exist at all (for example, the addition products of oximes and hydroxamic acids at the C≡N bond). Coordination to the metal centre stabilises these compounds and allows one to isolate such imino complexes in individual form. Coordination can also lead to stabilisation of the reaction products in a tautomeric form different from that in which the free compounds exist.

Due to the possibility of varying the nature of the metal, its oxidation state and ligand environment over wide ranges, a large number of nucleophiles of different strength can be used in addition reactions to coordinated nitriles and a broad spectrum of products can be synthesised. For example, complexes with imino and imidoylamidine ligands, as well as amidinium salts and free carboxamides, can be prepared by metal-mediated reactions of nitriles with oximes by varying the nature of the metal atom. In addition, the nature of the metal atom is responsible for the stoichiometric or catalytic character of the process. It should be noted that most known metal-mediated transformations of nitriles and HO-nucleophiles afford coordinated imines and require a stoichiometric amount of metal. The transformation products can be isolated in the free state as an additional step of the synthesis.

Examples of catalytic transformations of nitriles (hydrolysis and alcoholysis) are described in the literature. These reactions are of interest for the synthesis of compounds of commercial and/or pharmaceutical importance. Intermediates in catalytic systems are often too labile for preparative isolation and investigation. Model systems are used to understand the mechanisms of these reactions. Nitrile complexes of kinetically inert metals (for example, platinum) can serve as such models. The reactions of these complexes with nucleophiles give stable analogues of intermediates of catalytic processes. Studies of systems involving kinetically inert complexes would contribute to the design of new catalytic systems.

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