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Metal-mediated reactions of oximes

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Abstract. The published data on metal-mediated reactions of oximes are described systematically. The attention is focused on the reactions that serve as convenient methods for the synthesis of various organic compounds or models for the interpretation of the mechanisms of catalytic processes and the reactions resulting in new ligand systems. The bibliography includes 182 references.

I. Introduction

The permanent interest in ligand reactivity is caused, first of all, by the necessity of interpretation of the mechanisms of homogeneous metal-catalysed processes (including industrially important ones) in which a substrate is activated upon its coordination to a metal site. Usually it results in drastic changes in the substrate properties, particularly its electrophilicity (or nucleophilicity), acidity or redox properties. This alters the reactivity of the ligands to such an extent that the chemical reactions, impossible for a free ligand, become achievable. Books and reviews [1–25] concerning ligands' reactions are mainly focused on complexes with 'simple' (containing only one reaction site) ligands: hydrides,[11] carbonyls,[12] alkenes,[13] dinitrogen,[14] azides,[15] cyanides,[16] nitrosyls,[17] nitriles,[18,19] isonitriles,[20] amines,[21] sulfoxides,[22] sulfides and thiols,[23] pseudohalides[24] and phosphines.[25] Their chemical transformations mimic some catalytic processes and organic reactions taking place in the presence of metal complexes.

In contrast to the above-mentioned ligands, a coordinated oxime contains three active sites (C, N and O atoms) and an OH group the acidity of which increases drastically upon coordination.[26] Virtually all types of metal-mediated transformations are possible for the coordinated oximes, *viz*., nucleophilic and electrophilic reactions, intramolecular redox reactions, template synthesis,[27,28] metal-induced Beckmann rearrangement, *etc*.

Abundant experimental material on these transformations and on the metal-catalysed reactions of oximes and their complexes was considered in several reviews.[29–37] However, the problem is still topical, which is circumstantially proved by quite a number of recent papers on the subject. New reports together with previously non-reviewed results lead to a new insight into reactions of metal-activated oximes.

Retention or loss of integrity of the oxime fragment C = NOH during the coordination was the main characteristic used for our systematisation of metal-mediated reactions of oximes. According to this feature, all reactions are divided into two large groups.

The first group comprises transformations occurring with the cleavage of the O – N, O – H and C = N bonds. Two sub-groups within this first group involve non-redox reactions (first of all, addition or elimination of water molecules) and redox reactions.

Metal-mediated reactions of oximes with retention of the C = NOH fragment involve mostly the oxygen atom (less common, N and C atoms) of the oximes, they are represented by the nucleophilic addition reactions to substrates containing multiple bonds. Reactions involving peripheral groups in oxime and oximate complexes also belong to this category.

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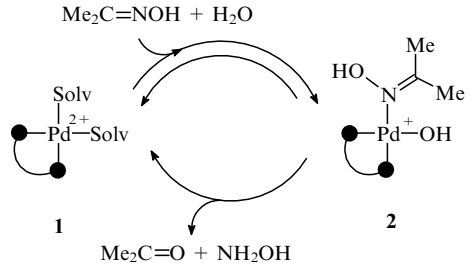
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II. Reactions with loss of integrity of the C = NOH fragment

1. Metal-mediated hydrolysis of oximes

Examples of metal-mediated hydrolytic cleavage of oximes occurring without change in the oxidation state of the nitrogen atom are discussed below.

A study of a catalytic process of acetone oxime hydrolysis in the presence of *cis*-$[Pd(en)(Solv)_2]^{2+}$ or *cis*-$[Pd(dtod)(Solv)_2]^{2+}$ (**1**) [en is ethylenediamine, dtod is 3,6-dithiaoctane-1,8-diol, Solv is H_2O or $(CD_3)_2CO$], including its kinetics, was reported.[38] A mechanism of the Pd-catalysed hydrolysis of acetone oxime has been proposed.

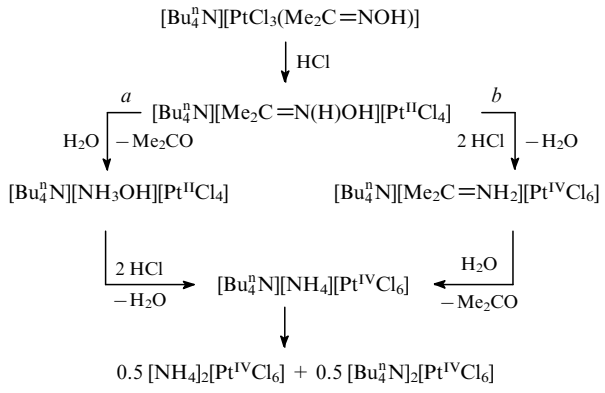


Palladium centre coordinates both the oxime and the hydroxide ion in the first step of the process yielding complex **2**. In the second step the C = N bond activated due to metal coordination is subject to intramolecular nucleophilic attack by the hydroxyl

ligand. As a result, the bond is hydrolytically cleaved to form acetone. The last and the rate determining step of the process is release of hydroxylamine upon dissociation of its Pd(II) complex. This step significantly reduces the efficiency of the catalytic process (the turnover number of the catalyst does not exceed 4). The presence of acetone and hydroxylamine (both free and coordinated) was confirmed by NMR spectroscopy.

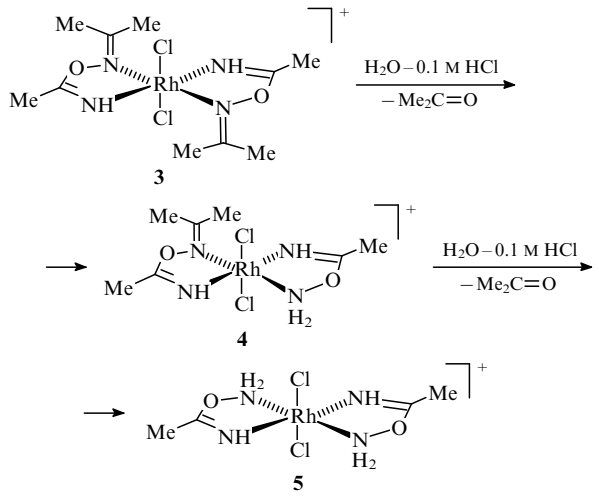
Treatment of the complex $[Bu^n_4N][PtCl_3(Me_2C=NOH)]$ with concentrated hydrochloric acid for 30 days at room temperature leads to two products, *viz*., $[NH_4]_2[PtCl_6]$ and $[Bu^n_4N]_2[PtCl_6]$,[39] which presumably result from consecutive redox and hydrolytic processes. Two alternative pathways of the process are presented in Scheme 1: acid hydrolysis of the oxime in the starting complex followed by intramolecular oxidation of Pt(II) to Pt(IV) by the eliminated $[NH_3OH]^+$ cation (path *a*), or oxidative deoxygenation of the oxime followed by hydrolysis of the produced iminium fragment (path *b*).

Scheme 1



However, no solid evidence in favour of one or another mechanism has been obtained. Nevertheless, it has to be stressed that both hydrolysis and oxidative deoxygenation of acetone oxime in this case are mediated by platinum(II).

Study on the reactivity of rhodium imino complexes formed in the nucleophilic addition of acetone oxime to rhodium(III) nitrile complexes reveals[40] that it is the oxime fragment of the imino-ligand that undergoes hydrolysis at pH 1 and 80 °C, while the imine fragment† manifests enormus stability under the same conditions. This implies that Rh(III) selectively activates the C=N bond of the oxime fragment.



^{1}H NMR study of this reaction has shown that the starting complex **3** completely transforms into a mixed-ligand product **4** in 36 h; the formation of acetone was also observed. When complex **4** was treated under the same conditions for 4 weeks, hydrolysis of the second imino-ligand occurred to give new bis-chelate complex **5**, which was isolated and structurally characterised. It is of note that the reaction proceeds faster in the absence of HCl, however the selectivity decreases substantially. In this case, considerable amount of by-products prevents isolation of compounds **4** and **5** in individual state.

Technetium imine-oxime complexes behave similarly.[41]

2. Dehydration of oximes

Synthesis of nitriles by dehydration of the corresponding aldoximes is long known and successfully employed in organic chemistry.[42,43] However, there are few examples of metal-mediated conversions of R(H)C=NOH into RCN.

Thus synthesis of two osmium nitrile complexes $[(\eta^6\text{-}C_6H_6)OsH(NCR)(PMeBu^t_2)]^+$ (R = Me, Ph) by reactions of $[(\eta^6\text{-}C_6H_6)OsHI(PMeBu^t_2)]$ with aldoximes RCH=NOH in the presence of $AgPF_6$ used for abstraction of the iodide ligand was described.[44] Tungsten nitrile complexes $[W(NCR)(CO)_5]$ (R = Me, Ph, C_6H_4OMe-*p*) were obtained from the corresponding aldoximes and $[W(THF)(CO)_5]$.[45]

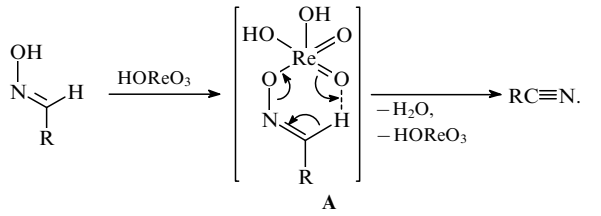
The reaction of $RuBr_3$ with benzaldoxime in 6 M aqueous HBr furnishes the mixed-valence ruthenium complex $[RuBr_3(NCPh)_5][RuBr_4(NCPh)_2]$.[46] Refluxing of the osmium acetonitrile trinuclear cluster $[Os_3(CO)_{11}(NCMe)]$ with anthracene-9-carbaldoxime in chloroform for 5 h resulted in the anthracenecarbonitrile complex $[Os_3(CO)_{11}(NCC_{14}H_9)]$ in 46% yield.[47] The formation of N-coordinated oxime intermediates in the initial stages of the above-mentioned reactions was suggested.[44–47] The electron density on the aldoxime nitrogen atom increases as a result of coordination to the metal (due to dative interaction of the occupied d-orbitals of a metal with the unoccupied π*-orbitals of a ligand), which facilitates cleavage of the N–O bond followed by dehydration and formation of a nitrile.

A number of studies on the dehydration of oximes assisted by Ru and Os complexes were reported. It is known that these metal sites possess strong affinities for nitriles. Obviously, the formation of highly stable nitrile complexes is one of the main driving forces of the reaction. This suggestion was indirectly supported by the results of a study[48] where it was shown that the reaction of the ruthenium complex $[Ru(NH_3)_5(H_2O)]^{2+}$ with the ketoximes Me(R)C=NOH [R = C(O)Me, C(O)Ph and CH(OH)Ph] leads to the acetonitrile complex $[Ru(NH_3)_5(NCMe)]^{2+}$ and elimination of ROH. The affinity of Ru(II) to nitrile is so high that even the cleavage of the ketoxime C–C bond becomes favourable.

Attanasi *et al.*[49] have shown that refluxing of aldoximes in acetonitrile in the presence of catalytic amounts of $Cu(OAc)_2\cdot H_2O$ produces the corresponding nitriles in good yield (85%–98%). Refluxing of benzaldoxime with AlI_3 (molar ratio 1:2) in acetonitrile for 2 h resulted in benzonitrile (92%).[50] Aldoximes undergo dehydration under mild conditions in the presence of titanium and indium trifluoromethanesulfonates [$TiCl_3(OTf)$[51] and $In(OTf)_3$[52]] affording the corresponding nitriles. Heterogeneous ruthenium catalysts obtained by adsorption of $[RuCl_2L_2]$ (L is *p*-cymene) on activated charcoal[53] or molecular sieves[54] are also used for conversion of aldoximes into nitriles.

Various aldoximes are converted into the corresponding nitriles in less than 1 h in more than 95% yields by azeotropic distillation with toluene or mesitylene in the presence of catalytic amounts of perrhenic acid $HOReO_3$ (1 mol.%, an aqueous solution).[55] A plausible reaction mechanism consists of nucleophilic addition of aldoximes to rhenium with formation of six-membered M,H-cyclic intermediates **A** which are split to give the corresponding nitriles:

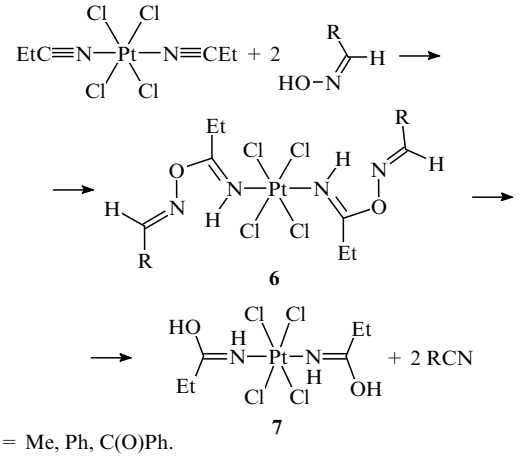
† It is known that non-coordinated imines are readily hydrolysed at low pH values.



A

Solid-phase dehydration of oxime ligands is also known.[56–58] The formation of PhCN as a result of thermal decomposition of the copper complex $[Cu\{2\text{-}OC_6H_4C(Ph)=NOH\}_2]$ was proved by combination of TGA and mass spectrometry.[56] Pyrolysis of Co(II) dimethylglyoximate and cyclohexanedione-1,2-dioximate complexes afforded acetonitrile and hexanedinitrile, respectively.[57] Lead(II) bis(salicylaldoximate) decomposes in the temperature range from 160 to 200 °C yielding the nitrile complex $[NCC_6H_4OPb]_2O$ with elimination of water.[58] Unfortunately, the formation of this product was confirmed only by elemental analysis.

An example of promotion of aldoxime dehydration by a coordinated ligand is known.[59] Thus the nucleophilic addition of aldoximes R(H)C=NOH to the platinum(IV) nitrile complex *trans*-$[PtCl_4(NCEt)_2]$ results in iminoacyl (imidate) derivatives *trans*-$[PtCl_4\{HN=C(Et)ON=CHR\}_2]$ (**6**).



6

7

R = Me, Ph, C(O)Ph.

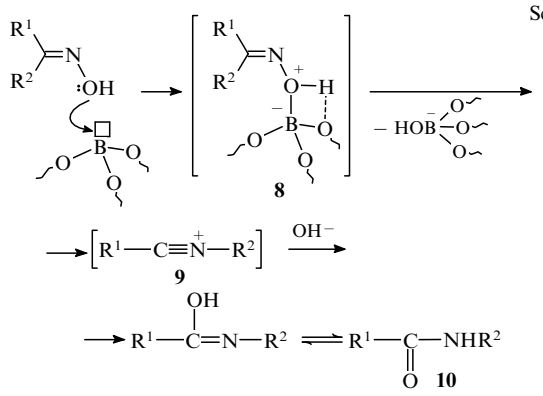
Complexes **6**, when stored in a solution, decompose yielding a Pt(IV) propionamide complex **7** (where the amide is stabilised in the imidic form) and the corresponding nitriles. This was confirmed by ^1H and ^{13}C NMR spectroscopy, thin layer chromatography and mass spectrometry. Comparison of the results presented in two papers (Refs 47 and 59) suggests that the reaction of the Os cluster (Ref. 47) also proceeds *via* an osmium iminoacyl intermediate, its decomposition results in anthracene-9-carbonitrile, which further reacts with Os.

3. Metal-mediated Beckmann rearrangement

The Beckmann rearrangement is still the simplest and the most convenient method of oxime conversion[60,61] into the corresponding amides both in laboratory and industry.‡ Strong Brønsted or Lewis acids are normally used as catalysts of this conversion.

The mechanism of the reaction was studied for borophosphates as Lewis acids.[62] In the first step, oximes react with borophosphates to form intermediate **8** (Scheme 2) stabilised by a hydrogen bond. Decomposition of the latter yields nitrilium cation **9**, which is converted into an amide **10** upon the reaction with the hydroxide ion.

Scheme 2



8

9

10

The rearrangement of oximes into amides is also catalysed by metal ions. For instance, benzamide was obtained from benzaldoxime in the presence of $CuCl_2$.[63] Later, it was shown[64] that monosaccharide oximes are converted into the corresponding aldonamides upon refluxing in 1,4-dioxane in the presence of $Cu(OAc)_2 \cdot H_2O$. Presumably,[64] copper(II) oximate complexes isolated from the reaction mixture are intermediates of this conversion. Unfortunately, no other experimental data on the reaction mechanism have been obtained.

Studies on the Beckmann rearrangement of various aldoximes into the corresponding amides catalysed by nickel(II) salts were carried out.[65–67] In particular, in the presence of catalytic amounts of $Ni(OAc)_2 \cdot 4H_2O$, aldoximes isomerise into amides in xylene or water in high yields. The role of the metal in this process was studied in detail[68,69] using rearrangement of a number of aldoximes into the corresponding amides in the presence of catalytic amounts of the complexes $[M(acac)_2]$ (M = Pd, Ni) or $[Pd(CH_2NO_2)(acac)(PPh_3)]$ as a model reaction. The reaction mixtures contained aldoxime and $[Pd(acac)_2]$, the presence of small amounts of acetonitrile was revealed by GLC and ^1H NMR spectroscopy. Heating of a three-component mixture Me(H)C=NOH – $PhCH_2CN$ – $[Pd(acac)_2]$ results in the conversion of acetaldoxime into acetonitrile and of phenylacetonitrile into phenylacetamide. Thus, a stepwise mechanism was suggested,[68,69] which includes dehydration of the aldoxime into the corresponding nitrile and hydrolysis of the latter into the amide.

$$R(H)C{=}NOH \xrightarrow[-H_2O]{} RC{\equiv}N \xrightarrow{H_2O} RC(O)NH_2\,.$$

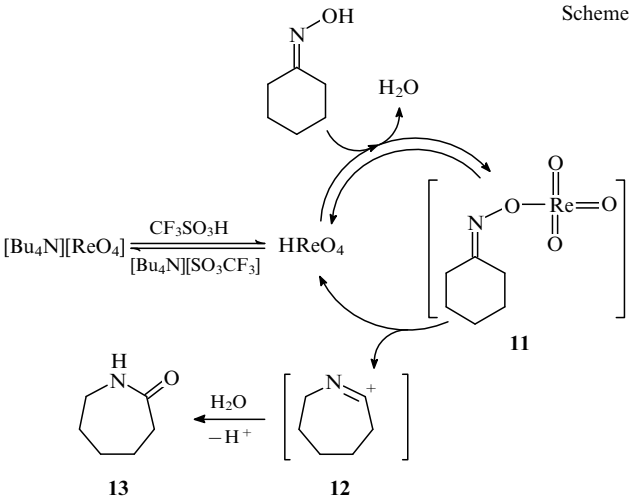
Similar mechanism was suggested for the conversion of aldoximes into amides in the presence of catalytic amounts of the Wilkinson complex $[RhCl(PPh_3)_3]$ (DMF, 150 °C).[70] In this case, the formation of small (~8%) amounts of nitriles was also observed. Unsuccessful attempts of rearrangements of ketoximes and *O*-alkylaldoximes into amides were yet another evidence in favour of the suggested stepwise mechanism of this reaction.

It was shown[71,72] that various ketoximes were converted in high yields into amides upon refluxing in nitromethane as the result of the Beckmann rearrangement catalysed by a mixture of $[Bu_4N][ReO_4]$ and CF_3SO_3H. No reaction occurs in the absence of $[Bu_4N][ReO_4]$. It was suggested that oxime perrhenate **11** (Scheme 3) is an intermediate of this process in the case of cyclohexanone oxime. This intermediate **11** decomposes yielding a seven-membered cation **12** and $HReO_4$. Hydrolysis of the cation **12** yields ω-caprolactam (**13**).

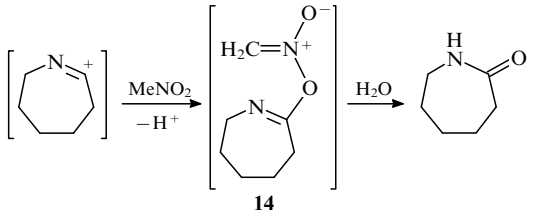
To increase the yield of ω-caprolactam, $NH_2OH \cdot HCl$ was added to the reaction mixture in order to bind the ketone formed as a by-product. The use of $MeNO_2$ as a solvent also increases the yields of amides, which is explained by possible formation of

‡ This is an industrial method for the manufacture of ω-caprolactam.

Scheme 3



intermediate **14**, *i.e.*, an adduct of nitromethane (in aci-nitro form) to the cation **12**, which is easily hydrolysed to give ω-caprolactam.



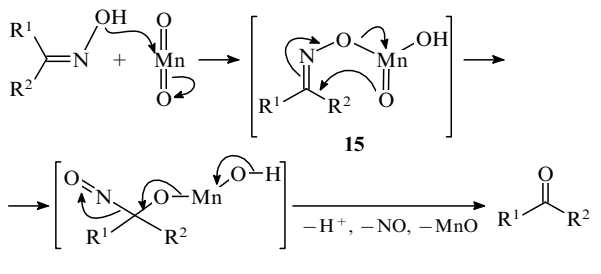
$[Yb(OTf)_3]$ [73] and $[La(OTf)_3]$ [74] appeared to be very efficient catalysts of the Beckmann rearrangement of some ketoximes. Unfortunately, the role of metal in this process was not discussed.

Analysis of the published data shows that the role of the metal in the metal-mediated Beckmann rearrangement is reduced to the dehydration of aldoximes, on one hand, and, on the other hand, to activation of the nitriles formed with respect to hydrolysis, which affords amides (for metal-mediated hydrolysis of nitriles, see a review [75]).

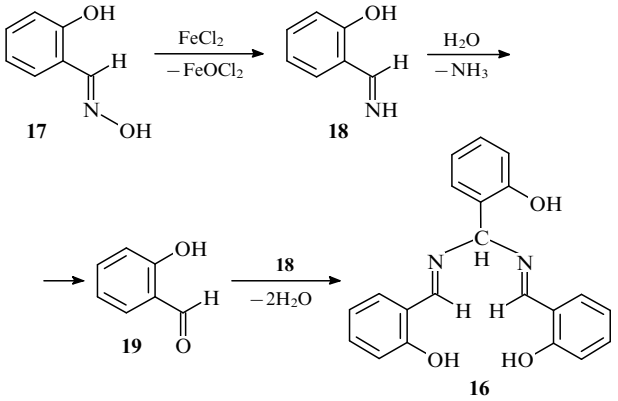
4. Reductive and oxidative deoximation

Among the methods for conversion of oximes into carbonyl compounds, reductive and oxidative deoximation are of the greatest interest, particularly, the reactions occurring in the presence of various metal compounds. These reactions are accompanied by changes in the oxidation state of the oxime nitrogen atom followed by hydrolytic cleavage of the C—N bond resulting in carbonyl compounds.

For instance, oxidation of various aldoximes and ketoximes in the presence of activated MnO_2 in aprotic solvents (dichloromethane, chloroform) proceeds under mild conditions (room temperature) and produces the corresponding carbonyl compounds in very high yields.[76] A plausible reaction mechanism involving the metal site was suggested. In the first step of the process, addition of an oxime to MnO_2 occurs to yield intermediate **15**, which then undergoes a [2,3]-sigmatropic shift followed by decomposition of the complex and formation of the carbonyl compound:



Reaction of ferrous chloride $FeCl_2$ with salicylaldoxime in the presence of triethylamine leading to the formation of the trinuclear complex $[Fe^{III}_3(\mu_3\text{-}O)(\mu_2\text{-}OPh)]^{6+}$ is an example of oxidative deoximation (see Ref. 77). The reaction proceeds in methanol in an atmosphere of argon. The formation of 2-[bis(salicylideneimino)methyl]phenol (**16**) is explained by reductive deoxygenation of the starting oxime **17** into the corresponding imine **18**, hydrolysis of the imine **18** to salicylaldehyde **19** and condensation of the latter with the imine **18** (the ratio **18** : **19** = 2 : 1).



Numerous experimental papers on the subject in question published before 2001 were thoroughly analysed in a review.[78] Therefore, only the data published after 2000 are discussed in the present review with indication of the oxidising agents used.

Quaternary heterocyclic halochromates [HetH](CrO_3X) (Het is pyridine, methylpiperidine, quinoline; X = Cl, F),[79–85] $Mg(HSO_4)_2$ in the presence of wet SiO_2,[86] MnO_2,[87] $[Cu(NH_3)_4](MnO_4)_2$,[88] $LnCl_3$ [89] and $KMnO_4$ [90] were used as oxidants in the oxidative deoximation.

Reductive deoximation of oximes to the corresponding carbonyl compounds proceeds in high yield using a suspension of zinc powder in non-dried MeCN in the presence of tungsten(VI) and molybdenum(VI) chlorides.[91]

Microwave irradiation was shown to effect oxidative deoximation. For example, oximes are cleaved in the presence of $BiCl_3$ in refluxing THF in 10 h (the yield of ketones is 40%). The same reactions under microwave irradiation are completed in a few minutes and in high yields, which allows smooth conversion of even such a sterically hindered substrate as camphor oxime into the corresponding ketone.[92]

Thus, reductive and oxidative deoximation of oximes can be effected with various oxidants or reductive agents and can be used as a method of synthesis of carbonyl compounds.

5. Oxime-mediated nitrosylation of metals

In the previous Section, we discussed the method of synthesis of carbonyl compounds from oximes by reductive and oxidative cleavage of the oxime C=N bond with involvement of metal complexes. Nitroso complexes of metals formed upon oxidation of the oxime nitrogen atom are intermediates in these processes. In this Section, we present examples of obtaining stable metal nitroso complexes by splitting of oximes. We assume that these examples are complementary and, therefore, their discussion in one paper will provide more detailed understanding of the mechanism of the oxidative deoximation.

The possibility of application of oximes as nitrosylating agents was demonstrated by the synthesis of the molybdenum nitroso complex $[Mo(acac)_2(NO)\{MeC(NH_2)NO\}]$ by reaction of acetamideoxime $MeC(NH_2)=NOH$ with $[MoO_2(acac)_2]$ in methanol at room temperature.[93] The structure of the complex was confirmed by X-ray diffraction analysis. Nitroso complexes were also obtained from acetone oxime and various Mo(VI) oxo complexes.[94] For instance, the complex $[Mo(acac)_2(NO).\{Me_2C=NO\}]$ was obtained by refluxing $[MoO_2(acac)_2]$ with acetone oxime in methanol for 5.5 h. The formation of nitroso

complexes in these reactions is explained [94] by hydrolytic splitting of acetone oxime to hydroxylamine followed by reductive nitrosylation of Mo(VI). The mechanism of reductive nitrosylation of molybdenum oxo complexes with hydroxylamine in water was studied in detail [95] and may be illustrated as follows:

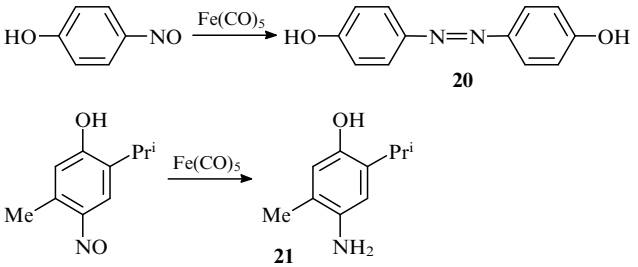
$$[Mo^{VI}O]^{4+} + NH_2OH \longrightarrow [Mo^{VI}(NH_2O)O]^{3+} + H^+,$$

$$[Mo^{VI}(NH_2O)O]^{3+} \longrightarrow [Mo^{II}(NO)]^{3+} + H_2O.$$

The ruthenium(III) nitroso complex $[NH_4]_2[RuCl_5(NO)]$ was prepared by reaction of various oximes (acetaldoxime, acetone oxime, cyclohexanone and cyclopentanone oximes) with $RuCl_3 \cdot x\,H_2O$.[96,97] The formation of the same product in all cases is explained by metal-mediated hydrolysis of oximes resulting in hydroxylamine and further disproportionation of the latter into nitrosyl and ammonium ion. High affinity of ruthenium to the nitrosyl ligand is yet another factor favouring the formation of the nitroso complexes.

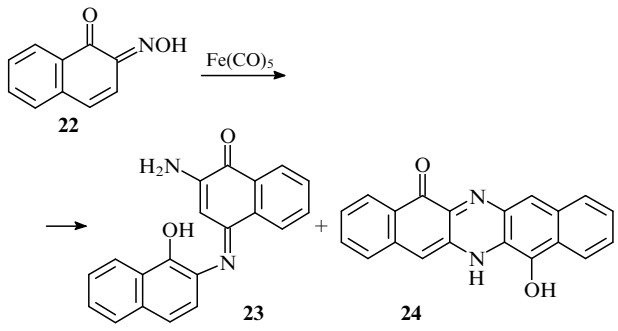
6. Reductive deoxygenation

Alper and Edward [98] have shown that the reaction of *p*-nitrosophenol (a tautomeric form of *p*-quinone monoxime) with $Fe(CO)_5$ results in 4,4′-dihydroxyazobenzene (**20**). However, 2-isopropyl-5-methyl-4-nitrosophenol is converted into 4-amino-2-isopropyl-5-methylphenol (**21**) under the same conditions.



Later, the process of metal-mediated reductive deoxygenation of quinone and benzoquinone oximes in the presence of $Fe(CO)_5$ (Ref. 99) or the trinuclear ruthenium carbonyl cluster $Ru_3(CO)_{12}$ (Ref. 100) was studied in detail. In both cases, the reactions of quinone oximes with metal carbonyls were carried out in refluxing THF under argon.

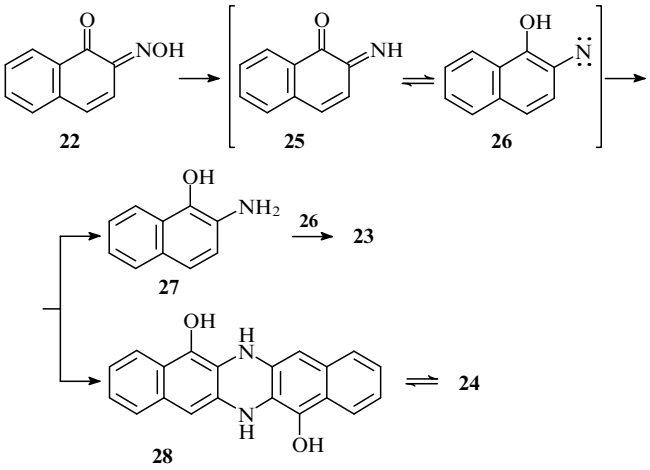
In the reaction of 1,2-naphthoquinone 2-oxime (**22**) with $Fe(CO)_5$, 2-amino-N^4-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine (**23**) and 5-hydroxydibenzo[*b*,*i*]phenazin-12(6*H*)-one (**24**) were identified.



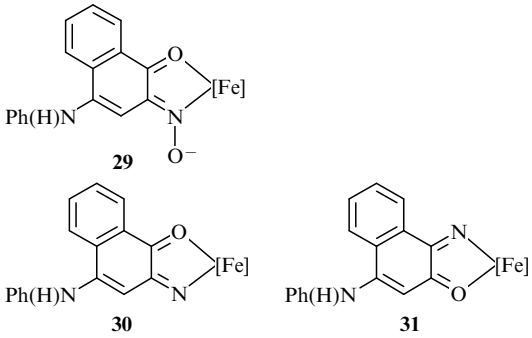
The formation of these products is explained [99] by conversion of the quinone oxime into a quinone imine **25** (as a result of deoxygenation) (Scheme 4) followed by possible formation of nitrene intermediate **26**, which is readily converted into aminonaphthol **26** (due to proton abstraction) or into dihydroxyphenazine derivative **28** (due to recombination).

Iron(II) quinone oximate complex **29** (the main product) and trace amounts of isomeric quinone imine complexes **31** and **31** are

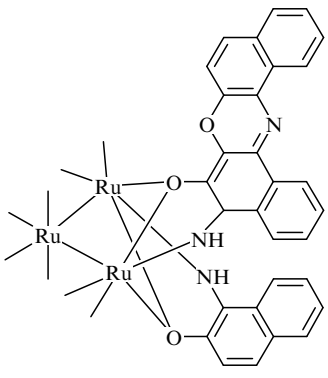
Scheme 4



formed alongside with compounds **23** and **24** in the presence of aniline.

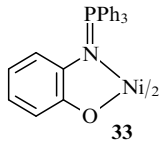


Mononuclear ruthenium naphthoquinone oximate complexes are the main products in similar reactions with $Ru_3(CO)_{12}$.[100] In addition to these complexes, mixed-ligand cluster **32** was isolated in the case of 1,2-naphthoquinone 1-oxime.



Presumably,[100] two types of ligands in the cluster **32** are formed as a result of deoxygenation of 1,2-naphthoquinone 1-oxime in the presence of $Ru_3(CO)_{12}$, which yields a nitrene intermediate of the type **26**, and its further conversions, similar to those shown in Scheme 4.

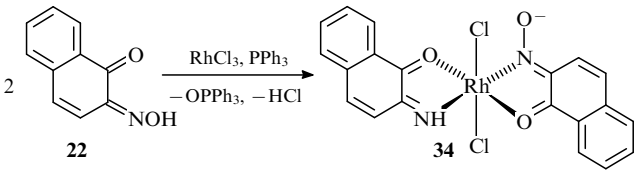
Reactions of quinone oximate complexes of 3d metals [Cu(II), Ni(II), Zn(II) and Fe(III)] with PPh_3 and RNH_2 afford compounds similar to those described previously (see Scheme 4).[101–105] It has to be noted, that in reactions with Cu(II) and Fe(III) complexes, [101] only mixtures of unidentified products with low oxidation states of the metal sites have been obtained. Reaction of a Ni(II) quinone oximate complex with PPh_3 [105] yields a triphenyl(*o*-hydroxyphenylimino)phosphorane complex **33**.



33

Ketoximes unable to tautomerise into nitroso-derivatives yield either the corresponding imines in reactions with $Fe(CO)_5$,[106] or ketones.[107]

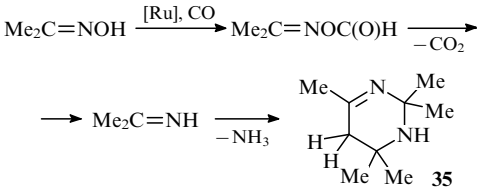
The reaction of $RhCl_3 \cdot 3H_2O$ with 1,2-naphthoquinone 2-oxime (**22**) in the presence of P- or N-donors (triphenylphosphine, pyridine or its 4-phenyl derivatives) [108] results in a mixture of Rh(III) complexes. Mixed-ligand complex **34** was isolated from this mixture and its structure was determined by X-ray crystallography.



22 **34**

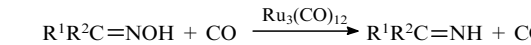
Steinborn *et al.*[41] have found that the rhodium glyoximate $[Rh(dmgH)_2(PPh_3)_2]^-$ (hereinafter referred to as $[Rh]^-$) ($dmgH_2$ is dimethylglyoxime) reacts with dihalomethanes CH_2X_2 (X = Br, Cl) producing both previously known compounds of the $[Rh]-CH_2X$ type and the new imino-oximate complexes $[Rh(CH_2X)\{ON=C(Me)-C(Me)=NH\}(dmgH)(PPh_3)]$. The complex $[RhCl_2(dmgH)(dmgH_2)]$ reacts with trialkylphosphines in the presence of $NaBH_4$ to afford an imino-oximate complex $[Rh(dmgH)(bdioH)(PR_3)_2]Cl$ (bdioH is butane-2,3-dione 2-imine-3-oximate).[109] Unusually high resistance of the newly formed imine bond against hydrolysis has been noted.[39] The boron–technetium imino-oximate binuclear complex obtained in the reaction of $[^{99}TeCl_3(NCMe)(PPh_3)_2]$ with $dmgH_2$ and $EtB(OH)_2$ appeared to be stable as well. This binuclear complex was isolated using 1 M HCl.[110] Reactions of salicylaldoximes with $[RuCl_2(PPh_3)_3]$ [111] and $[ReOCl_3(PPh_3)_3]$ [112] demonstrated a possibility of synthesising imino-oximate complexes.

Deoxygenation of ketoximes in the presence of catalytic amounts of the complex $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}Me_2C=NO)_2 \cdot (Me_2C=NOH)_2]$ resulting in imines has been studied.[113] 2,3,4,5-Tetrahydro-2,2,4,4,6-pentamethylpyrimidine (**35**), CO_2 and NH_3 are formed upon deoxygenation of acetone oxime with CO. A plausible mechanism of this process includes carbonylation of acetone oxime followed by decarboxylation of an unstable intermediate $Me_2C=NOC(O)H$ to yield the imine $Me_2C=NH$. This undergoes trimerisation with elimination of NH_3.



35

It was shown [114] that, in the presence of $Ru_3(CO)_{12}$, various ketoximes are converted (CO, 20 atm) into the corresponding ketimines in virtually 100% yield:



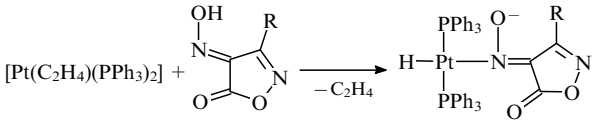
The mechanism of this process was not studied in detail. Taking into account the fact that *o*-benzylpropiophenone oxime and *o*-acetylacetophenone oxime are inactive in this reaction, it was suggested that the initial stage of the process is the reductive cleavage of the N–O bond.

7. Oxidative addition of oximes

Oxidative addition of oximes to electron-rich metal sites may proceed with cleavage of both the O–H bond and the N–O bond resulting in complexes with bridging or monodentate ligands.

a. Oxidative addition of oximes as a result of the O–H bond cleavage

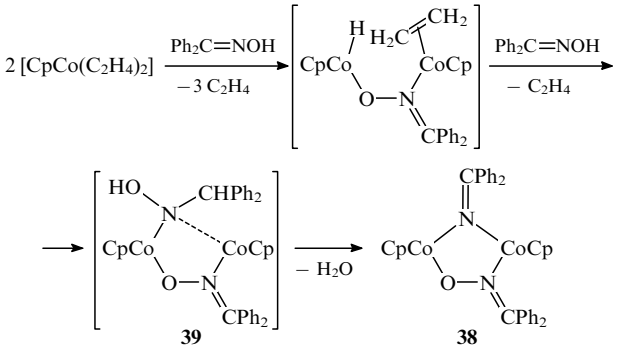
For the first time, the reaction of oxidative addition with cleavage of the O–H bond was performed by Beck and co-workers [115] with heterocyclic oximes as examples. The platinum(0) complex $[Pt(C_2H_4)(PPh_3)_2]$ reacts with heterocyclic oxime **36** in toluene at room temperature yielding Pt(II) hydride-oximate complexes **37**. It has to be noted, that up to now this reaction is the only example of formation of monodentate N-coordinated oximate fragment in a complex formed as a result of the O–H bond cleavage.



36 **37**

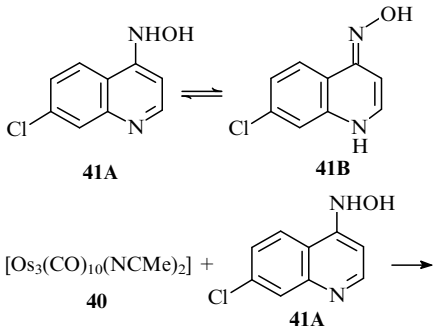
R = Me, Ph.

It was shown by Floriani and co-workers [116] that the reaction of benzophenone oxime with the complex $[CpCo(C_2H_4)_2]$ in toluene at room temperature leads to the formation of the μ_2-imidooximate cobalt cluster $[\{CpCo\}_2(\mu_2\text{-}N=CPh_2) \cdot (\mu_2\text{-}ON=CPh_2)]$ (**38**). The suggested reaction mechanism includes the following steps: oxidative addition of oxime to Co(I) with cleavage of the O–H bond, intramolecular nucleophilic addition of the hydride ion to the carbon atom of the second N-coordinated oxime moiety and dehydration of the intermediate **39** with formation of the complex **38**.



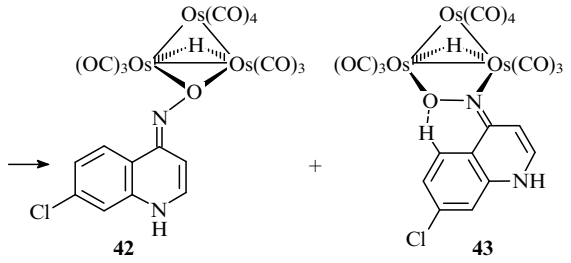
39 **38**

The reaction of the cluster $[Os_3(CO)_{10}(NCMe)_2]$ (**40**) with 7-chloro-4-(hydroxyamino)quinoline (**41**) existing in two tautomeric forms **A** and **B**, in a mixture of dichloromethane and acetone at room temperature produces the clusters $[Os_3(\mu_2\text{-}H)(\mu_2\text{-}\eta^1\text{-}OC_9H_6N_2Cl)(CO)_{10}]$ (**42**) and $[Os_3(\mu_2\text{-}H)(\mu_2\text{-}\eta^2\text{-}ONC_9H_6NCl) \cdot (CO)_{10}]$ (**43**) in 37% and 23% yields, respectively.[117] The complex **42** is completely converted into the complex **43** when kept in acetone for two days at room temperature.



41A **41B**

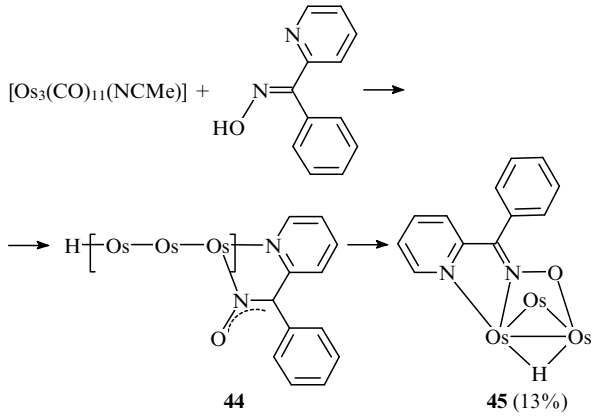
40 **41A**



42 **43**

Acetone oxime reacts with the cluster **40** in the same way.[118] The formed hydride-oximate complex $[Os_3(\mu_2\text{-H}).(\mu_2\text{-ON}=CMe_2)(CO)_{10}]$ isomerises into the hydroxo-imide complex $[Os_3(\mu_2\text{-OH})(\mu_2\text{-N}=CMe_2)(CO)_{10}]$ on refluxing in octane. It was suggested[118] that isomerisation proceeds with formation of the oxime intermediate $[Os_3(\mu_2\text{-HON}=CMe_2)(CO)_{10}]$ (of the type **43**) in which the N–O bond cleavage takes place as a result of oxidative addition. This type of oxidative addition of oximes will be discussed in detail in the next Section of the review.

2-Benzoylpyridine oxime reacts with another osmium cluster $[Os_3(CO)_{11}(NCMe)]$ in dichloromethane at 25 °C yielding the complex $[Os_3H(CO)_{11}\{\eta^2\text{-ON}=CPh(NC_5H_4)\}]$ (**44**) (carbonyl groups in formulas **44** and **45** below are omitted). Another cluster $[Os_3(\mu_2\text{-H})(CO)_9\{\mu_2\text{-}\eta^3\text{-ON}=CPh(NC_5H_4)\}]$ (**45**) was obtained by refluxing the complex **44** for 3 h in toluene under argon.[119]



44 **45** (13%)

Oximato-silane complexes were obtained by heating $(\pi\text{-}C_5Me_5)_2Si$ with $R^1R^2C=NOH$ in toluene for several hours at 60 °C:[120]

$$(\pi\text{-}C_5Me_5)_2Si + R^1R^2C{=}NOH \longrightarrow (\sigma\text{-}C_5Me_5)_2Si(H)(ON{=}CR^1R^2)$$

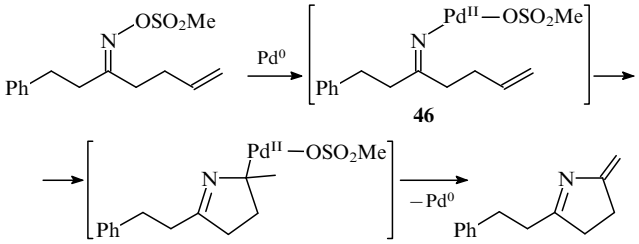
$R^1 = H$, $R^2 = Me$; $R^1-R^2 = (CH_2)_5$.

b. Oxidative addition of oximes with cleavage of the N–O bond

The first example of oxidative addition of acetone oxime to the rhenium complex *trans*-$[Re^{I}Cl(N_2)(dppe)_2]$ with cleavage of the N–O bond was described in 1998.[121] The reaction was carried out in THF in the presence of $TlHSO_4$. The hydroxo-complex *trans*-$[Re(OH)(NCMe_2)(dppe)][HSO_4]$ was obtained upon addition of the oxime to the Re(I) complex. Later, other oximes $R^1R^2C=NOH$ [$R^1 = H$: $R^2 = Me$, Ph; $R^1-R^2 = (CH_2)_4$, $(CH_2)_5$] were introduced in reactions with this complex.[122]

Afterwards, Tillack *et al.*[123] have shown that reactions of titanocene derivatives with *O*-silylated oximes $R^1R^2C=NOSiMe_3$ [$R^1 = R^2 = Me$, $R^1-R^2 = (CH_2)_5$] in refluxing hexane for 5 h resulted in complexes $[Cp_2Ti(N=CR^1R^2)(OSiMe_3)]$ in 45% and 50% yields, respectively.

The oxidative addition of oxime derivatives to palladium catalysts was used to synthesise key intermediates in the preparation of various heterocycles.[124–127] Thus unsaturated *O*-substituted ketoximes are converted into various nitrogen heterocycles (pyrroles, pyridines, isoquinolines, spiroimines and azaazulenes) on heating in DMF (110 °C, 30 min) in the presence of catalytic amounts of $Pd(PPh_3)_4$ and triethylamine. It was suggested that these reactions occur *via* alkylideneaminopalladium intermediate of the type **46** (as a result of oxidative addition of the oxime to Pd^0) followed by intramolecular amination (similar to the Heck reaction) of the alkene fragment of the molecule.[124–127]



46

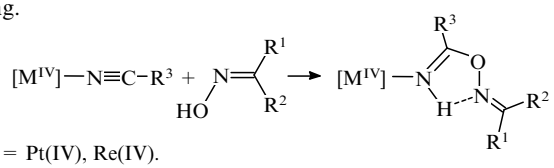
Thus, oxidative addition of oximes to a metal site, which occurs with cleavage of the O–H or N–O bond (depending on the character of the metal), may result in both hydride-oximate (N- or O-coordinated) and hydroxoalkylideneamine metal complexes.

III. Reaction with retention of the C=NOH fragment

1. Nucleophilic addition of oximes to multiple bonds

a. Metal-mediated addition reactions of oximes to nitriles

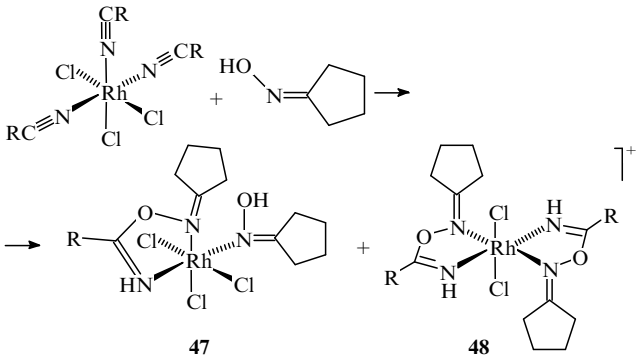
Vast amount of experimental data are known to date concerning metal-mediated nucleophilic addition of oximes to nitriles with formation of iminoacyl ligands.[18, 19, 128] Reactions of nitrile complexes of metals in higher oxidation states [Pt(IV),[129–134] Re(IV) [135]] with various oximes in aprotic media (nitriles, chloroform, CH_2Cl_2) are highly selective and result in monodentate N-coordinated iminoacyl derivatives in high yields. *E*-Isomers of iminoacyl ligands are stabilised by an intramolecular hydrogen bond between the hydrogen atom of the imine and the nitrogen atom of the acyl fragment with formation of a 5-membered N–H-ring.



M = Pt(IV), Re(IV).

In these reactions, the metal centre activates the carbon atom of the nitrile ligand and then stabilises the coordinated imine formed.

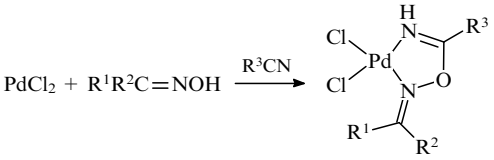
In contrast to Pt(IV) and Re(IV) nitrile complexes, a Rh(III) nitrile complex, *viz.*, *mer*-$[RhCl_3(NCR)_3]$, reacts with oximes (for example, with cyclopentanone oxime) yielding rhodium(III) *N,N*-mono- (**47**) and *N,N*-bis-chelate (**48**) iminoacyl complexes.[136]



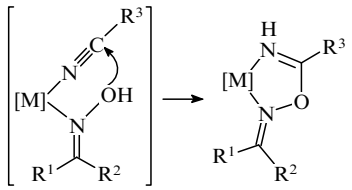
47 **48**

Bis-chelate complexes **48** were also obtained by a reaction of *mer*-$[RhCl_3\{HON=C(CH_2)_4\}_3]$ with acetonitrile in ethanol.[38] Previously, similar chelate iminoacyl compounds were formed on refluxing oxo-vanadium salicylaldoximate complex $[VOL_2]$

(L is salicylaldoxime) in acetonitrile.[137, 138] Prolonged refluxing of $PdCl_2$ with various ketoximes in nitrile media afforded monochelate iminoacyl complexes $[PdCl_2\{\underline{N}H=C(R^3)O\underline{N}=CR^1R^2\}]$ (hereinafter, underlined are atoms coordinated to a metal).[139]



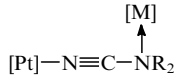
Various oxime complexes were isolated in the initial stage of the reaction. These can be regarded as stable intermediates of this process, similarly to those in the case of rhodium complexes.[38, 136] Labile and chelate-forming Rh(III) and Pd(II) ions favour further substitution of nitrile for one of the N-coordinated oximes resulting in an unstable mixed-ligand intermediate **49**. This is converted into N,N-chelate complex **50** as a result of intramolecular nucleophilic addition of the oxime oxygen atom to the nitrile.



49 **50**

M = Rh(III), Pd(II)

Platinum(II) cyanamide complexes, *viz.*, *cis*-$[PtCl(N\equiv CNR^3_2)(PPh_3)_2][BF_4]$ and *cis*-$[Pt(N\equiv CNR^3_2)_2(PPh_3)_2].[BF_4]_2$, react with oximes in the presence of Ag^+ or Cu^{2+} salts (CH_2Cl_2, 20–25 °C) to form azametallacycles $[Pt\{\underline{N}H=C(NR^3_2).O\underline{N}=CR^1R^2\}(PPh_3)_2][BF_4]_2$.[140] The oxime-cyanamide intermediate *cis*-$[Pt(N\equiv CNEt_2)(HON=CR^1R^2)(PPh_3)_2][BF_4]_2$ was isolated at R^3 = Et, which serves as indirect evidence for the above-mentioned mechanism of formation of chelate iminoacyl complexes. It was suggested [140] that the Ag^+ or Cu^{2+} ions favour additional electrophilic activation of the carbon atom of the cyanamide group and allow this reaction to take place even in the case of relatively inert Pt(II) complexes.



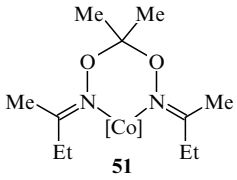
[M] = Ag^+, Cu^{2+}.

Sulfur-containing dioximes react with nitriles in the presence of $Ni(ClO_4)_2\cdot 6H_2O$ yielding mono- and binuclear Ni(II) iminoacyl complexes.[141, 142]

b. Metal-mediated addition reactions of oximes to carbonyl compounds

Oxime complexes of Pt(II), *viz.*, *trans*-$[PtCl_2(R^1R^2C=NOH)_2]$ [$R^1 = R^2$ = Me, $R^1-R^2 = (CH_2)_4$, $(CH_2)_5$], react with *m*-chloroperoxybenzoic acid in acetone to give platinum(IV) compounds $[PtCl_2\{\underline{O}CMe_2O\underline{N}=CR^1R^2\}_2]$.[143] Presumably, oxidation of Pt(II) to Pt(IV) takes place in the initial stage of the reaction followed by O-coordination of two acetone molecules accompanied by intramolecular nucleophilic attack of the oxime oxygen atom on the acetone carbonyl carbon atom.

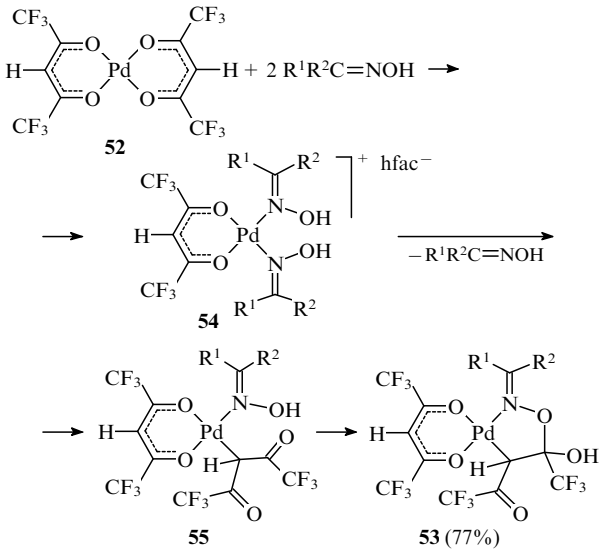
Complex **51** was obtained in the reaction of $CoI_2\cdot 2H_2O$ with an excess of butan-2-one oxime in dry acetone in the presence of trimethyl orthoformate and its structure was determined by X-ray crystallography.[144]



51

It was suggested that this reaction proceeds with formation of a cobalt dioxime complex. Coordination of the nitrogen atoms to the Co centre significantly increases the acidity of the OH groups,[35] which later undergo electrophilic attack by the carbonyl carbon atom to form the diacyl ligand. The rate of this reaction and the yield of the final product increase when the reaction is carried out in basic media. This fact may be regarded as indirect evidence in support of the suggested machanism.[144]

The reaction of the oxime $R^1R^2C=NOH$ (L) with $[Pd(hfac)_2]$ (**52**) (Hhfac is hexafluoroacetylacetone) in CH_2Cl_2 at room temperature yields the complex **53**.[145]



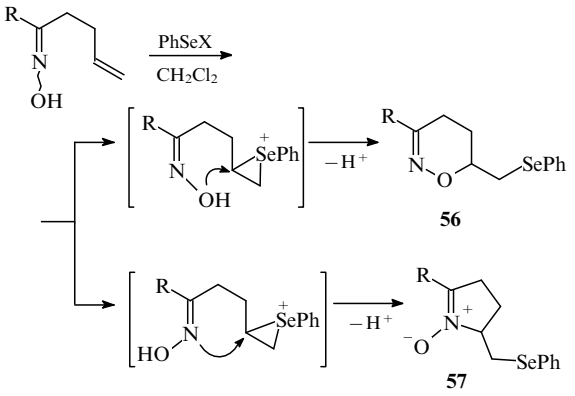
52 **54** **55** **53** (77%)

Monitoring of this reaction by ^{19}F NMR ($CDCl_3$, −30 °C) has shown that the complex $[Pd(hfac)L_2](hfac)$ (**54**) is formed. This complex was regarded as the first reaction intermediate.[145] Substitution of hfac, which is a monodentate ligand coordinated to Pd(II) through the carbon atom, for one oxime ligand is accompanied by formation of an unstable intermediate **55**, which is converted to the final product **53** as a result of nucleophilic addition of the oxime.

c. Nucleophilic addition reactions of oximes to coordinated C=C bonds

The intramolecular cyclisation of unsaturated alkenyl- and allenyl-oximes resulting in heterocyclic compounds (oxazoles and oxazines) and cyclic nitrones is one of the best studied and often employed reactions of this type. Thus it was shown [146, 147] that α,β-unsaturated oximes $HON=CR^1-CR^2=CR^3H$ ($R^1 = R^3$ = Ph, R^2 = H; $R^1 = Bu^t$, R^2 = H, R^3 = Ph; R^1 = Ph, R^2 = Me, $R^3 = Pr^i$) were converted into the corresponding isoxazoles by refluxing in benzene in the presence of equimolar amount of $[PdCl_2(PPh_3)_2]$ and a fivefold excess of NaOPh. Presumably,[146, 147] a Pd σ,π-oxime complex, in which the palladium centre is linked to the nitrogen atom and the ethylene fragment, is formed in the initial stage of the reaction. The electrophilically activated C=C bond then undergoes intramolecular nucleophilic attack by the oxygen atom of the oxime moiety resulting in closure of the isoxazole ring.

Depending on the configuration, γ-alkenyl oximes are converted into either 1,2-oxazines **56** or cyclic nitrones **57** in the presence of selenium compounds PhSeX (X = Cl, Br) at room temperature in acetonitrile or dichloromethane.[148, 149]

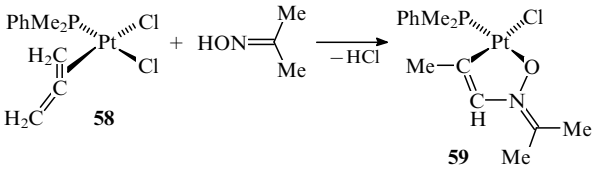


The structure of the final products depends on the spatial configuration of the starting oximes. The O-nucleophilic attack on the carbon atom of the C=C bond takes place in the case of *E*-isomers; in the case of *Z*-isomers, N-nucleophilic attack occurs.

Cyclic nitrones are also formed from *Z*-isomers of γ-alkenyl oximes in the presence of mercury(II) acetate in THF at 25 °C[150] as well as from *E*-isomers of δ-unsaturated oximes upon refluxing in THF in the presence of $PdCl_2$ or $[PdCl_2(NCMe)_2]$.[151] Allenic oximes are converted into unsaturated cyclic nitrones in high yields at room temperature in dichloromethane in the presence of Ag^+.[152]

Various oximes are converted into oxime ethers or cyclic nitrones in the presence of catalytic amounts of the complex $[Pd(PPh_3)_4]$ or a system of reagents $Pd(NO_3)_2-PPh_3$ (1:4) as a result of intermolecular nucleophilic addition (O- or N-) to butadiene.[153] Presumably,[153] electrophilic activation of butadiene is a result of formation of a palladium π-allyl intermediate.

The reaction product of coordinated allene in *cis*-$[PtCl_2(C_3H_4)(PMe_2Ph)]$ (**58**) with acetone oxime is the only example known so far of a stable complex obtained upon nucleophilic addition of the oxime to the C=C bond.[154]

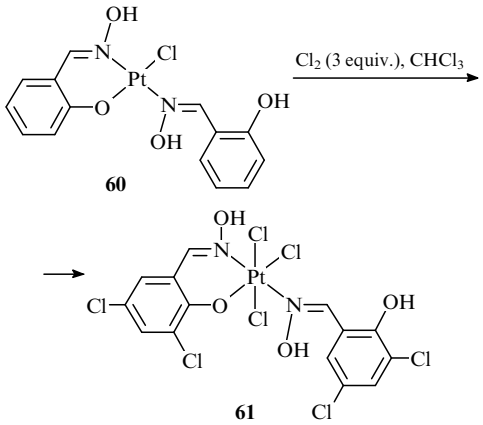


Allene electrophilically activated by coordination to Pt undergoes intramolecular nucleophilic attack by the nitrogen atom of the O-coordinated oximate ligand, which is accompanied by 1,3 prototropic shift and closure of a five-membered C,O-chelate ring giving rise to complex **59**.

2. Reactions of peripheral groups in oxime- and oximate complexes

Peripheral groups of coordinated ligands may undergo different transformations; such reactions are well known in coordination chemistry. However, there are very few examples of such processes in the chemistry of oxime and oximate complexes. These will be discussed in this Section.

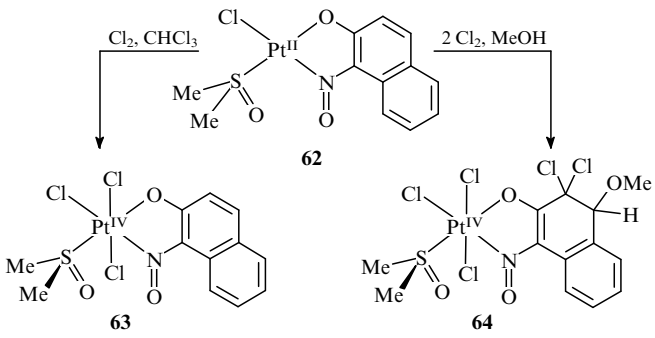
Chlorination of various platinum(II) salicylaldoximate complexes was studied in detail.[155, 156] Thus chlorination of oxime-oximate complex **60** afforded the complex *trans*-(N,N)-$[PtCl_3(3,5\text{-}Cl_2\text{-}2\text{-}OC_6H_2CH{=}NOH)(3,5\text{-}Cl_2\text{-}2\text{-}HOC_6H_4CH{=}NOH)]$ (**61**); its structure was determined by X-ray crystallography.



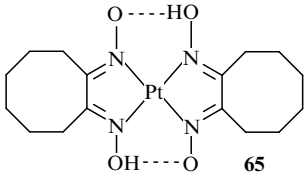
Other platinum(II) salicylaldoximate complexes, *e.g.*, the bis-chelate complex $[Pt(o\text{-}OC_6H_4CH{=}NOH)_2]$[157] and mixed-ligand complexes *trans*-(S,N)-$[PtCl_2(o\text{-}HOC_6H_4CH{=}NOH)(Me_2SO)]\cdot H_2O$ and *trans*-(S,N)-$[PtCl(o\text{-}OC_6H_4CH{=}NOH)(Me_2SO)]$[155] undergo similar transformations upon chlorination. The reactions of these complexes with an excess of Cl_2 are selective: the chlorine atoms in the products occupy *ortho*- and *para*-positions of the benzene ring relative to the OH group. Conversely, the chlorination of non-coordinated salicylaldoxime is non-selective and results in a large number of products.

Chlorination of complex **62** with an excess of Cl_2 in chloroform at room temperature yielded complex **63**. The same reaction in methanol afforded complex **64** in 24% yield.

Chlorination of non-coordinated 1,2-naphthoquinone 1-monoxime under the same conditions resulted in the corresponding methoxylated oxime in less than 3% yield. This suggests that the methoxylation is metal-mediated.[157] The following mechanism of formation of the complex **64** was suggested: oxidation of Pt(II) into Pt(IV), chlorination of the naphthalene fragment and subsequent methoxylation.



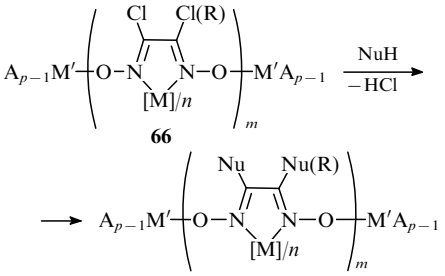
Chlorination of the platinum(II) bis-oximate chelate complex $[Pt^{II}\{C_8H_{12}(=NO)_2H\}_2]$ (**65**) with $PhICl_2$ in CH_2Cl_2 produces the platinum(III) binuclear complex $[Pt^{III}Cl\{C_8H_{12}(=NO)_2H\}_2]_2$, which is converted into $[Pt^{IV}Cl_2\{C_8H_{12}(=NO)_2H\}_2]$ under the action of an excess of $PhICl_2$.[159]



Oxidation of the platinum(II) *cis*- and *trans*-acetone oxime complexes $[PtCl_2(Me_2C{=}NOH)_2]$ with excess chlorine in $CHCl_3$ yields $[Pt(IV)Cl_4(Me_2C{=}NOH)_2]$.[160] In both cases,[159, 160] chlorination affects only the platinum site with retention of the oxime and oximate ligands.

Thus, in spite of different chlorination conditions (different solvents and chlorinating agents) and various starting Pt(II) complexes, the oxime fragment was not changed upon chlorination. The metal site serves in all these reactions as a protecting group, which prevents the Piloty reaction [158] (chlorination of 'free' oximes) and/or oxidative deoximation (see Section II.4).

Voloshin *et al.*[161–172] have shown that functionalisation (change of peripheral environment) of clathrochelate complexes with encapsulated metal ions (Fe^{2+}, Co^{+}, Co^{2+}, Co^{3+}, Ru^{2+}) follows two principal pathways, *viz*., incorporation of a substituent (*e.g*., a chlorine atom) into chelating edge fragments of the cage (edge functionalisation) and substitution in tripod linking fragments. In the case of edge functionalisation of the macrobicyclic cage framework, the substituent and encapsulating metal site have substantial electronic and spatial impacts on each other, which are especially strong in the case of polyenic clathrochelate complexes of transition metals with a conjugated system of π-bonds in the chelating fragments. The presence of a system of σ- and π-bonds provides effective transfer of both inductive and mesomeric effects of functional substituents to the encapsulated metal ion. For instance, the presence of reactive chlorine atoms in molecules of tris-dioximate clatrochelates **66** enables their further functionalisation under mild conditions in the nucleophilic substitution with various H-nucleophiles (NuH) and synthesis of compounds with predetermined properties.



66

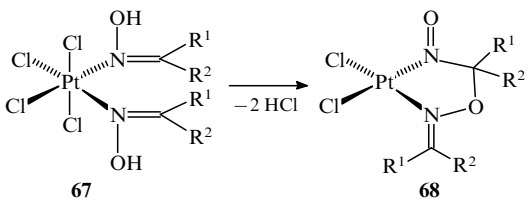
M = Fe^{2+}, Co^{+}, Co^{2+}, Co^{3+}, Ru^{2+}; M′ = B^{3+}, Sn^{4+};
R = Me; A = F, Bu^n, Ph; NuH — O-, S- and N-nucleophiles.

Chemically stable cage structures with pendent substituents, highly biologically active materials,[173] new liquid-crystalline systems,[172] luminescent labels [174] and selective reagents for sequencing of nucleic acids [168] have been synthesised by this method.

IV. Miscellaneous oxime reactions involving metal complexes

The reactions of oximes that do not comply with the classification used in the previous Sections are discussed in this Section.

Oxidation of platinum(II) oxime complexes *cis*-[$PtCl_2$.$(R^1R^2C{=}NOH)_2$] with chlorine in $CHCl_3$ yields the platinum(IV) coordination compounds *cis*-[$PtCl_4(R^1R^2C{=}NOH)_2$] (**67**), which are spontaneously converted into platinum(II) chelate derivatives [$PtCl_2\{\underline{N}(=O)CR^1R^2O\underline{N}=CR^1R^2\}$] (**68**) on storage in aqueous acetone for 3 h.

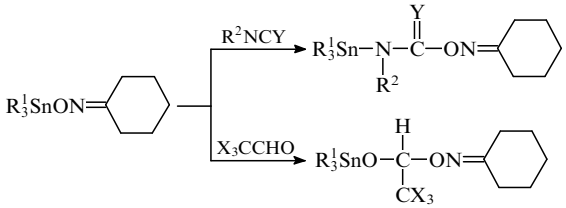


67 **68**

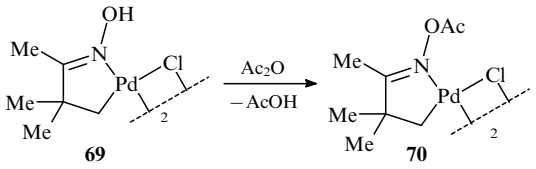
$R^1 = R^2 = Me$; $R^1 - R^2 = (CH_2)_4$, $(CH_2)_5$.

Complexes [$PtX_2\{\underline{N}(=O)CR^1R^2O\underline{N}=CR^1R^2\}$] isostructural to the complex **68** were obtained in the reaction of *trans*-[$PtX_2(R^1R^2C{=}NOH)_2$] [X = Cl, Br; $R^1 = R^2 = Me$; $R^1 - R^2 = (CH_2)_4$, $(CH_2)_5$] with *m*-chloroperoxybenzoic acid in DMF at 40 °C.[175] While the formation of the chelate **68** is a result of intramolecular two-electron redox interaction between Pt(IV) and the nitrogen atom of the oxime ligand, the formation of its isostructural analogue in DMF (see Ref. 175) occurs as an intermolecular oxidation of the nitrogen atom of the coordinated oxime with *m*-chloroperoxybenzoic acid.

Reactions of *O*-trialkylstannyl oximes with alkyl and aryl isocyanates, their thia analogues and aldehydes result in compounds that can formally be regarded as the insertion products into the Sn − O bond.[176]

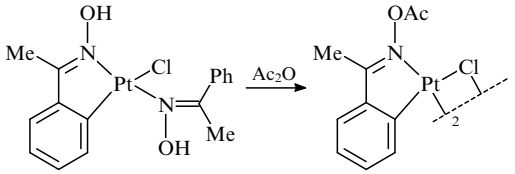


Refluxing of the palladium(II) dimeric bridged oxime complex [$Pd(\mu\text{-}Cl)(CH_2CMe_2CMe{=}NOH)]_2$ (**69**) in acetic anhydride yields complex **70** with an *O*-acylated oxime.[177]



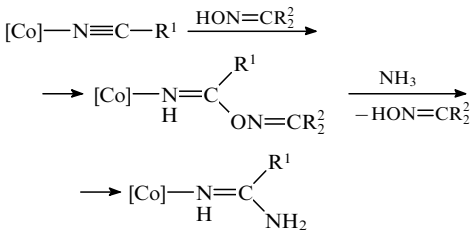
69 **70**

A platinum(II) dimeric bridged complex **71**, *viz*., [$Pt(\mu\text{-}Cl)$.$\{o\text{-}C_6H_4C(Me){=}NOAc\}]_2$ containing an *O*-acylated oxime fragment was obtained by refluxing [$PtCl\{o\text{-}C_6H_4C(Me){=}NOH\}$.$(HON{=}CPhMe)$] in acetic anhydride for 1 h.[178]



71

Reactions of nitriles with ketoximes in the presence of salts of 3d metals were studied.[179–182] Thus nitriles R^1CN are converted into the corresponding amidines at 50 °C in 8 h on treatment with ketoximes $R^2_2C{=}NOH$ in the presence of $Co(NO_3)_2 \cdot 6H_2O$ in a molar ratio of 4 : 1. These amidines were isolated as nitrates [$R^1C(=NH_2)NH_2](NO_3)$.[179] In the case of acetonitrile, a stable intermediate [$Co(NCMe)_2(H_2O)_4](NO_3)_2$ was isolated and structurally characterised. Acetic acid, which is a product of the two-step hydrolysis of the nitrile, was also detected. A suggested [179] reaction mechanism is based on iminoacylation of a nitrile (see Section III.1.a) coordinated to Co(II) followed by intermolecular nucleophilic attack of NH_3 on the imidate carbon atom (a product of two-step hydrolysis of R^1CN) and amidine formation.

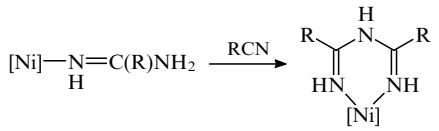


R^1 = Me, Et, Pr^n, Bu^n; R^2_2 = Me_2, $(CH_2)_5$.

Catalytic hydrolysis of nitriles into the corresponding carboxamides $R^1C(O)NH_2$ was performed in the presence of a system $ZnX_2 - R^2_2C{=}NOH$ [X = Cl, NO_3, CF_3SO_3; R^2_2 = Me_2, $(CH_2)_4$, $(CH_2)_5$; the molar ratio of the zinc salt to oxime being equal to

1 : 4].[180] The highest efficiency was achieved in the hydrolysis of *p*-methoxyphenylacetonitrile in the presence of a system $Zn(NO_3)_2 \cdot 6H_2O - Me_2C{=}NOH$. In this case, the turnover number of the catalyst was equal to 1000. A zinc(II) oxime complex $[Zn(NO_3)_2(Me_2C{=}NOH)_2]$ was the only stable intermediate isolated in the process. Presumably,[180] the formation of an imine complex $[Zn]-NH{=}C(R^1)ON{=}CR^2_2$ is the first step of the putative mechanism of the process. Hydrolysis of the imino-ligand into carboxamide in the coordination sphere of zinc and recovery of the catalyst due to hydration of the complex complete the catalytic cycle.

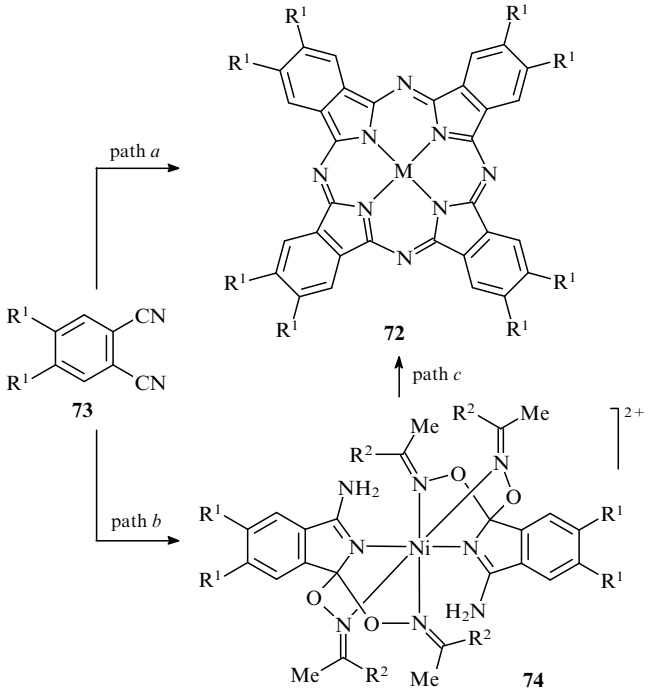
The nickel(II) imidoylamidine complexes $[Ni\{\underline{N}H{=}C(R).NHC(R){=}\underline{N}H\}_2]^{2+}$ (see [181]) were obtained in high yields (65% – 91%) by refluxing $NiCl_2 \cdot 2H_2O$ in nitrile solvents in the presence of acetone oxime. As in the two previously described cases (see [179, 180]), the plausible mechanism of the reaction includes the formation of an $[Ni]-NH{=}C(R)ON{=}CMe_2$ intermediate, which hydrolyses later with elimination of NH_3. Ammonia formed reacts with another coordinated nitrile to give amidine. Nucleophilic addition of this amidine to the ligand RCN results in nickel imidoylamidine complexes.



A novel efficient method for the synthesis of industrially important symmetrical (**72**) and asymmetrical phthalocyanines and their complexes with Ni(II), Cu(II), Zn(II) and Cd(II) by reactions of substituted phthalocyanines **73** with the corresponding metal chlorides in the presence of an oxime $Me(R^2)C{=}NOH$ (Scheme 5, path *a*) was proposed.[182]

Chelate **74** was obtained by refluxing $NiCl_2 \cdot 2H_2O$ in acetone for 24 h in the presence of an oxime and various phthalonitrile derivatives (the molar ratio oxime : phthalonitrile = 2 : 1). Complex **74** is the nucleophilic addition product of two oxime molecules to one nitrile group (Scheme 5, path *b*) and this is the first example of such type of metal-mediated reactions of oximes. Nickel phthalocyanines **72** (M = Ni) can be obtained under 'mild' conditions (refluxing in methanol, 24 h) and in high yields (~60%) when complex **74** is used as a phthalogen (Scheme 5, path *c*).

Scheme 5



(*a*) MX_2 [M = Ni(II), Cu(II), Zn(II), Cd(II)]; 4 equiv. of $Me(R^2)C{=}NOH$ (R^2 = Me, Et);
(*b*) $NiCl_2 \cdot 2H_2O$, boiling in Me_2CO, $Me(R^2)C{=}NOH$;
(*c*) $R^1_2C_6H_2(CN)_2$, boiling in MeOH, 24 h.

V. Conclusion

The data discussed in the present review on metal-mediated and metal-catalysed reactions of free and coordinated oximes and their derivatives show that nowadays the development of new methods of organic synthesis and design of new models for the interpretation of mechanisms of catalytic processes are in the focus of attention. Particularly, methods of dehydration and reductive deoxygenation of aldoximes in the presence of metal complexes giving nitriles in high yield have been developed; new reactions of oxidative and reductive deoximation resulting in carbonyl compounds have been discovered. The search for efficient catalysts of the Beckmann rearrangement is underway. It appeared that application of various rhenium(VII) derivatives allows smooth conversion of cyclohexanone oxime into industrially important ω-caprolactam. A new catalytic method of hydration of nitriles into amides in the presence of oximes and zinc nitrate as well as simple and inexpensive method of amidine synthesis from oximes and cobalt(II) nitrate in nitrile media were developed. A new efficient method for the synthesis of industrially important symmetrical and asymmetrical metal phthalocyanines by reactions of various phthalonitriles with an excess of oximes in the presence of Ni(II), Cu (II), Zn(II) and Cd(II) chlorides has been found.

Significant attention is still paid to metal-mediated reactions of oximes resulting in new ligand systems: loss of integrity of the C = NOH fragment in reactions of reductive deoxygenation of oxime ligands leads to mixed-ligand imine-oxime complexes. New methods of synthesis of nitrile complexes of W, Ru and Os by dehydration of the starting oxime adducts as a result of cleavage of the N—O bond of the oxime fragment are developed. Stable nitroso complexes of Mo(VI) and Ru(III) are obtained by hydrolytic and redox processes in aqueous media. Reactions of oxidative addition of oximes to electron-rich sites resulting in imide-oximate or hydride-oximate ligands have been studied. Hydroxoalkylideneamine ligands, generated by oxidative cleavage of the N—O bond, are regarded as the key intermediates of the palladium-catalysed Heck reaction in the synthesis of heterocycles. New types of imino-ligands have been synthesised by nucleophilic addition of oximes to coordinated nitriles. Depending on the character of the metal, either monodentate N-coordinated molecular complexes or N,N-chelate products are formed. Nickel(II) imidoylamidine chelates or phthalocyanines are obtained in oxime – nitrile template transformations in the presence of nickel(II) chloride.

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