

# Oxime and oximate metal complexes: unconventional synthesis and reactivity

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## Abstract

The chemistry of oxime/oximato metal complexes has been investigated actively since the beginning of 20th century and aspects such as traditional synthetic routes leading to oxime/oximato complexes, structural and solution chemistry and analytical applications of oxime species have been reviewed extensively. Despite a fairly large number of reviews and books on different aspects of the chemistry of oxime/oximato metal compounds, data on their metal-mediated reactions are just beginning to actively emerge. Apparently, our review (V.Yu. Kukushkin, D. Tudela, A.J.L. Pombeiro, *Coord. Chem. Rev.* 156 (1996) 333) published in this journal in 1996 was the first attempt for classification of such reactions. In this article we carry on the description, systematization and analysis of metal-mediated reactions of oxime species with special emphasis on research of the last few years and also work produced in our group. In addition, data on unconventional routes for preparation of oxime/oximato complexes are also included and ascribed to certain reaction modes. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Oxime; Coordinated oxime; Synthesis of oxime; Synthesis of oxime complexes; Oxime ligand reactivity; Metal-mediated reactions

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## 1. Introduction

The chemistry of oxime/oximato metal complexes has been investigated actively since the time of the first synthesis, e.g. preparation of nickel(II) dimethylglyoximate, and recognition of the chelate five-membered character of this complex by Chugaev [1], and has been reviewed (refs. 31–52 in [2] and [3–5]) from 1974 onwards, however, without attention being directed to the reactions of oxime/oximato complexes and the ligand reactivity. While structural, traditional synthetic coordination and analytical chemistry of the title compounds has now reached a stage of maturation, that of their metal-mediated reactions is just beginning to actively emerge.

Apparently, our review [2] published in this journal in 1996 was the first attempt for the classification of such reactions. The review illustrates the fact that the chemistry of oxime/oximato metal complexes is rich since these species display an amazing variety of reactivity modes. This fact and also new works in the field of oxime chemistry, constantly appearing in literature, allow us to assume that the reactivity of oxime species is very far from being explored. In addition, in a number of cases intriguing reactions were discovered but were not later developed in a

systematic way. All this together with our permanent interest in the reactivity of oxime metal complexes initiated writing of a new article on the subject. We also added to this paper a section on syntheses which is absent in the previous work. We attempted to avoid duplication of material and overlapping of references between the first and the current reviews. However, in order to keep a logical consequence, in a few places in this article, we include a very brief account of work previously surveyed by us [2].

The first part of this article is devoted to synthetic routes for preparation of the title compounds. We do not describe well known methods for preparation of oxime/oximato complexes which are based on direct addition of an oxime ligand to any source of metal ion. Our main goal now is accumulation and consequent systematization of data on unconventional routes for preparation of these complexes. Therefore, synthetic methods to prepare the oxime/oximato species are reviewed selectively.

The second part represents those reactions which were not earlier overviewed. These include reactions which only became available in the last 2 or 3 years, and some less common—although eventually not less important—reactions which were missed as a result of our rather wide approach. Indeed, although we are interested in reactions occurring with the oxime group and, in many cases, without special attention to other groups in a molecule, we examine together complexes of both simple oximes (which merely have the oxime group as a coordination site) and functionalized oximes, i.e. with an additional coordination site in the  $\alpha$  or  $\beta$  position to the oxime moiety. Taking into account the great variety of types of both simple and functionalized oximes, gaps become easily understood.

Kozma Prutkov (a pseudonym of the four Russian authors, i.e. A.K. Tolstoy and Zhemchuzhnikov brothers) correctly pointed out that ‘one cannot embrace the immensity’. In accord with him, this review is just a new approach to the immensity of oximes rather than a work pretending to be comprehensive.

## 2. Unconventional synthesis of oxime/oximato metal compounds

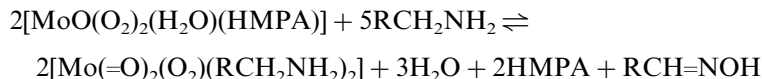
### 2.1. Reduction of organic nitroalkanes

The reduction of an aliphatic nitro compound containing an  $\alpha$ -hydrogen,  $RR'CHNO_2$ , may be stopped at the oxime,  $RR'C=NOH$ , stage. Numerous methods for this transformation including reductions with low-oxidation-state metal ions (for example, Sn(II) and Cr(II)) have been developed in organic chemistry [6,7].

Oxygen donors that contain N–O or N=O bonds, for instance nitroalkanes [8], are used widely for the oxygenation of coordinated CO and its conversion into  $CO_2$ . The formation of oximes is a plausible intermediate step [9] in the reduction of  $RNO_2$  to amines by iron carbonyls. Thus,  $Fe_3(CO)_{12}$  reacts with one equivalent of 2-nitropropane in toluene at 80°C to give a mixture of products. The main product of the reaction, which turned out to be the bridged oximato complex  $Fe_2(CO)_6(\mu-O,N-ONCMe_2)(\mu-NHCHMe_2)$ , was isolated by TLC and characterized by X-ray crystallography.

## 2.2. Oxidation of aminoalkanes by metal(oxo) compounds

The peroxymolybdenum compound  $[\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})(\text{HMPA})]$  (HMPA = hexamethylphosphoramide) catalyzes olefin oxygenation by  $\text{H}_2\text{O}_2$  [10]. Porta and co-workers [10] have shown that this complex can also oxidize benzylic primary amines,  $\text{RCH}_2\text{NH}_2$  ( $\text{R} = \text{Ph}$ , 2,4- $\text{Cl}_2\text{C}_6\text{H}_3$ , 2- $\text{ClC}_6\text{H}_4$ , 3,4-( $\text{OMe}$ ) $_2\text{C}_6\text{H}_3$ ), to afford the corresponding oximes,  $\text{RCH}=\text{NOH}$  and/or the Schiff bases,  $\text{RCH}=\text{NCH}_2\text{R}$ . The latter presumably forms on hydrolysis of the oximes followed by their condensation with unreacted amines. The oxidation proceeds in accord with the following equation:

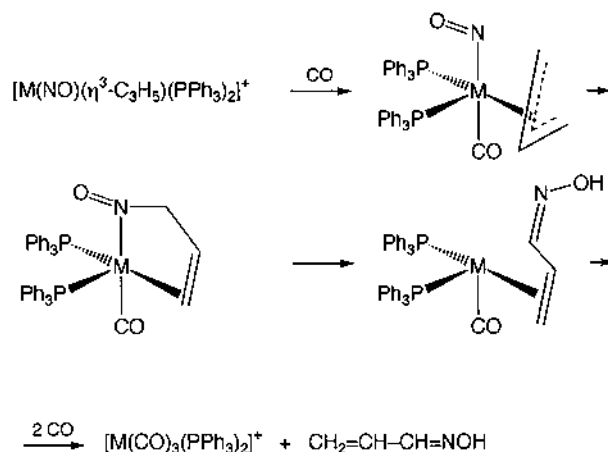


The reaction becomes catalytic in the presence of hydrogen peroxide. A plausible mechanism for the conversion involves an electrophilic transfer of one oxygen atom of the peroxide ring in  $\text{Mo}(\text{O}_2)$  moiety to the amines. The oxidation of cyclohexylamine by  $[\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})(\text{HMPA})]/\text{H}_2\text{O}_2$  proceeds likewise to the oxygenation of benzylic amines, giving cyclohexanone oxime along with cyclohexanone and nitro-cyclohexane [11]. Conversion of  $\text{C}_6\text{H}_{11}\text{NH}_2$  into  $\text{C}_6\text{H}_{10}\text{NOH}$  can also be achieved in the process where the complex  $\text{oxo}[\text{N}-(2\text{-oxidophenyl})\text{salicylidenaminato}]\text{vanadium}$  in combination with cyclohexyl peroxide in dichloroethane oxidizes cyclohexylamine to give the corresponding oxime in 72% yield, along with precipitated vanadium compounds [12]. The addition of cyclohexyl hydroperoxide to the precipitate regenerated the peroxo complex. The photochemical excitation of  $[\text{Bu}_4\text{N}]_4[\text{W}_{10}\text{O}_{32}]$  in the presence of  $\text{C}_6\text{H}_{11}\text{NH}_2$  and oxygen gives a catalytic process in which cyclohexanone oxime as a major component of a mixture of products is formed [13].

In all examples listed in this section the formation of oxime complexes—rather than free oximes—was not observed. Nevertheless, the synthetic method for the oximes has been well established and its application to the preparation of oxime complexes by this type of in situ generation of the oxime can be anticipated for non-catalytic systems.

## 2.3. Tautomerization of nitrosoalkanes

Primary and secondary nitrosoalkanes are usually irreversibly rearranged to give the corresponding oximes [14,15]. This reactivity mode is preserved when nitrosoalkane species are coordinated to a metal center. *N*-coordinated ligands  $\text{R}_1\text{R}_2\text{HC}-\text{N}=\text{O}$ , undergo a spontaneous tautomerization into the oxime ligands,  $\text{R}_1\text{R}_2\text{C}=\text{NOH}$ . Thus, Schoonover et al. [16] have found that the allyl/nitrosyl complexes  $[\text{M}(\text{NO})(\eta^3\text{-C}_3\text{H}_5)(\text{PPh}_3)_2]^+$  ( $\text{M} = \text{Rh}$ ,  $\text{Ir}$ ) react readily with carbon monoxide to give acrolein oxime and  $[\text{M}(\text{CO})_3(\text{PPh}_3)_2]^+$ . A plausible mechanism for the conversion involves the tautomerization of a nitrosopropene intermediate to the more stable oxime, Scheme 1.

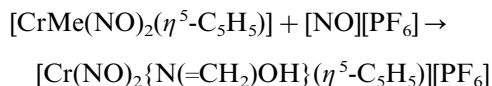


Scheme 1.

Tertiary nitrosoalkanes are frequently stable towards conversion into oximes. However, some halogenated forms can still be used as precursors for the generation of oximato complexes, e.g. King and Douglas [17] treated  $Na_2Fe(CO)_4$  with 2-bromo-2-nitrosopropane,  $BrC(N=O)Me_2$ , and isolated the Fe–Fe 2-propanone oximato complex  $Fe_2(CO)_6(\mu_2-N=CMe_2)(\mu-(N,O)-ON=CMe_2)$  whose structure was determined later by Khare and Doedens [18]. Analogously, the reaction between  $NaMo(CO)_3(\eta^5-C_5H_5)$  and  $BrC(N=O)Me_2$  leads to the oximato compound  $Mo(\eta^2-O,N-ON=CMe_2)(CO)_2(\eta^5-C_5H_5)$  and NaBr as a by-product [19].

#### 2.4. Insertion of nitrosyl into a metal–methyl bond

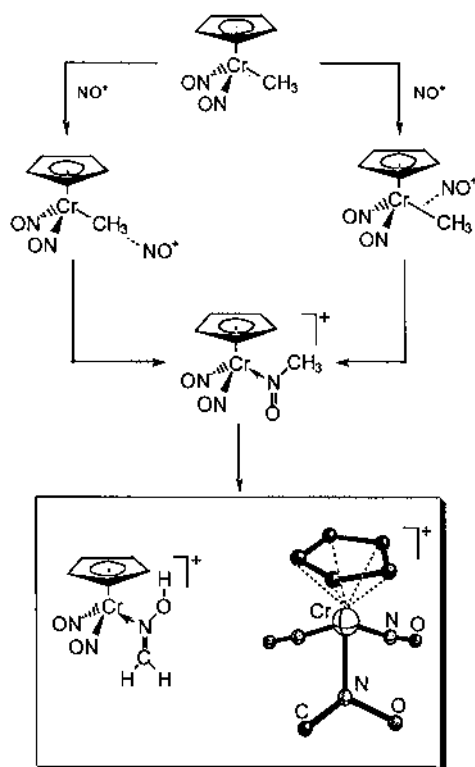
The first example of the insertion of the nitrosonium ion into a metal–carbon bond was reported in 1986 [20]:



The structure of the formaldoxime product,  $[Cr(NO)_2\{N(=CH_2)OH\}(\eta^5-C_5H_5)][PF_6]$ , has been confirmed by single-crystal X-ray diffraction. The mechanistic pathways for the insertion of  $NO^+$  into metal–carbon bonds have been described in the literature [20], Scheme 2. It would be of considerable interest to extend this reaction to the preparation of other formaldoxime compounds. However, the nitrosation has so far only one precedent [20–23].

#### 2.5. Nitrosation of $\beta$ -diketonate and similar complexes

It has already become a classical issue in coordination chemistry that the  $\gamma$ -H of metal  $\beta$ -diketonates, as with organic aromatic rings, can be chlorinated or nitrated



Scheme 2.

[24]. However, the reactivity of these complexes in other electrophilic reactions, e.g. nitrosation, is different. Thus, Djordjevic et al. [25,26] reported that the treatment of  $[\text{M}(\text{acac})_2]$  ( $\text{M} = \text{Ni}, \text{Pd}$ ; Hacac = acetylacetonate) with  $\text{NOCl}$  in benzene affords a

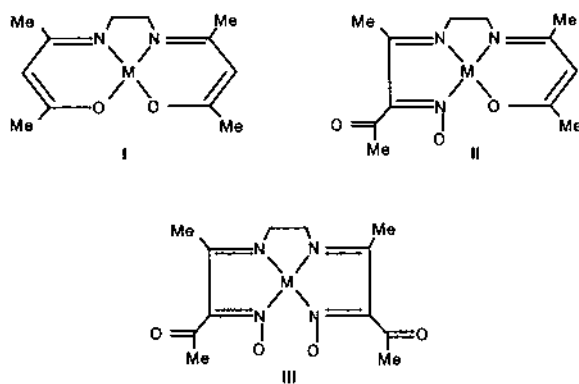


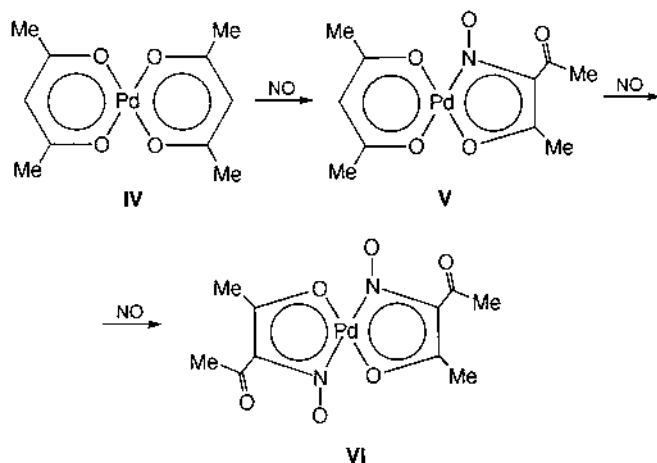
Fig. 1.

compound which is thought to be either an oxime or nitroso derivative but its exact structure was not elucidated. Later, Masuda and colleagues [27] discovered that complexes of the type **I** (see Fig. 1;  $M = \text{Cu(II)}$ ,  $\text{Ni(II)}$  and  $\text{Pd(II)}$ ) which are rigid analogs of the  $\beta$ -diketonate complexes react with NO in benzene to form oxime complexes **II** ( $M = \text{Cu}$ ,  $\text{Ni}$ ) and **III** ( $M = \text{Cu}$ ,  $\text{Ni}$ ,  $\text{Pd}$ ), Fig. 1. White [28] then repeated an investigation of the reaction reported previously [25,26] between  $[\text{Pd}(\text{acac})_2]$  (**IV**) and NO in  $\text{C}_6\text{H}_6$  at room temperature where he isolated and identified complex **V**, formed in low yield. With longer reaction times, the nitrosation proceeds further to give **VI**, Scheme 3. It is remarkable that the latter complex was also obtained in independent synthesis starting from the isonitroso-derivative of Hacac and  $[\text{PdCl}_4]^{2-}$  [28]. Moreover, a comparison of the data presented by Djordjevic and colleagues [25,26] with those obtained by White [28] have shown that the former workers prepared complex **V** in the course of nitrosation of  $[\text{Pd}(\text{acac})_2]$ .

Eventually, Herberhold and Kratzer [29] described the photonitrosation of  $[\text{Co}(\text{acac})_3]$  in benzene or toluene solutions which leads to the oximato complex tris(3-hydroxyimino-pentane-2,4-dionato)cobalt. All products prepared from nitrosation of  $\beta$ -diketonates and similar complexes correspond to a formal substitution of the  $\gamma$ -H of chelate rings by nitric oxide and subsequent linkage isomerization.

## 2.6. Nitrosation of hydrocarbons activated by complexation

Nitrosation of organic carbanions in basic media is a useful reaction for the preparation of free oximes. In organic chemistry this approach was useful for the synthesis of oximes starting from aromatic hydrocarbons with benzylic hydrogens activated by ortho or para nitro groups. Similar activation can be reached by complexation of  $\text{ArCH}_2\text{R}$  with the  $\{\text{Cr}(\text{CO})_3\}$  moiety. Thus, in basic media,



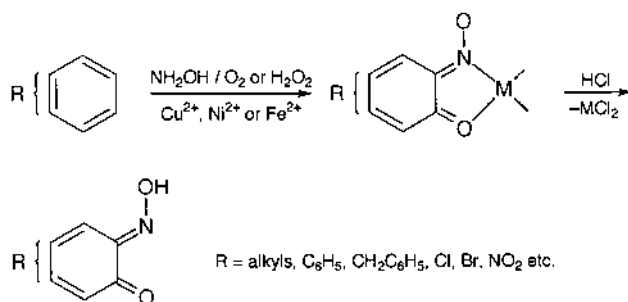
Scheme 3.

aromatic hydrocarbons and benzylmethylethers complexed by  $\{\text{Cr}(\text{CO})_3\}$  units are readily nitrosated at the benzylic position by  $\text{tBuONO}$  to give the corresponding oximes [30,31]. Despite the fact that synthesis of the oximes is metal-mediated, the  $=\text{N}-\text{OH}$  group remains uncoordinated and, therefore, these reactions are beyond the scope of this review.

### 2.7. The Baudisch reaction (metal-assisted oxidative nitrosation) and its modified version (nitrosation of phenols)

It is well-known in organic chemistry that conventional nitrosation of phenols with  $\text{HNO}_2$  always leads to *p*-nitrosophenols ( $\rightleftharpoons$  *p*-quinone monoximes), although *o*-nitrosophenols ( $\rightleftharpoons$  *o*-quinone monoximes) are formed as intermediates. The problems in preparation of *o*-quinone monoximes can be solved by utilizing the Baudisch reaction. According to Baudisch [32–36], Cronheim [37–39] and Konecny [40], the oxidative nitrosation of aromatic compounds proceeds by simultaneous introduction of the nitroso and hydroxyl groups into adjacent positions on the nucleus when treated with nitrosyl hydride and oxygen or hydrogen peroxide. *o*-Nitrosophenols formed are trapped in the form of their reddish violet copper salts; some other metal ions can also be employed [40]. In some cases the ligands were isolated as free species on acidifying the complexes with  $\text{HCl}$  followed by extraction in petrol ether, Scheme 4. A plausible mechanism of the Baudisch reaction has been suggested [41–44]. The presence of copper salts is necessary to stabilize the nitrosyl radical, to form stable complexes and to prevent in this way the formation of *p*-quinone monoximes. It is also believed [37–39] that the trapping of *o*-quinone monoximes as their complexes prevents further oxidation to *o*-nitrophenols

If the reaction is applied to phenols instead of non-hydroxyl benzene derivatives, the interaction gives essentially the same products, e.g. copper complexes with *o*-quinone monoximes. However, due to a better solubility of phenols in water, the reaction proceeds considerably faster and typically in higher yields [45].



Scheme 4.



## 2.8. Condensation of aldehydes and ketones with hydroxylamine or hydroxylamido ligands

The condensation of primary amines with  $RR'C=O$  compounds was first reported by Schiff in 1864 and since then a great number of these reactions were performed and reviewed [46]. When hydroxylamine and its O-alkyl or O-acyl derivatives are employed, the condensation gives oximes, O-alkyl oximes or O-acyl oximes, respectively, along with water as a by-product. The experimental conditions depend mostly on the nature of the parent materials and basicity of the reaction medium; usually, reactions proceed smoothly at pH close to neutral [46].

Most likely Bush was the first who in 1963 [47] described briefly results of his unpublished work on condensation of coordinated hydroxylamine in the palladium(II) complex  $[PdCl_2(NH_2OH)_2]$  and  $MeC(=O)C(=O)Me$  which led to the dimethylglyoxime derivative  $[PdCl_2(MeC(=NOH)C(=NOH)Me)]$  and  $H_2O$ . In accord with Bush's observations, heating of  $[PdCl_2(NH_2OH)_2]$  in acetone also brings about an easy transformation of the starting material into the 2-propanone oxime complex  $[PdCl_2(Me_2C=NOH)_2]$  which was characterized by X-ray diffraction [48].

Complexes with N-bonded hydroxylamine species, e.g. *cis*- and *trans*-isomers of  $[PtCl_2(NH_2OH)_2]$ , and also the Alexander's base,  $[Pt(NH_2O)_2(NH_2OH)_2] \cdot 2H_2O$  (often formulated as  $[Pt(NH_2OH)_4][OH]_2$ ), react with acetaldehyde in alkaline media to produce  $[PtCl_2(Me_2C=NOH)_2]$  and  $[Pt(Me_2C=NOH)_4]Cl_2$ , correspondingly, isolated in good yields [49].

Müller et al. reported the condensation between the side-on bonded hydroxylamido(1-) ligand in the molybdenum complex  $[Ph_4P][Mo(\eta^2-O,N-ONH_2)(NO)(NCS)_4]$  and  $Me_2C=O$  which proceeds in refluxing acetone for 1 h and brings about transformation of the starting material into the oximato compound  $[Ph_4P][Mo(\eta^2-O,N-ONCMe_2)(NO)(NCS)_4]$  [50,51]. The condensation in refluxing diethylketone proceeds analogously giving  $[Mo(\eta^2-O,N-ONCMe_2)(NO)(NCS)_4]^-$  [52]. The mechanism of the processes has not been investigated.

In none of the above mentioned works a mechanistic pathway of the condensations was studied. In organic chemistry, it is generally believed that reactions of  $RR'C=O$  and hydroxylamine at pH close to neutral occurred through nucleophilic attack of the nitrogen electron pair to the electrophilically activated  $C=O$  carbon, while in strongly basic media the attacking agent is most likely the anion  $N^-HOH$  or  $NH_2O^-$  [46]. In complexes, the electron pair of the nitrogen atom of  $NH_2OH$  is blocked by coordination. Concurrently, coordination gives rise to a dramatic increase of acidic properties of coordinated hydroxylamine. These factors make the mechanism which proceeds via interaction between deprotonated forms of coordinated hydroxylamine and  $RR'C=O$  rather favorable. However, the condensation might also proceed dissociatively. Further work in this area could well be aimed at improving the understanding of kinetics of processes involved in the condensations and this may impact the development of new synthetic methods for the preparation of oxime complexes.

### 3. Reactivity of oximes and oxime-containing metal complexes

#### 3.1. Self-assembly of oxime/oximato metal complexes due to their stepwise deprotonation. Unusual types of hydrogen bonding

The hydrogen bond is frequently used in designing supramolecular arrays. Significant progress has been reached in the construction of organic aggregates held by H-bonds, while the use of transition metal complexes for assembly or self-assembly by hydrogen bonding has received much less attention (see, for example Refs. [53,54] and cit. loc.).

As it was shown in the previous review [2], the *N*-coordination of oximes to a platinum(II) center leads to a dramatic change in reactivity expressed in a sharp decrease of  $pK_a$  values. The latter brings about the possibility of an easy conversion of an oxime ligand into oximato species. Thus, the conjugate acid and base, which are coordinated to the Pt(II) ion, may be present in the same complex. Therefore, the formation of hydrogen bonding between protons of the OH groups of coordinated oximes and oximato oxygen(s) can be expected. In that case mixed oxime/oximato complexes of platinum(II) could be used as building elements for designing complexes with extended arrays whose shapes and bonding structures are controlled by the geometrical configuration of the building elements and direction and number of hydrogen bonds.

Kukushkin and co-authors [55,56] have prepared a number of 2-propanone oxime and or mixed 2-propanone oxime/2-propanone oximato complexes of platinum(II) and characterized them by X-ray diffraction. Some compounds display interesting hydrogen bonding modes.

Indeed, in *cis*-[PtCl(Me<sub>2</sub>C=NO)(Me<sub>2</sub>C=NOH)<sub>2</sub>], two crystallographically independent molecules form the repeat unit for a novel type of self-assembly that produces infinite one-dimensional polymeric chains held by strong H-bonds; a novel type of self-assembly shown in Fig. 2 was reported.

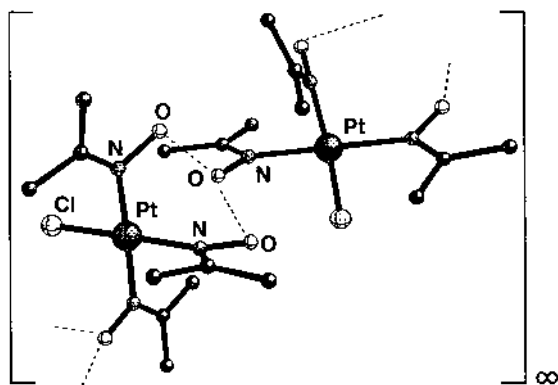


Fig. 2.

$[\text{Pt}(\text{Me}_2\text{C}=\text{NO})_2(\text{Me}_2\text{C}=\text{NOH})_2] \cdot 2\text{H}_2\text{O}$ , as compared with vic-dioxime Pt(II) complexes, displays stronger intramolecular hydrogen bonds and shows the absence of columnar stacking. In addition, the solvation  $\text{H}_2\text{O}$  molecules connect the Pt(II) building elements by intermolecular H-bonds to form a layered two-dimensional network.

In  $[\text{Pt}(\text{Me}_2\text{C}=\text{NOH})_4]\text{Cl}_2$ , the flexibility of the oxime/oximato species around the Pt–N bond allows the formation of intermolecular  $-\text{O}^- \cdots \text{HO}-$  hydrogen bonds, hydrogen bonds with counterion,  $(\mu_4-\text{Cl}^-) \cdot \text{cis}-[(\cdots \text{H}-\text{O}-)_2(\cdots \text{H}-\text{CH}_2-)_2]$ , and  $\text{Pt} \cdots \text{H}-\text{CH}_2-$  interactions, thus building the caged complex (Fig. 3). Another interesting structural feature of  $[\text{Pt}(\text{Me}_2\text{C}=\text{NOH})_4]\text{Cl}_2$  is the interaction between methyl hydrogens and platinum indicated in Fig. 3.

### 3.2. Acylation of coordinated oximes

Ryabov and co-workers [57,58] have described the high-yield acylation of coordinated functionalized oxime in the platinum(II) complex proceeding under reflux conditions in neat acetic anhydride for ca. 1 h (Scheme 5). As a result of the acylation and loss of an acylated oxime ligand, the chloro-bridged dimer is formed. A plausible reason for its formation is that the acylation of both oximes of the parent monomeric compound which would afford a sterically demanded material. Analogously, treatment of the palladium chloro-bridged dimer,  $[\text{Pd}_2(\mu-\text{Cl})_2(\text{CH}_2\text{CMe}_2\text{CMe}=\text{NOH})_2]$ , with acetic anhydride led to the acylated product  $[\text{Pd}_2(\mu-\text{Cl})_2(\text{CH}_2\text{CMe}_2\text{CMe}=\text{NOC}(=\text{O})\text{Me})_2]$  [59].

### 3.3. Iminoacylation of oximes due to their addition to coordinated nitriles

In organic chemistry, oximes are ambidentate nucleophiles and their N- or O-alkylation, acylation and arylation have been studied and reviewed extensively [60]. Similar processes involving metal complexes are also known although scarce

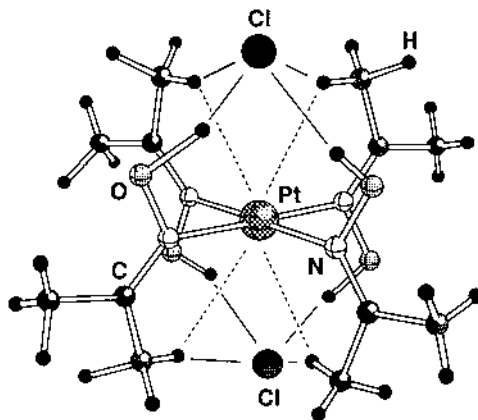
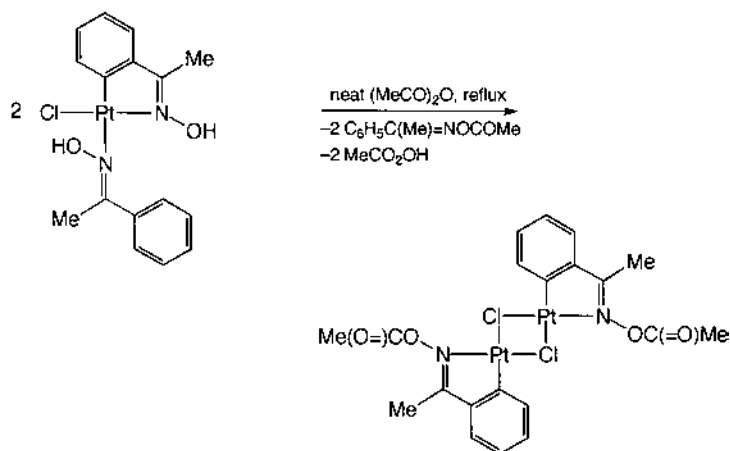


Fig. 3.



Scheme 5.

(Section 3.2). Metal-mediated iminoacylation of oximes is an even lesser explored area and only a few examples of such a reaction have been so far observed (see Refs. 65 and 67 in [2] and also [61]). Recently the authors of this review have reported on a high-yield systematic way for facile metal-assisted addition of oximes to coordinated nitriles to give iminoacylated species [62]. The reaction of ketoxime or aldoxime with the platinum(IV) complexes *trans*-[PtCl<sub>4</sub>(RCN)<sub>2</sub>] (R=Me, CH<sub>2</sub>Ph, Ph) proceeds under relatively mild conditions to yield stable iminoacyl compounds *trans*-[PtCl<sub>4</sub>(NH=C(R)ON=CR'R'')<sub>2</sub>] (R' = R'' = Me, R'R'' = C<sub>4</sub>H<sub>8</sub>, C<sub>5</sub>H<sub>10</sub>, (H)Ph, (H)C<sub>6</sub>H<sub>4</sub>(OH)-*o*), Scheme 6. Evidence in favor of metal-mediated path were presented and it is assumed that complexes are formed by nucleophilic attack of the oxime oxygen on the highly electrophilically activated carbon atom of the organonitrile.

#### 3.4. Reaction of the oxime OH group with Lewis acids (syntheses of clathrochelates)

Compounds containing an encapsulated metal ion in the three-dimensional cavity of a macropolycyclic ligand (Fig. 4; substituents are omitted for clarity) are of

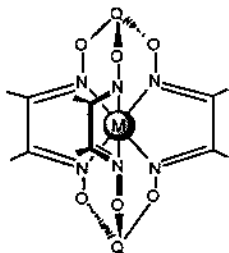
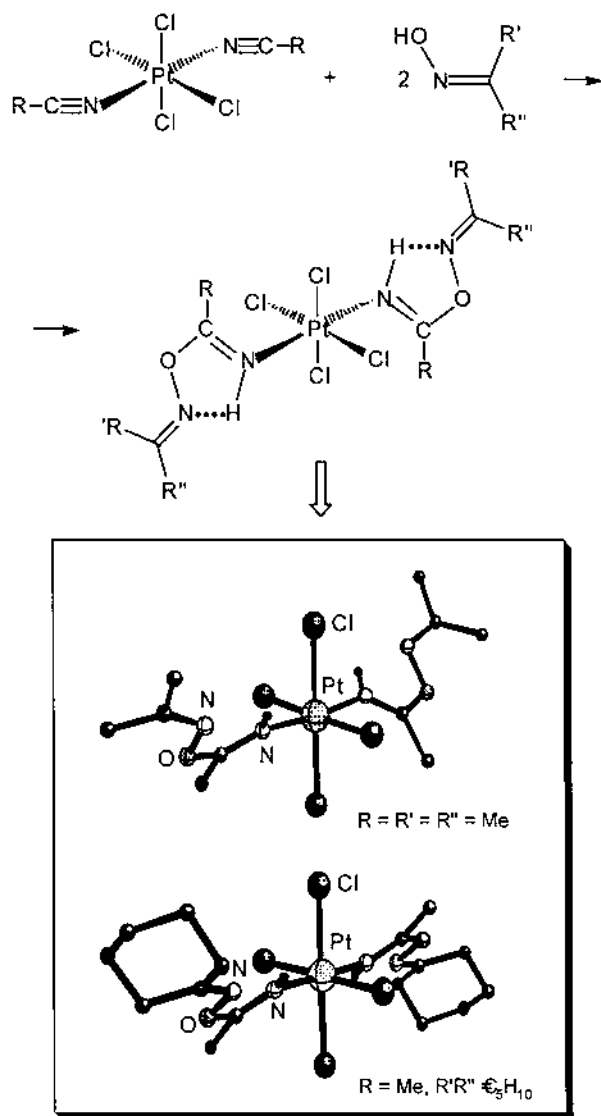


Fig. 4.

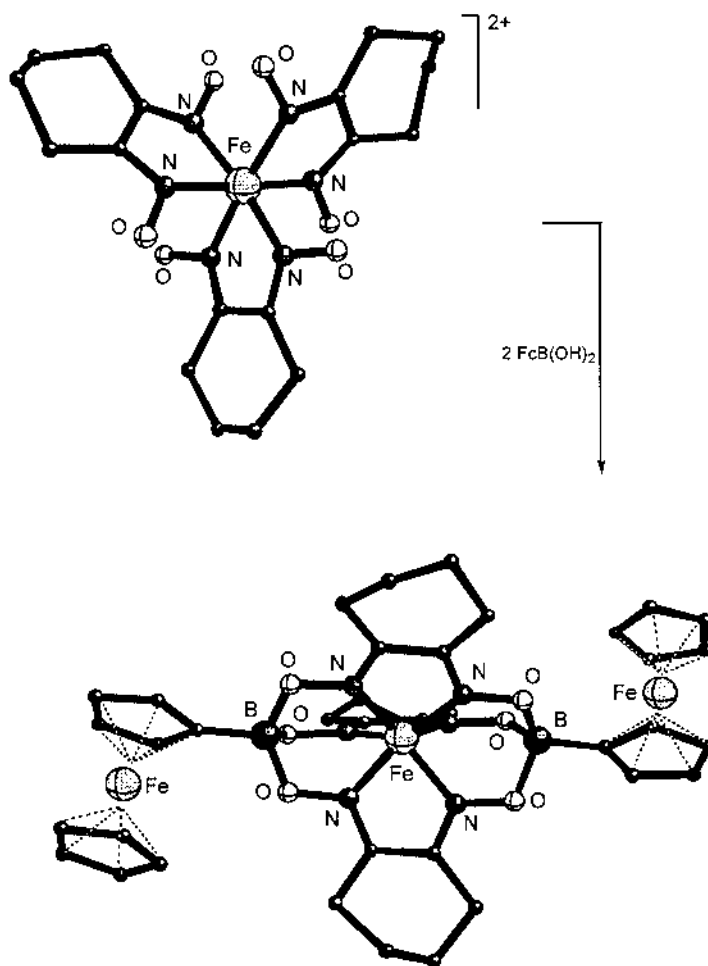


Scheme 6.

interest mainly due to their unique physicochemical properties displayed by the caged central atom [63,64].

Two general approaches were developed to synthesize clathrochelates which originate from tris-dioximate complexes. The first one is based on a reaction between the OH groups of a tris-dioximate precursor and appropriate Lewis acid. Usually this method gives high yields of final products but requires an additional

stage in achieving this goal, i.e. isolation of the tris-dioximate compound. The second approach—which is commonly called ‘the template condensation’—is based on the preparation of a tris-oximate complex in situ from a source of metal ion and a vic-dioxime. Addition of a Lewis acid after generation of the dioximate complex terminates cross-linking giving the clathrochelate. This technique gives lower yields but, nevertheless, is more often employed due to its superior simplicity. It is a wide spread opinion that the exceptional stability of clathrochelates drives the reaction [64]. Both methods were applied successfully to the synthesis of the ferrocenyl trinuclear macrobicyclic iron(II) compound [65,66] depicted in Scheme 7 and the route starting from  $[\text{Fe}(\text{1,2-cyclohexanedionedioxime})_3]^{2+}$  [67] is illustrative.



Scheme 7.

Currently a variety of clathrochelates (biscapped tris-dioximates) or semi-clathrochelates (monocapped tris-dioximates) of Fe(II), Fe(III), Ru(II), Co(II), Co(III), Ni(II) and Tc(III) with B, Si, Ge, Sn and Sb as a cap were isolated. A comprehensive survey of these compounds including their preparations with literature coverage until 1991 has been published [64]. Among recent work in this field, attention should be drawn to publications by Chaudhuri [68,69], Voloshin [65,70–73] and their co-workers. Cross-linking of square planar dioximate complexes is also well-documented [74].

### 3.5. Dehydration to give nitriles

Over the years, a number of methods have been described for the conversion of aldoximes into nitriles. Most of these methods, surveyed by Fatiadi [75] and Freidrich [76], employed very reactive dehydration reagents, otherwise reactions require harsh conditions.

As far as the metal-assisted dehydration of oxime species is concerned, work in this area is relatively scarce, although several reports describing the dehydration of oximes and the formation of metal-bound nitriles have been published. These examples include concerted deaquation and dealkylation of ketoximes,  $\text{MeRC}=\text{NOH}$ , by the ruthenium(II) complex  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  to give  $[\text{Ru}(\text{NH}_3)_5(\text{N}=\text{CMe})]^{2+}$  [77], conversion of the aldoximes during the reaction between  $[(\eta^6\text{-C}_6\text{H}_6)\text{OsHI}(\text{PMe}'\text{Bu}_2)]$  and  $\text{AgPF}_6$  in the presence of  $\text{HON}=\text{CHR}$  to produce  $[(\eta^6\text{-C}_6\text{H}_6)\text{OsH}(\text{N}=\text{CR})(\text{PMe}'\text{Bu}_2)]^+$  [78], and dehydration of  $\text{HON}=\text{CHR}$  on treatment with  $[\text{W}(\text{CO})_5(\text{THF})]$  [79]. In addition, some workers have studied the solid-state thermal elimination of water from oxime-containing complexes but no convincing evidence for formation of nitriles was given [80,81].

Relatively recently, the reaction between ruthenium(III) bromide and benzaldehyde oxime in aqueous 6 M HBr has been studied [82]. This results in facile metal-assisted dehydration of the oxime and concomitant partial reduction of ruthenium(III) to produce the mixed-valence ruthenium(III)–ruthenium(II) compound  $[\text{RuBr}(\text{N}=\text{CPh})_5][\text{RuBr}_4(\text{N}=\text{CPh})_2]$ . The latter was characterized by X-ray diffraction as the mono benzyl alcohol solvate. It was suggested that the reaction proceeds via N-coordination of the oxime to the metal ion which promotes increased unsaturation at the bonded nitrogen atom—a phenomenon generally attributed to back-bonding from the 4d orbitals of Ru(II) or Ru(III) to the empty  $\pi^*$  orbitals on  $\text{sp}^2$ - or  $\text{sp}$ -hybridized nitrogen—thus facilitating the dehydration. As a rule, syntheses of oximes from aldehydes and hydroxylamine are much easier than those of the corresponding nitriles. Thus, the Ru-assisted dehydration of oximes may be useful in the synthesis of complexes with difficult-to-obtain and/or commercially unavailable nitriles.

Among other work relevant to the dehydration of oximes, attention should be drawn to observations by Tillack and colleagues [83] who attempted to perform the reaction between  $\text{PhC(H)}=\text{NOSiMe}_3$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{Me}_3\text{SiC}_2\text{SiMe}_3)$  which gave a mixture of unidentified products. An IR spectrum of this mixture, after its short exposure in air, shows a vibration band at  $2228\text{ cm}^{-1}$  which was attributed to

$\nu(\text{C}\equiv\text{N})$  in benzonitrile. Although PhCN-containing species or benzonitrile itself were not isolated, these observations seem to be reasonable because the tendency to form nitriles during reaction of O-alkylaldoxime ethers with metal complexes was already described [77].

Further, Levin patented [84] the preparation of 2-hydroxybenzonitrile by reacting  $\text{NH}_2\text{OH}$  and salicylaldehyde which is at least partially in the form of a salt/or complex of Groups IIA, IIIA, IVA, or VIA metals, followed by dehydration of the salicylaldoxime formed. No more details have been disclosed in the patent [84]. Thermal decomposition of 2-oximido carboxylic acids,  $\text{HO}_2\text{C}-\text{C}(\text{R})=\text{NOH}$  [85], or their alkali salts [86] is a useful synthetic route for the preparation of functionalized nitriles RCN which also gives water and carbon dioxide as by-products.

Undoubtedly, these rather scarce and non-systematic examples of the metal-mediated dehydration of oximes make generalization too speculative so far. However, we believe that further progress in this area could be targeted to studies of thermolysis of aldoximes in the presence of nitrilophilic metal ions such as, for instance, ruthenium(II).

### 3.6. Deoxygenation of oximes

Gouzerh and co-workers [87] attempted to react  $[\text{Mo}(\text{NO})(\text{acac})_2-\{\text{MeC}(\text{NH}_2)\text{NO}\}]$  and  $\text{PhC}(\text{=O})\text{NHNH}_2$ . Instead of the expected condensation giving the  $\text{Mo}\{\text{N}_2\text{C}(\text{=O})\text{Ph}\}$  moiety, the authors isolated the tetramolybdate  $[\text{MeC}(\text{NH}_2)_2]_2[\text{Mo}_4\text{O}_{12}\{\text{MeC}(\text{NH}_2)\text{NO}\}_2]$ . Although the mechanism of formation of this compound has not been verified, the identification of acetamidine provides a good argument in favor of deoxygenation of the oxime or, in other words, oxygen transfer from acetamidoxime to the molybdenum(II) center.

Oxime ligands can undergo dehydroxylation to form ligated methyleneamides ( $\text{N}=\text{CR}_1\text{R}_2$ ) as demonstrated by the synthesis of complexes of the type  $[(\eta^6\text{-C}_6\text{R}_6)\text{M}(\text{N}=\text{CR}_1\text{R}_2)(\text{L})][\text{PF}_6]$  [ $\text{M} = \text{Os}$  or  $\text{Ru}$ ;  $\text{R} = \text{H}$  or  $\text{Me}$ ;  $\text{CR}_1\text{R}_2 = \text{CPh}_2$ ,  $\text{CMe}(\text{Ph})$ ,  $\text{CMe}_2$  or  $\text{C}(\text{CH}_2)_5$ ;  $\text{L} = \text{organophosphine}$ ] which were obtained by Werner and co-workers [88,89] by reaction of the corresponding oximes  $\text{HON}=\text{CR}_1\text{R}_2$  with  $[(\eta^6\text{-C}_6\text{R}_6)\text{MHX}(\text{L})]$  ( $\text{X} = \text{Cl}$  or  $\text{I}$ ) in the presence of  $\text{AgPF}_6$ . This proceeds via the hydride-oxime intermediates  $[(\eta^6\text{-C}_6\text{R}_6)\text{MH}(\text{HON}=\text{CR}_1\text{R}_2)(\text{L})][\text{PF}_6]$  which, upon subsequent dehydration when chromatographed over  $\text{Al}_2\text{O}_3$ , yields the final products.

### 3.7. Oxidative additions of oximes to electron-rich metal compounds

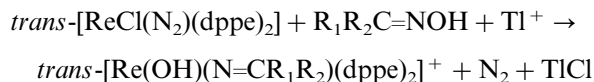
The oxidative addition of oximes to metal centers is a very little explored area. To the best of our knowledge, only one work, by Deeming et al. [90], has been published on the O–H bond splitting in the oxidative addition of 2-propanone oxime to the osmium cluster  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  giving the hydride/oximato compound  $[\text{Os}_3(\mu\text{-H})(\mu\text{-Me}_2\text{C}=\text{NO})(\text{CO})_{10}]$ . Thermal isomerization of this cluster leads to the hydroxo/imido isomer  $[\text{Os}_3(\mu\text{-OH})(\mu\text{-Me}_2\text{C}=\text{N})(\text{CO})_{10}]$  along with some other unidentified products. The mechanism of the latter conversion has not been studied. If it includes the intermediate formation of  $[\text{Os}_3(\mu\text{-Me}_2\text{C}=\text{NOH})(\text{CO})_{10}]$ —



as it was suggested by the authors [90]—the reaction can be considered as the oxidative addition of oximes due to the N–O bond splitting.

However, the first direct observation of oxidative addition, to a metal center, of an oxime with N–O bond splitting was only recently reported [91], involving an electron-rich metal site. Thus, treatment of the rhenium(I) complex *trans*-[ReCl(N<sub>2</sub>)(dppe)<sub>2</sub>] (dppe = 1,2-bis(diphenylphosphino)ethane) with 2-propanone oxime in the presence of the halide-abstractor Tl[BF<sub>4</sub>]/Tl[HSO<sub>4</sub>] and in sunlight (to promote dinitrogen loss) afforded the hydroxo-methyleneamide complex *trans*-[Re(OH)(N=CMe<sub>2</sub>)(dppe)<sub>2</sub>][HSO<sub>4</sub>] which was characterized by X-ray diffraction, Fig. 5.

The generality of the reaction was established [92] by extending it to various oximes R<sub>1</sub>R<sub>2</sub>C=NOH (CR<sub>1</sub>R<sub>2</sub> = CMe<sub>2</sub>, C(CH<sub>2</sub>)<sub>4</sub>, C(CH<sub>2</sub>)<sub>5</sub>, CHMe or CHPh); it proceeds according to the following equation:



This oxidative addition reaction of an oxime to an electron-rich metal centre constituted a novel route for the synthesis of methyleneamide complexes. The hydroxide ligand in some of the hydroxo-methyleneamide products can undergo ready replacement by fluoride, upon treatment with HBF<sub>4</sub>, to give the corresponding fluoro-complexes *trans*-[Re(F)(N=CR<sub>1</sub>R<sub>2</sub>)(dppe)<sub>2</sub>][BF<sub>4</sub>] [92].

Recently Tillack and colleagues [83] have observed the N–O bond cleavage in O-silylated oximes, R<sub>1</sub>R<sub>2</sub>C=NOSiMe<sub>3</sub> (R<sub>1</sub>R<sub>2</sub> = Me<sub>2</sub>, {CH<sub>2</sub>}<sub>5</sub>), occurring on treatment with the titanocene compound depicted in Scheme 8. These oxidative additions were carried out on heating the reactants in *n*-hexane at 60°C for 5 h and the final compounds were isolated in 45–50% yield [83].

The formation of methyleneamide complexes from oximes by simple oxidative addition (via N–O bond cleavage) to a metal centre is distinct from the above

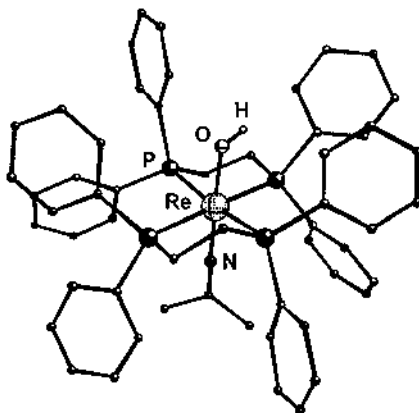
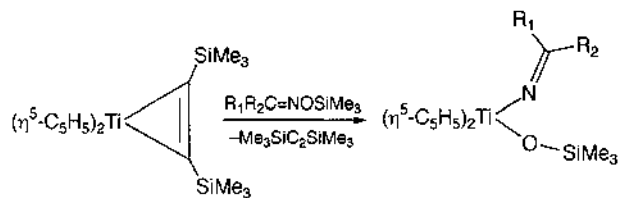


Fig. 5.



Scheme 8.

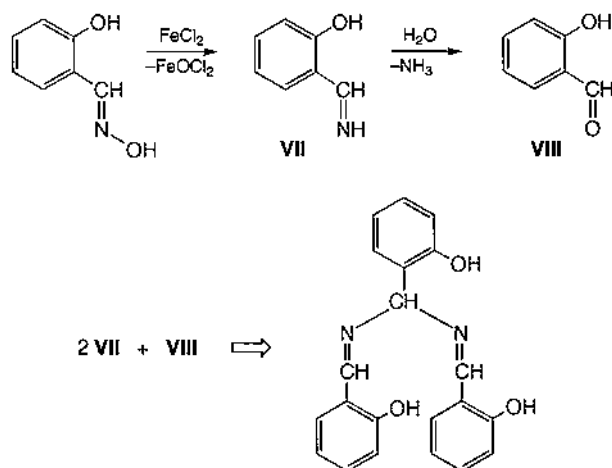
mentioned dehydration of the hydride-oxime species  $[(\eta^6\text{-C}_6\text{R}_6)\text{MH}(\text{HON}=\text{CR}_1\text{R}_2)(\text{L})][\text{PF}_6]$ , on treatment with  $\text{Al}_2\text{O}_3$  [88,89], which also leads to methyleneamide products. In fact, the latter process, as described in the previous section, is not an oxidative addition of the oxime to the metal (the oxidation state of which is preserved), requires the presence of an hydride co-ligand as a source of a leaving proton, and also the use of a dehydrating agent.

### 3.8. Redox and non-redox hydrolysis involving metal compounds

The conversion of oximes into the parent carbonyl compounds requires in general reductive or oxidative cleavages, strongly basic or acidic media. In addition, yields are low. Attanasi and co-workers [93] proposed a facile method based on copper(II)-assisted hydrolysis. In a typical experiment, a ketoxime or aldoxime is refluxed in  $\text{MeOH}$ – $\text{THF}$  mixtures in the presence of approximately three-fold excess  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Released carbonyls  $\text{RR}'\text{C}=\text{O}$  were extracted in diethyl ether and thus separated from metal-containing species. Although intermediates were not detected, the difference between regular and metal-mediated conditions led the authors [93] to the conclusion that reaction is metal-assisted and involves the reaction of electrophilically activated coordinated oxime ligands.

Oxidative deoxygenation of oximes was discussed in our previous review [2]. Since that time some additional work on deoxygenation involving  $\text{NH}_4\text{CrO}_3\text{Cl}$  [94–97] and  $\text{KMnO}_4$  [98] has appeared along with a review on the subject although published in a journal of limited availability [99].

The reaction between salicylaldehyde and  $\text{Ti(III)}$ ,  $\text{Fe(II)}$ ,  $\text{V(III)}$ ,  $\text{Cr(III)}$ ,  $\text{Mn(III)}$  and  $\text{Co(III)}$  ions in methanolic solutions under argon leads to complexes with unusual triangular  $[\text{M}_3^{\text{III}}(\mu_3\text{-O})(\mu_2\text{-OPh})]^{6+}$  core [100,101]. These compounds also contain the deprotonated ligand 2-(bis(salicylideneamino)methyl)phenol which is generated in situ in the course of the reaction. Its formation—in case of the metal ions with strong reducing properties, e.g.  $\text{Ti(III)}$  and  $\text{Fe(II)}$ —was explained on the basis of the reductive hydrolysis path, involving deoxygenation of the oxime by the metal center (a type of reaction we have described above), Scheme 9. However, occurrence of this reaction with the other metal ions suggest that two more routes for the hydrolysis—oxidative deoxygenation and regular metal-mediated path—are also possible.



Scheme 9.

### 3.9. Nitrosylation of metal centers by oximes

Acetamidoxime,  $\text{MeC}(\text{NH}_2)=\text{NOH}$ , can act as a nitrosylating reagent toward  $[\text{MoO}_2(\text{acac})_2]$ , yielding the seven-coordinate acetamidoximate complex  $[\text{Mo}(\text{NO})(\text{acac})_2\{\text{MeC}(\text{NH}_2)=\text{NO}\}]$  [102]. Similar compounds were obtained with propanamidoxime and chloroacetamidoxime as reagents [87]. Further nitrosylation of metal centers involving oximes were observed when  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  was treated with acetaldoxime, 2-propanone oxime, cyclohexanone oxime and cyclopentanone oxime [103,104]. In all these cases the nitrosyl compound  $[\text{NH}_4]_2[\text{RuCl}_5(\text{NO})]$  was isolated but in some cases this product was contaminated with  $[\text{NH}_4]_2[\text{RuCl}_6]$ . The authors [103,104] believe that both the nitrosyl and ammonium ion arises from ruthenium ion mediated hydrolysis/disproportionation of the oximes; high nitrosylophilicity of the ruthenium drives the overall process.

### 3.10. Metal-mediated Beckmann rearrangement

The Beckmann rearrangement is often used for conversion of oximes into amides or lactams in organic synthesis [105–107]. This reaction generally requires the use of excess amounts of strong Brønsted or Lewis acids. Metal ions, like typical Lewis acids, can also promote the rearrangement. Metal-mediated isomerization of an aldoxime to amide appears to have been observed first by Comstock, who reported as early as 1897, that benzamide can be synthesized starting from benzaldoxime when this reagent is heated in benzene or toluene in the presence of  $\text{CuCl}_2$  [108]. Later Bryson and Dwyer [109,110] observed conversion of furfuraldoxime to furamide during a study of coordination compounds of nickel(II) with the oxime. This observation was developed thoroughly in subsequent work by Field et al. [111] who investigated the Beckmann rearrangements of a variety of aldoximes catalyzed

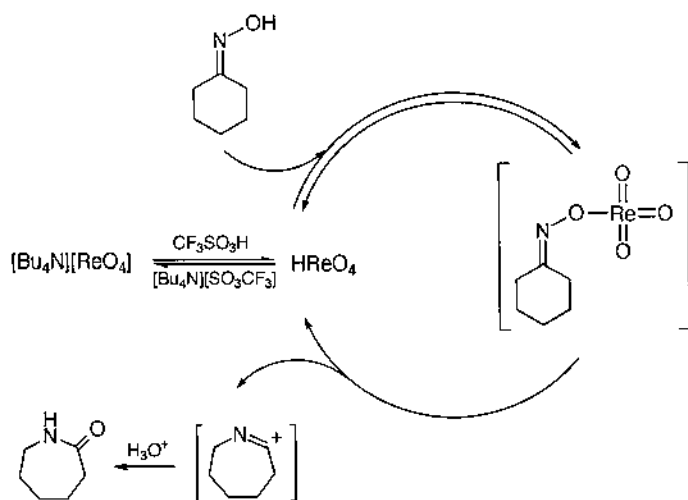
by  $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ . The reactions were performed in either xylene, xylene + piperidine mixtures or water depending on whether the nature of an aldoxime and appropriate amides were isolated in preparative yields. Zhdanov et al. [112] have studied the Cu(II)-mediated Beckmann rearrangement of monosaccharide-based aldoximes into the appropriate amides which proceeds on heating the oximes and  $\text{Cu}(\text{CH}_3\text{CO}_3)_3$  in a 2:1 molar ratio in dioxane. The authors [112] reported that they isolated (oxime)copper(II) complexes as intermediates of the reaction, but no details of their conversion were given.

An approach to the understanding of influence of metal ions on the Beckmann rearrangement was presented by Leusink and colleagues [113] who investigated rapid isomerization of aldoximes ( $\text{MeCH}=\text{NOH}$ ,  $\text{PhCH}=\text{NOH}$ , 4- $\text{HOC}_6\text{H}_4\text{CH}=\text{NOH}$ ) to the corresponding amides catalyzed by  $[\text{M}(\text{acac})_2]$  ( $\text{M} = \text{Pd}$ ,  $\text{Ni}$ ) and  $[\text{Pd}(\text{CH}_2\text{NO}_2)(\text{acac})(\text{PPh}_3)]$  complexes.  $^1\text{H}$ -NMR and GLC monitoring of the catalytic system composed from  $\text{MeCH}=\text{NOH}$  and  $[\text{Pd}(\text{acac})_2]$  revealed the presence of a small amount of acetonitrile in the mixture. During heating of the system  $\text{MeCH}=\text{NOH}/\text{PhCH}_2\text{CN}/[\text{Pd}(\text{acac})_2]$ , acetaldoxime was converted into acetonitrile while an equivalent amount of benzylicyanide was transformed into phenylacetamide. In the authors opinion [113], these experiments give an argument in favor of consecutive dehydration–hydration path of the process in which acetaldoxime is converted into acetonitrile and then the nitrile is converted into amide. Indeed, both metal-assisted reactions are well-documented in coordination chemistry, e.g. dehydration of oximes was surveyed in Section 3.5 of this article while metal-mediated hydration of nitriles was the subject of a number of reviews [114–120].

In contrast to aldoximes, the metal-mediated Beckmann rearrangement of ketoximes is a rare reaction and, in fact, only one example of such conversion is at our disposal. Thus, Narasaka and co-workers [121,122] reported that the Beckmann rearrangement of ketoximes is catalyzed by tetrabutylammonium perrhenate,  $[\text{Bu}_4\text{N}][\text{ReO}_4]$ , and trifluoromethanesulfonic acid in refluxing nitromethane. In the absence of  $[\text{Bu}_4\text{N}][\text{ReO}_4]$ , the reaction does not proceed at all. Concurrently, when *O*-acetyl cyclohexanone oxime was employed instead of the oxime  $(\text{C}_5\text{H}_{10})\text{C}=\text{NOH}$ , the rearrangement hardly occurred with the catalyst under the same reaction conditions. These observations led the authors [121,122] to the conclusion that the reaction involves intermediate formation of oxime perrhenate, accordingly to Scheme 10 of the catalytic cycle. In this process, the by-production of ketones was efficiently suppressed by addition of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  and the target products, e.g. amides and lactams, were isolated in good yields.

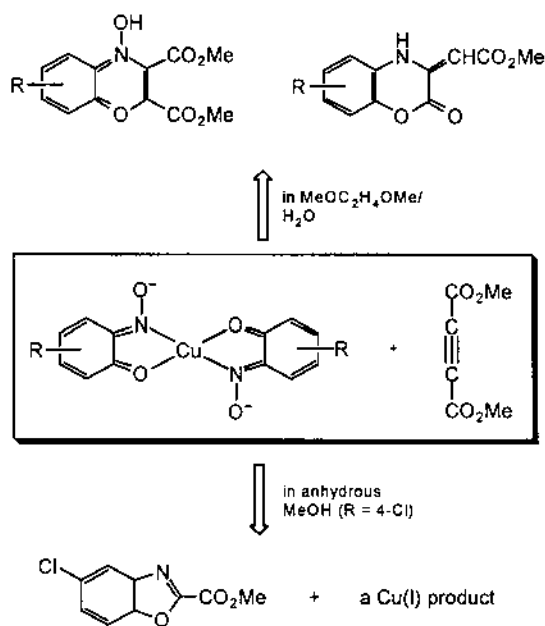
### 3.11. Synthesis of *N*-containing heterocycles from metal oximates

Copper(II) [123,124] or nickel(II) [124] complexes with *o*-quinone monoximes react with dimethyl acetylenedicarboxylate (DMAD) in aqueous 1,2-dimethoxyethane under reflux conditions to give the corresponding benzoxazines and benzoxazin-2-ones [123,124] (see Scheme 11 for the case of copper complex). Model experiments show that appropriate free ligands [123,124] or their =NOMe



Scheme 10.

ethers [123] are either completely unreactive towards DMAD [123] or form the open chain adducts  $RC_6H_3\{=O\}\{=NOC(CO_2Me)=C(CO_2Me)H\}$  [124]. These observations favor a metal-mediated reaction.



Scheme 11.

Castellani and Millini [125] further investigated these reactions and discovered that in anhydrous methanol, the metal-mediated [4 + 2] cycloaddition does not occur and reaction of bis(4-chloro-1,2-benzoquinone-2-oximato)copper(II) with  $\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me}$  leads to methyl 5-chloro-1,3-benzoxazole-2-carboxylate rather than the benzoxazine, Scheme 11. A diamagnetic residue of Cu(I)-containing species was also detected as a by-product and this observation means that in the course of the reaction both the oxime nitrogen and copper(II) ion were reduced [125]. Unfortunately, the role of a metal in the [4 + 2] additions is not completely understood. Indeed, DMAD react with the nickel(II) complex, e.g. bis(4-chloro-1,2-benzoquinone-2-oximato)nickel(II), in the presence of water but much slower as compared with the analogous copper(II) compound; there is no reaction in anhydrous MeOH [3]. Further, DMAD fails to react with Co(III) *o*-quinone monoxime complexes [123].

Brown and co-workers [126] investigated products and the mechanism of pyrolysis of the benzyl cobaloxime (**IX**) by using mass spectrometry in conjunction with DTA methods. All thermolysis experiments were conducted under an argon atmosphere. Apart from loss of dimethylglyoxime and 4-methylpyridine the authors detected products due to chemical conversions, 3,4-dimethyl-5-phenylisoxazole (**X**), and its plausible precursor, e.g. a monoxime intermediate (**XI**), Fig. 6. Benzyl derivatives of cobaloxime decompose easily not only in the solid state but also in a high-boiling solvent such as *m*-xylene, to afford 5-aryl-2,3-dimethylisoxazoles in yields substantial enough (40–60%) to regard the procedure as a synthetic route to these heterocycles. A plausible mechanism for isoxazole formation includes a free-radical-based pathway [127].

### 3.12. Miscellaneous

The heating of salicylaldoxime with  $[\text{VO}(\text{acac})_2]$  in methanol results in the formation of the unusual compound indicated in Fig. 7. The authors [61] did not

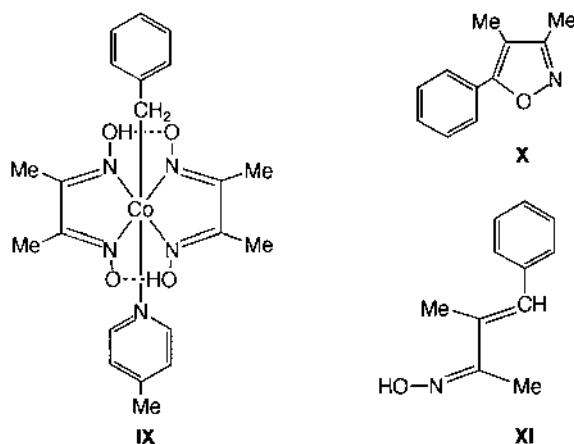


Fig. 6.

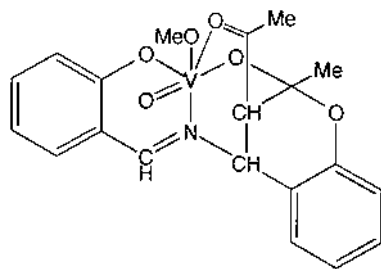


Fig. 7.

discuss plausible mechanistic pathways of its formation but pointed out that the tetradentate ligand derives from coupling of acetylacetone with salicylaldimine and salicylaldehyde.

It is known that free ketoximes and aldoximes in the course of the Piloty reaction [128] can be chlorinated to generate chloronitrosoalkanes,  $RR'ClC-N=O$ , and chloroximes,  $RC(Cl)=NOH$  (via  $RCH(Cl)-N=O$ ), respectively. Furthermore, chlorination of free  $\alpha$ -dioximes in many instances leads to furoxans [129]. Reaction of the salicylaldoxime platinum(II) complexes *trans*-(S,N)-[PtCl<sub>2</sub>(*o*-HOC<sub>6</sub>H<sub>4</sub>CH=NOH)(Me<sub>2</sub>SO)]·H<sub>2</sub>O and *trans*-(S,N)-[PtCl(*o*-OC<sub>6</sub>H<sub>4</sub>CH=NOH)(Me<sub>2</sub>SO)] with excess Cl<sub>2</sub> leads to oxidation of the Pt(II) centre and—instead of the Piloty reaction or oxidative deoximation (see Section 3.8)—chlorination in *para* and *ortho* positions of the benzene ring giving, as a result of the overall process, the platinum(IV) complex *trans*-(S,N)-[PtCl<sub>3</sub>{Cl<sub>2</sub>(O)C<sub>6</sub>H<sub>2</sub>CH=NOH}(Me<sub>2</sub>SO)] [130]. The metal plays the role of a protecting center which prevents oxidation of the oxime nitrogen, Fig. 8. Concurrently, the oxo(1-)-substituent in the phenyl ring is apparently facilitating the chlorination (as compared to the neutral salicylaldoxime) and orienting the chlorination towards the *ortho* and *para* positions.

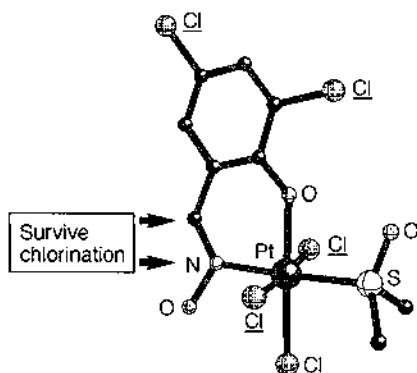


Fig. 8.

Coordinated oxime can reduce platinum(IV) ion in the acetoxime compound *cis*-[PtCl<sub>4</sub>(Me<sub>2</sub>C=NOH)<sub>2</sub>] to give the platinum(II) chelate [PtCl<sub>2</sub>{N(=O)CMe<sub>2</sub>ONC-Me<sub>2</sub>}] [131]. Furthermore, Bléaupré and Holland investigated the extraction of H<sub>2</sub>[Pt<sup>IV</sup>Cl<sub>6</sub>] from aqueous solutions of HCl in the pH range 0.00–2.00 by methylethylketone oxime and 4-heptanone oxime [132]. They reported that the [Pt<sup>IV</sup>Cl<sub>6</sub>]<sup>2-</sup> ion is reduced to give a platinum(II) species but neither of these complexes was isolated nor was the nature of the reducing agent elucidated. In contrast to these observations, reactions [133] of [(*n*-Bu)<sub>4</sub>N][PtCl<sub>3</sub>(Me<sub>2</sub>C=NOH)] or a mixture of Me<sub>2</sub>C=NOH and K<sub>2</sub>[PtCl<sub>4</sub>] with concentrated (ca. 36%) aqueous HCl lead to the oxidation of Pt(II) species and concurrent reductive hydrolysis of the oxime to give (NH<sub>4</sub>)<sub>2</sub>[Pt<sup>IV</sup>Cl<sub>6</sub>] and either [(*n*-Bu)<sub>4</sub>N]<sub>2</sub>[Pt<sup>IV</sup>Cl<sub>6</sub>] or K<sub>2</sub>[Pt<sup>IV</sup>Cl<sub>6</sub>]. Apparently, these examples were the first to show the redox duality of oximes towards one and the same metal.

Kagan and co-workers [134] reported on the reduction of salicylaldoxime by SmI<sub>2</sub> in methanol as a solvent. Two major products, benzylamine and 1,2-diphenyl ethyl amine, were isolated. It was later established that the reduction exclusively gives benzylamine if the samarium diiodide–base (LiNH<sub>2</sub> or KOH) system in THF is employed [135]. Similarly, other aldoximes and ketoximes, e.g. PhCH=NOH, (2-HOC<sub>6</sub>H<sub>4</sub>)CH=NOH, Ph<sub>2</sub>C=NOH, (4-ClC<sub>6</sub>H<sub>4</sub>)PhC=NOH and PhMeC=NOH, were reduced to the appropriate amines [135]. The intimate mechanism of these reactions was not revealed.

#### 4. Conclusions

The above discussions illustrate a wide variety of metal-mediated reactions towards the syntheses of oxime (or oximate) complexes, as well as the promotion of further reactivity.

Oxime complexes can be obtained, either in a conventional way upon reaction of an oxime with a metal center (a subject not treated in this review) or, less commonly, upon generation in situ of the oxime ligand from convenient precursors. The unconventional ways, which does not require the previous synthesis of the oxime, include a number of distinct types of sources of the organic (=CRR') and/or the inorganic (=NOH) moieties of the oxime (RR'C=NOH).

In fact, although the oxime precursor can already contain the {CNO} fragment, e.g. an organic nitroalkane (RR'CHNO<sub>2</sub> which generates the oxime upon reduction, route 2.1) or a nitrosoalkane (e.g. RR'HC–N=O which can tautomerize to the oxime, route 2.3), the most frequent situations involve distinct sources for the organic and the inorganic moieties. Hence, the former moiety can be supplied by a ketone or an aldehyde (RR'C=O following a Schiff-type condensation with an hydroxylamine or hydroxylamide ligand, route 2.8), an aromatic compound (the Baudisch and related reactions, route 2.7), an alkyl ligand (upon insertion of nitric oxide into the metal–carbon bond, route 2.4), a benzyl ligand (susceptible to nitrosation at the methylenic position, route 2.6) or a β-diketonate ligand (prone to nitrosation at the γ-position, route 2.5). Nitric oxide (routes 2.4 and 2.5), nitrosyl



hydride formed in situ (route 2.7), hydroxylamine or hydroxylamide ligands (route 2.8), or an organonitrite (route 2.6) can behave as the {NO} sources, whereas an organonitrogen compound such as an amine can be used (route 2.2) as a source of the oxime {NC} group which, upon oxygenation by an metal(oxo) compound, generates the oxime.

Other potential sources, yet unexplored, of the oxime components can be envisaged and the generality of some of those synthetic methods, including their dependence on the type of metal centre, as well as the investigation of their mechanisms have still to be explored. Moreover, the activation of oximes by transition metal centres towards further reactions should also constitute a fruitful area of research in view of the interesting cases already reported, although limited in number, that can be grouped as follows.

(i) Reactions involving the O atom of the oxime (oximate) ligand, with retention of the {CNO} fragment, accounted for by its basic and/or nucleophilic character: hydrogen-bond formation (Section 3.1), O–H cleavage with loss of  $H^+$  that can be replaced by a Lewis acid (Section 3.4), an acyl (Section 3.2) or an iminoacyl (via nucleophilic addition to a nitrile ligand, Section 3.3) group.

(ii) Reactions centred at the N atom of the oxime ligand with preservation of the {CNO} group: rare cycloaddition with an electrophilic acetylene ([4 + 2] cycloaddition of an *o*-quinone monoxime with acetylenedicarboxylate to give a benzoxazine, Section 3.11).

(iii) Reactions with loss of the integrity of the {CNO} group, in particular involving:

(a) N–O bond cleavage: oxidative addition of the oxime to an electron-rich metal centre (route for methyleneamide ligands, Section 3.7), deoxygenation (which can also lead to ligating methyleneamides, Section 3.6), dehydration (to generate nitriles, Section 3.5), conversion into amides or lactams (Beckmann and related rearrangements, Section 3.10) or into amines (Section 3.12), and rare couplings to an acetylene (some reactions of an *o*-quinone monoxime with acetylenedicarboxylate to form a benzoxazin-2-one or a benzoxazole-carboxylate, Section 3.11) or to an acetylacetonate ligand (reaction of salicylaldoxime with a vanadylacetylacetonate, Section 3.12).

(b) N=C bond cleavage: hydrolysis (that can occur via the deoxygenation by the metal, i.e. via N–O bond cleavage, Section 3.8) and nitrosylation of the metal (Section 3.9).

Some of the above reactions are still quite rare (e.g. coupling to acetylacetonate ligands or to acetylenes), and not always defined clearly (e.g. deoxygenation by the metal), but further examples are expected to be reported allowing their full establishment. Nucleophilic additions of oximes to organonitriles have been recently well established and should be extended to other types of unsaturated species. Applications in syntheses of organonitrogen products, including N-containing heterocycles, are particularly promising and should be further explored.

Systematic studies are usually still lacking and deserve a greater attention, hoping to recognize and rationalize relationships between the electronic/structural properties of the binding metal centres and the types of reactions they induce at the ligated oximes, whose mechanisms, moreover, have to be established also.

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