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Metal-ion assisted reactions of oximes and reactivity of oxime-containing metal complexes

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Abstract

The syntheses, structures and solution chemistry of oxime- and oximato-containing metal complexes have been extensively studied and described in a large number of books and reviews. However, metal-ion assisted reactions of oximes and reactivity of oxime-containing metal complexes have received much less attention and no general overview of these processes has been presented. The goal of this review is to fill this gap. Along with consideration of experimental results illustrating a rich chemistry of coordinated oximes, an attempt is made to show general features of some reactions and to systematize reaction types. In order to provide a clearer picture of different reactivity modes, possible reaction pathways are discussed and evidence for these mechanisms is provided. In conclusion the article points out certain metal-ion assisted reactions which (from the viewpoint of the authors) need more attention.

Keywords: Coordinated oxime; Oxime; Oxime-containing metal complex

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1. Introduction

A great number of publications on oxime-containing complexes appeared after the pioneering works of Hantzch and Werner in 1890 [1], Chugaev in 1905 [2], and Hieber and Leutert in 1927 [3,4]. Areas covering the organic [5–21], solution and analytical [22–30] and general inorganic and organometallic chemistry of oximes and their complexes (Table 1) have been extensively explored as shown by the significant number of books and review articles [31–52] produced.

Nevertheless, with the exception of a few papers, where data on reactivity were discussed only briefly, no review has been published on the reactivity of coordinated oximes and oxime complexes. This omission is somewhat surprising from the viewpoint of the intrinsic interest in reactions of coordinated ligands [53–55]. Here, metal-ion assisted reactions of oximes and reactions of oxime complexes are discussed and classified. We have not restricted our scope by considering only so-called "simple" oximes, e.g. ligands which have merely one oxime group as the only coordination site, but also have included reactions of *vic*-dioximes and substituted oximes. Our main interest is in the systematic classification rather than an encyclopedic listing of experimental results. Hence, the coverage is more selective than exhaustive. The references provided lead to the original work as well as to subsequent reviews so that the reader may select the information to pursue.

The different coordination modes of oxime and oximato species, depicted in Fig. 1 indicate a versatile electronic distribution within the ligands. This, in turn, suggests that the chemistry of metal-bonded oximes should be rich. The inspection of data accumulated in the literature confirms this assumption. In this article we focus our attention on the following reactivity modes of oximes and oxime complexes.

(i) Oximes, being weak oxygen acids, react with bases and undergo deprotonation. The N-coordination of oxime ligands to a metal center leads to a dramatic increase in their acidic character and the formation of oximato ligands is favorable upon coordination.

Table 1
Selected reviews on the general inorganic and/or organometallic chemistry of oximes published after 1970

Description of article	Authors/Year of publication	Refs.
Comprehensive review with 298 Refs. on the structural chemistry of simple oximes, *vic*-dioximes, nitrosophenols (quinonemonoximes), carbonyl-, imine-, pyridine-, azo-, hydroxy-, amine- and amido-oximes. Some aspects of the chemistry and reactivity are also discussed	A. Chakravorty/1974	[31]
Synthesis and structural studies and some reactions of oximato-containing organometallics	A. Singh, V.D. Gupta, G. Srivastava and R.C. Mehrotra/1974	[32]
Preparations, structures and spectroscopic studies of isonitrosoketones, $RC(=O)C(=NOH)R'$	B.C. Haldar/1974	[33]
Transition metal complexes of isonitroso-β-ketoimines	K.S. Bose and C.C. Patel/1974	[34]
Metal and metalloid complexes with oximes	R.C. Mehrotra, A.K. Rai, A.K. Singh, and R. Bohra/1975	[35]
Preparation, properties, electronic, IR and NMR spectra as well as structures of the transition metal oxime complexes	C. Varhelyi and Z. Firta/1976	[36]
Oxime-bridged complexes of transition metals	J.A. Bertrand and P.G. Eller/1976	[37]
Cobaloximes as models for studies of vitamin B_{12}	G.N. Schrauzer/1976	[38]
Transition metal complexes of isonitroso-β-ketoimines and related ligands	N.S. Dixit and C.C. Patel/1977	[39]
Metal complexes with oximes. No more information is given in Chemical Abstracts	S. Yamada and H. Kuma/1978	[40]
Coordination compounds of Co^{III} with dioximes	V.N. Shafranskii, I.L. Fasu, D.D. Buburuz, I.V. Dranka and Yu.Ya. Kharitonov/1981	[41]
Structure and reactivity of complexes of Cu^{II}, Ni^{II} and Pd^{II} with dimethylglyoxime and salicylaldoxime	N. Voiculescu and L. Dominte/1983	[42]
Structural aspects of the *trans*-influence in Co^{III} complexes with dioximes	Yu.A. Simonov, A.I. Shkurpelo, S.S. Budnikov, M.M. Botoshanskii and T.I. Malinovskii/1983	[43]
Structure, ligand bonding, synthesis and some reactions of transition metal hydroxyoxime complexes	M.E. Keeney, K. Osseo-Asare and K.A. Woode/1984	[44]
Structure and reactivity of Pd and Pt arylazooximates	A. Chakravorty/1984	[45]
Concise review on structures, syntheses and reactivity of complexes containing "simple" and *vic*-dioximes	R.C. Mehrotra/1987	[46]
Unusual electric and optical behavior of Pt and Ni *vic*-dioximates	I. Shirotani/1987	[47]
Axial ligation to low spin Fe^{II} oxime complexes. Implications of kinetic and equilibrium data to the understanding of metal-ligand bonding	D.V. Stynes/1988	[48]
First row transition metal chemistry of aromatic *o*-hydroxyalkoximes	R.P. Singh and N.K. Singh/1991	[49]

Table 1 (*continued*)

Description of article	Authors/Year of publication	Refs.
Preparation and characterization of cobaloxime complexes in which axial positions are occupied by some anionic ligands or derivatives of imidazole	K.C. Dash/1991	[50]
Chemistry of complexes with azomethine ligands including oxime species	A.D. Garnovsky/1993	[51]
Brief review on structure and modes of coordination of oxime ligands in metal complexes	N.N. Gerasimchuk and K. Bowman-James/1994	[52]

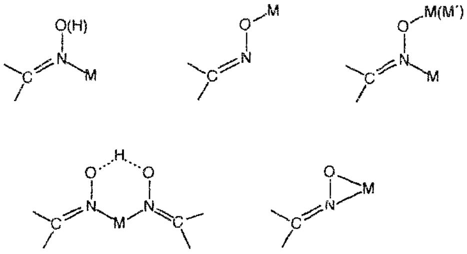


Fig. 1. Coordination modes of oxime and oximato species.

(ii) Oximes behaving as protic nucleophiles towards nitriles, similarly to alcohols or amines, involving the addition of the oxime O–H group to the nitrile C≡N bond.

(iii) Oximes behaving also as nucleophiles towards other unsaturated species, such as ketones, olefins or arenes, and involving the nucleophilic addition via either the O or the N atom.

(iv) Aldoximes being activated by a transition metal binding site towards dehydration to form a coordinated nitrile, or towards deoxygenation to form aldimine ligands; also ketoxime ligands forming nitriles by elimination of alcohols.

(v) Oxidation of oxime ligands involving deprotonation and coupling via nucleophilic attack at the C atom to form, e.g. nitrosoalkyl species.

(vi) Reductive or oxidative deoximation of oximes involving metal complexes or metal ions. Aldehydes and ketones are main products in these processes.

(vii) Metal-assisted deoxygenation to form nitriles, azavinylidenes, imines or μ_2-imides; alcohols and amines being also possible reduction products.

(viii) Metal-assisted rearrangement of oximes to amides (the Beckmann rearrangement), formation of clathrochelates, hydrosilylation of oximes to N-silylamines, insertion of isocyanates and aldehydes into the metal–oximato bond, etc.

2. Prototropic acid–base reactions of N-coordinated oximes and generation of oximato complexes

Oximes, like most weak oxygen acids, undergo deprotonation at fairly high pH values. Thus, the pK_a in water of 12.4 and 12.3 have been reported for acetoneoxime and acetaloxime, respectively [56,57]. However, Bordwell and Ji [58] have concluded that these pK_a values are merely lower limits. Despite uncertainty in the exact K_a constants of the oximes, it is clear that free oximes exhibit only weak acidic properties. Grinberg and Stetsenko [59–62] and then Kukushkin and co-workers [63,64] have established that the coordination of oxime ligands gives rise to a dramatic increase in their acidic character. This, in turn, reflects the fact that reactivity of oximes changes significantly when these ligands are coordinated to a metal center. Additionally this explains certain reactivity modes of coordinated oximes which will be discussed in appropriate Sections of the article. K_a values for some oxime complexes of Pt^{II} obtained from potentiometric and ^1H NMR spectrophotometric studies are summarized in Table 2.

Inspection of the data presented in Table 2 show that: (i) Acidities of cationic complexes are higher than those for neutral compounds, apparently due to the effect of the positive charge in the former case; (ii) Acidities of aldoxime complexes are higher by one or two orders of magnitude as compared with the appropriate acetoxime derivatives; (iii) In $[PtCl_2(oxime)L]$ replacement of amine ligand (L is NH_3) by

Table 2
Acid dissociation constants of platinum(II) oxime complexes in water (potentiometry, $c = 10^{-2}$–10^{-3} mol·L^{-1}, $\mu = 0.3$, 25.0±0.1°C)

Complex	K_{a1}	K_{a2}	Refs.
cis-$[PtCl_2(Me_2C{=}NOH)(NH_3)]$	$(1.0 \pm 0.1) \times 10^{-7}$		[63]
cis-$[PtCl_2(MeCH{=}NOH)(NH_3)]$	$(1.0 \pm 0.1) \times 10^{-6}$		[63]
cis-$[PtCl_2(Me_2C{=}NOH)(Me_2SO)]$[a]	1×10^{-6}		[63]
trans-$[PtCl_2(Me_2C{=}NOH)(Me_2SO)]$	$(2.0 \pm 0.1) \times 10^{-7}$		[64]
cis-$[PtCl_2(MeCH{=}NOH)(Me_2SO)]$[a]	1×10^{-5}		[63]
trans-$[PtCl_2(MeCH{=}NOH)(Me_2SO)]$	$(7.0 \pm 0.1) \times 10^{-7}$		[64]
cis-$[PtCl_2(Me_2C{=}NOH)_2]$	$(7.4 \pm 0.8) \times 10^{-7}$	$(3.6 \pm 0.9) \times 10^{-10}$	[62]
trans-$[PtCl_2(Me_2C{=}NOH)_2]$	$(8.6 \pm 0.9) \times 10^{-8}$	$(4.1 \pm 1.0) \times 10^{-10}$	[62]
cis-$[PtBr_2(Me_2C{=}NOH)_2]$	$(9.3 \pm 1.0) \times 10^{-7}$	$(9.2 \pm 3.0) \times 10^{-10}$	[62]
trans-$[PtBr_2(Me_2C{=}NOH)_2]$	$(1.4 \pm 0.2) \times 10^{-7}$	$(4.7 \pm 1.3) \times 10^{-10}$	[62]
cis-$[Pt(Me_2C{=}NOH)_2(NH_3)_2]Cl_2$	$(2.7 \pm 0.2) \times 10^{-6}$	$(7.3 \pm 0.8) \times 10^{-9}$	[59]
trans-$[Pt(Me_2C{=}NOH)_2(NH_3)_2]Cl_2$	$(2.2 \pm 0.2) \times 10^{-6}$	$(4.0 \pm 0.4) \times 10^{-8}$	[59]
trans-$[Pt(MeCH{=}NOH)_2(NH_3)_2]Cl_2$	$(2.0 \pm 0.2) \times 10^{-5}$	$(7.2 \pm 0.4) \times 10^{-6}$	[59]
cis-$[Pt(Me_2C{=}NOH)_2(NH_3)_2]Cl_2$[a,b]	2.9×10^{-6}	not determ.	[60]
trans-$[Pt(Me_2C{=}NOH)_2(NH_3)_2]Cl_2$[a,b]	3.4×10^{-6}	4.4×10^{-8}	[60]
$[PtCl(Me_2C{=}NOH)_3]Cl$[c]	$(2.8 \pm 0.1) \times 10^{-5}$	$(4.2 \pm 0.2) \times 10^{-8}$	[61]
$[Pt(Me_2C{=}NOH)_4]Cl_2$[d]	$(3.0 \pm 0.2) \times 10^{-4}$	$(1.9 \pm 0.2) \times 10^{-4}$	[61]
$[Pt(MeCH{=}NOH)_4]Cl_2$[e]	$(1.5 \pm 0.4) \times 10^{-2}$	$(1.6 \pm 0.1) \times 10^{-4}$	[59]

[a] Standard deviations are not given; [b] ^1H NMR study; [c] $K_{a3} = (0.8 \pm 0.1) \times 10^{-10}$; [d] $K_{a3} = (1-2) \times 10^{-11}$; [e] $K_{a3} = (3.1 \pm 0.2) \times 10^{-7}$, $K_{a4} = (2.7 \pm 0.3) \times 10^{-10}$.

dimethyl sulfoxide (L is Me_2SO), which exhibits strong π-acceptor properties, leads to an increase in the acidity constants of coordinated oxime ligands. Substitution of Cl for Br in $[PtX_2(oxime)_2]$ gives rise to a slight increase in acidity.

The increased acidity of oximes upon coordination should be taken into account in synthetic experiments. Thus, Stetsenko et al. [61] attempted to prepare $[Pt(Me_2C{=}NOH)_4][NO_3]_2$ via chloride abstraction from $[PtCl(Me_2C{=}NOH)_3]Cl$ by two equivalents of $AgNO_3$, filtration of AgCl formed followed by addition of excess oxime to the solution. However, instead of $[Pt(Me_2C{=}NOH)_4][NO_3]_2$ they prepared a compound which contains two deprotonated oximes, e.g. $[Pt(Me_2C{=}NO)_2(Me_2C{=}NOH)_2]$. This complex reacts with excess HCl to give $[Pt(Me_2C{=}NOH)_4]Cl_2$. In turn, upon the addition of two equivalents of NaOH to an aqueous solution of $[Pt(Me_2C{=}NOH)_4]Cl_2$, the oximato complex $[Pt(Me_2C{=}NO)_2(Me_2C{=}NOH)_2]$ is regenerated and precipitated.

3. Addition of oximes to ligands containing triple and double bonds

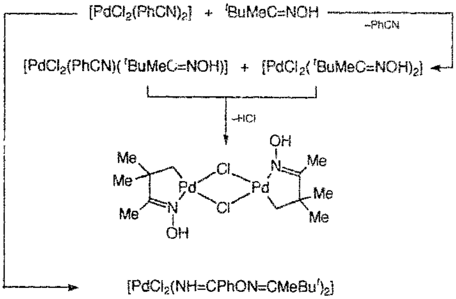
The addition reactions of free oximes often involve processes in which a variety of reagents add to the polarized C=N double bond, e.g. nucleophilic reagents attack the carbon atom of the azomethine linkage. N-coordinated oximes seem to be even more susceptible to the nucleophilic attack due to additional polarization by a metal center. However, electrophilic reagents or electrophilically activated ligands may add to the N or O donor centers. Reactions of both types will be discussed in Section 3.

3.1. *Addition of oximes to coordinated nitriles and vice versa*

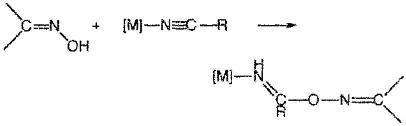
Natile and co-workers [65] have investigated the reaction between 3,3-dimethyl-2-butanone oxime, $^tBuMeC{=}NOH$, and $[PdCl_2(PhC{\equiv}N)_2]$. They isolated and characterized products of partial and complete substitution of the coordinated benzonitrile by the oxime, e.g. $[PdCl_2(PhC{\equiv}N)(^tBuMeC{=}NOH)]$ and $[PdCl_2(^tBuMeC{=}NOH)_2]$. These two complexes spontaneously underwent further reaction with the formation, inter alia, of the dinuclear metallated compound indicated in Scheme 1. Apart from the above mentioned species the authors isolated the product of addition of the oxime to coordinated $PhC{\equiv}N$-$[PdCl_2(NH{=}CPhON{=}CMeBu^t)_2]$ (Scheme 1).

This reaction involves a formal oxime O–H bond addition to the nitrile N≡C bond (Scheme 2).

This process is similar to the known [55,66] nucleophilic additions to nitrile ligands of other protic nucleophiles such as alcohols or amines. However, it should be noted that the concise form for presentation of the work [65] does not give answers to certain questions. Thus, as a general rule, organic ligands like $NH{=}CPhON{=}CMeBu^t$ form stable 5-membered rings with the metal (see later) and it is reasonable to assume that the formation of a Pd chelate should terminate the overall process. Despite some uncertainties the reaction reported is, most likely, the first example of addition of oximes to coordinated nitriles.



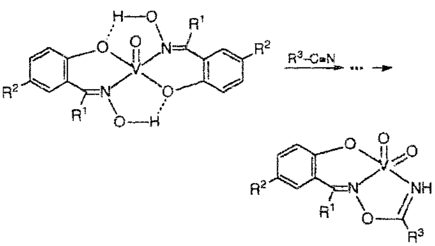
Scheme 1.



Scheme 2.

Fairly recently Grigg et al. [67] have reported the (formally) reverse reaction between a coordinated oxime and a nitrile. The authors studied the conversions of the oxovanadium(IV) aldoxime and ketoxime complexes under treatment with various nitriles (Scheme 3).

The product of one reaction, $[VO_2\{C_6H_4(O)CH{=}N{-}OC(Me){=}NH\}]$, has been structurally characterized. There is no evidence that the novel ligand is produced from a direct combination of the nitrile with the oxime. Therefore, a metal-ion assisted mechanism for this reaction was suggested. It is believed [67] that the mechanistic pathway of the reaction involves initial coordination of R^3CN to the oxovanadium(IV) centre, prior to oxidation. The loss of an oxime bidentate ligand



Scheme 3.

followed by addition of the oxime-OH group across the C=N bond carry on the process. The nature of the oxidant for the V^{IV} centre remains unelucidated.

3.2. Addition to ketones

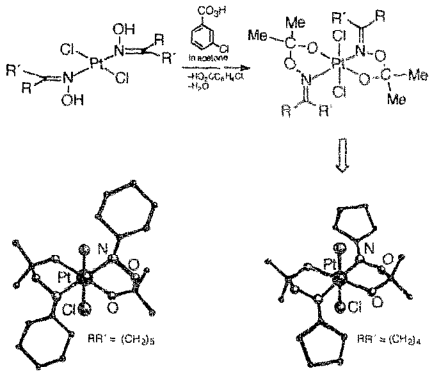
The platinum(II) complexes *trans*-[$PtCl_2(RR'C=NOH)_2$], where R=R'=Me, RR'=$(CH_2)_4$ and $(CH_2)_5$, react with *m*-chloroperoxybenzoic acid in Me_2CO to give the platinum(IV) complexes [$PtCl_2(OCMe_2ON=CRR')_2$] [68] (Scheme 4).

A possible explanation is that the reactions studied proceed via steps of oxidation of Pt^{II} by *m*-chloroperoxybenzoic acid and coordination of acetone molecules to two vacant sites formed on $Pt^{II} \rightarrow Pt^{IV}$ oxidation, followed by ring-closure with neighbouring oxime ligands.

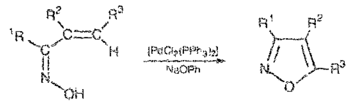
3.3. Addition to coordinated olefins, allene and arene ligands: reactions of alkylation and arylation

Oximes are ambidentate nucleophiles and their alkylation and arylation have been extensively studied in organic chemistry and are well-documented [69]. For instance, it is known that alkylation of oximes by alkyl halides preferentially gives O-alkyl ethers, whereas N-alkylation is a commonly occuring side reaction. Examples of alkylation or arylation involving metal complexes are scarce. A reaction of this type was reported for the first time by a group of Japanese workers [70,71] who examined the conversion of α,β-unsaturated oximes into isoxazoles. It was shown that $HON=C(R^1)-C(R^2)=C(R^3)H$ (R^1, R^3 are Ph, R^2 is H; R^1 is ^tBu, R^2 is H, R^3 is Ph; R^1 is Ph, R^2 is Me, R^3 is ^iPr) are transformed into isoxazoles by treatment with an equimolar amount of [$PdCl_2(PPh_3)_2$] in the presence of a five-fold excess of NaOPh in benzene under refluxing conditions (Scheme 5).

The products of this oxidative cyclization were isolated by distillation after removal



Scheme 4.



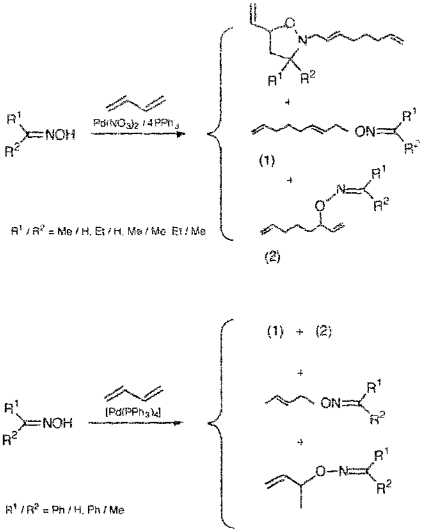
Scheme 5.

of the palladium black from the reaction mixture. The suggested mechanism of the reaction involves bidentate coordination of the oximes via their N-atom and olefinic group, followed by electrophilic activation of the C=C moiety and its subsequent intramolecular nucleophilic attack by the oxygen atom.

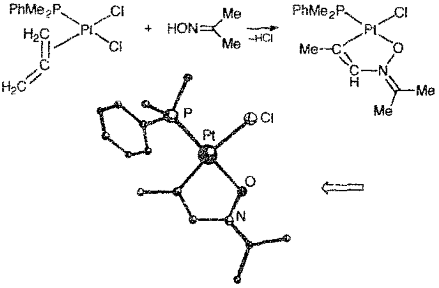
Baker and Nobbs [72] have shown that in the Pd-catalyzed reaction of oximes with butadiene, alkylation proceeds at either oxygen or nitrogen to yield oxime ethers and nitrones, the latter reacting with excess of butadiene to give N-alkylated isoxazolidines (Scheme 6).

The authors [72] believe that the ethers arise from the reaction of the oximes with π-allylpalladium intermediates formed in situ.

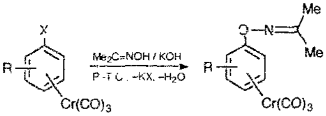
Show and co-workers [73] studied the addition of acetoxime to the allene in *cis*-$[PtCl_2(C_3H_4)(PMe_2Ph)]$. The overall process is depicted in Scheme 7 and involves nucleophilic attack by nitrogen, a 1–3 hydrogen shift, and ring closure. Strong electrophilic properties of the allene in the starting compound as well as the nucleophilic character of the oxime drive this reaction (Scheme 7).



Scheme 6.



Scheme 7.



Scheme 8.

It has been reported [74,75] that halogenarenes in $[\{\eta^6\text{-}(R)(X)C_6H_4\}Cr(CO)_3]$ (where R is H, Me, OMe; X is F, Cl in different combinations) electrophilically activated by the $Cr(CO)_3$ moiety, react smoothly with acetoxime under phase-transfer conditions to afford the corresponding O-aryloximes in good yields (Scheme 8).

This reaction can also be viewed as a nucleophilic substitution at coordinated arenes. Again the reaction was promoted by the electrophilicity of the coordinated arene ligand and the nucleophilic properties of the deprotonated oxime.

4. Dehydration and generation of free and metal-bonded nitriles

Oximes are starting materials for the synthesis of nitriles via dehydration for aldoximes or C–C bond cleavage with concomitant elimination of ROH for ketoximes. Reactions of this type are well-documented in the organic chemistry of oximes, and usually require stringent reaction conditions. In coordination chemistry, additional—and sometimes the main—driving force for the conversion of metal-bonded oximes into coordinated nitriles is the high stability of the metal–nitrile bond formed. An elegant example confirming this statement has been reported by Guengerich and Schug [76]. They have shown that the reaction between the ruthenium(II) complex $[Ru(NH_3)_5(H_2O)]^{2+}$ and the ketoximes MeRC=NOH, where R is –C(=O)Me, –C(=O)Ph and –CH(OH)Ph, has the overall stoicheometry

$$[Ru(NH_3)_5(H_2O)]^{2+} + MeRC{=}NOH \rightarrow [Ru(NH_3)_5(N{\equiv}CMe)]^{2+} + ROH + H_2O \tag{1}$$

The authors believe that the reaction proceeds via N-coordination of the oximes to the ruthenium center, followed by spontaneous carbon–carbon bond cleavage, elimination of ROH and stabilization of the nitrile complexes. This reactivity mode of coordinated oximes provides unambiguous evidence for the ability of Ru^{II} to promote increased unsaturation of bonded nitrogen atoms, a phenomenon generally attributed to strong back-bonding from the filled 4d orbitals of Ru^{II} to the empty π^* orbitals on sp^2- or sp-hybridized nitrogen. Additional insight into the driving forces for the formation of metal bonded nitriles can be obtained from the reactivity of O-alkyl aldoximes. Although the reactivity modes of these oxime derivatives are formally out of the scope of this review, the following paragraph is relevant in connection with the dehydration of oximes. Thus, following the appearence of the previously cited work [76], Geno and Dawson [77] reported the reaction between $[Ru(NH_3)_5(H_2O)]^{2+}$ and the O-alkyl aldoximes RON=CHR′ (R is Me, Et; R′ is Me, Ph)

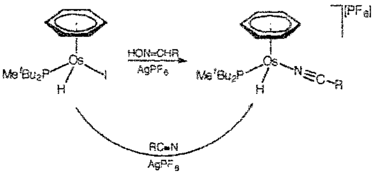
$$\begin{aligned}&[Ru(NH_3)_5(H_2O)]^{2+} + RON{=}CHR' \rightarrow \\ &\quad [Ru(NH_3)_5(N{\equiv}CR')]^{2+} + ROH + H_2O\end{aligned} \qquad (2)$$

The authors [77] postulate that Ru^{II} is back-bonding to the O-alkyl aldoxime via the nitrogen atom of the oxime. The back-bonding promotes increased unsaturation on the bound nitrogen donor atom, thereby facilitating rupture of the oxime N–O bond. Further strong driving force is the conversion of an sp^2-hybridized oxime nitrogen into an sp-hybridized nitrile nitrogen.

Osmium(II) centers have a similar pronounced ability to bind nitriles. Werner and co-workers [78] observed that when the hydride complex $[(\eta^6\text{-}C_6H_6)OsHI(PMe^tBu_2)]$ was treated with $AgPF_6$ in the presence of HON=CHR (R is Me, Ph) dehydration occurred and the nitrile compound was formed (Scheme 9).

The product $[(\eta^6\text{-}C_6H_6)OsH(N{\equiv}CR)(PMe^tBu_2)][PF_6]$ was also obtained in independent synthesis via halide abstraction from $[(\eta^6\text{-}C_6H_6)OsHI(PMe^tBu_2)]$ in the appropriate nitrile (Scheme 9).

Attanasi et al. [79] established that metal-ion assisted dehydration of aldoximes is of synthetic importance for the preparation of nitriles. The authors [79] described a catalytic method for the conversion of the alkyl and aryl aldoximes RCH=NOH, where R is n-C_7H_{15}, n-C_9H_{19}, $PhCH_2CH_2$, PhCH=CH, Ph, 4Me–C_6H_4, 4MeO–C_6H_4, $3NO_2$–C_6H_4, to the appropriate nitriles. The procedure consists of heating the aldoximes in boiling acetonitrile in the presence of a catalytic amount



Scheme 9.

of $Cu(OAc)_2 \cdot H_2O$. After completion of the reaction and subsequent work-up, the nitriles were isolated in 85%–98% yields. It was also shown that $CuCl_2 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$ are inactive as catalysts for the conversion. Based on these observations the authors [79] postulated that the overall process, probably, involves stages of coordination of the aldoximes to Cu^{II} ion, acylation of the ligand and elimination of acetic acid to afford the nitriles.

Other works on dehydration of aldoximes involving metal ions and complexes have been published. Konwar et al. [80] reported that AlI_3 is an efficient reagent for the dehydration and conversion of the aldoximes $ArCH{=}NOH$ and $PhCH_2CH{=}NOH$ into the corresponding nitriles. For example, addition of one equivalent of $PhCH{=}NOH$ to two equivalents of AlI_3 in MeCN and reflux for 2 h gave $PhC{\equiv}N$ in 92% yield. A mechanism involving initial formation of an aluminium oximato intermediate has been postulated but not confirmed experimentally. Czarkie and Shvo [81] have described the preparation of the aldimine complexes $[W(NH{=}CHR)(CO)_5]$ from $HON{=}CHR$ (R is Me, Ph, $p\text{-}C_6H_4OMe$) and $[W(CO)_5(THF)]$ (see Section 6.3.). Remarkably, deoxygenation and formation of the aldimine complexes were accompanied by deaquation and generation of the corresponding nitriles, $[W(N{\equiv}CR)(CO)_5]$. In fact, both aldimines and nitriles were isolated in comparable yields.

Among other works where the formation of nitriles was reported, attention should be payed to studies on solid-state thermal reactions of oxime-containing complexes [32,82,83]. Lalia-Kantouri and Hartophylles [82] described the thermal decomposition of various 2-hydroxyaryloxime complexes of Cu^{II}, Ni^{II} and Pd^{II} studied by DTA/TG method and mass-spectrometry. It was found that the copper complex $[Cu(2\text{-}HOC_6H_4CPh{=}NOH)_2]$, in contrast to nickel and palladium compounds of the same type, decomposes on heating with abstraction of $PhC{\equiv}N$. Olczak-Kobza has investigated the thermal conversion of bis(salicyloaldoximate)lead(II) [83]. It was found that at 160–220°C a water molecule is abstracted and the nitrile complex formulated as $[N{\equiv}CC_6H_4OPb]_2O$ is formed. Unfortunately, apart from satisfactory elemental analyses, no physicochemical data supporting the nitrile structure were given. It has been shown [32] that aldoximato derivatives of aluminium, $Al(ON{=}CHR)_3$, decompose when heated at 200°C under vacuum (0.2 mm). The volatile products formed during the thermal conversions appear to be nitriles as evidenced by the characteristic $\nu(C{\equiv}N)$ bands in the IR spectra. Other products were Al_2O_3 and H_2O.

Other examples of metal-assisted deoxygenation of oximes to give nitriles are mentioned below (Section 6.1.). They involve transition metal carbonyls, and other possible products are alcohols.

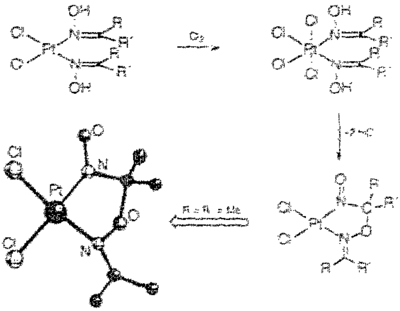
5. Metal-ion assisted oxidation of oximes

5.1. *Oxidation of coordinated oximes to generate nitrosoalkyl ligands*

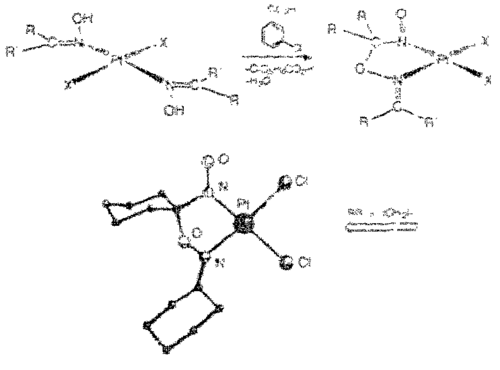
Kukushkin et al. [84,85] have demonstrated that the oxidation of *cis*-$[PtCl_2(RR'C{=}NOH)_2]$, where R, R' are Me, or R, R' are $(CH_2)_4$ and $(CH_2)_5$, by molecular chlorine yields *cis*-$[PtCl_4(RR'C=NOH)_2]$. The ketoxime ligands survive the reaction conditions, although it is known that free ketoximes can be easily converted into the nitroso compounds, RR'ClC–NO, by chlorination with Cl_2 [86]. The platinum(IV) compounds *cis*-$[PtCl_4(RR'C=NOH)_2]$, on standing in water-acetone solution, undergo an unusual spontaneous Pt^{IV}-mediated redox coupling leading to the platinum(II) chelate $[PtCl_2\{N(=O)CRR'ONCRR'\}]$ (Scheme 10).

It was found [87] later that the reaction between the platinum(II) compounds *trans*-$[PtX_2(RR'C=NOH)_2]$ (X is Cl, Br; CRR' is CMe_2, CC_4H_8, CC_5H_{10}) and *m*-chloroperoxybenzoic acid (MCPBA) in dimethylformamide gives the products $[PtX_2\{(N=O)CRRONCRR'\}]$ (Scheme 11).

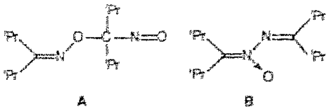
It is interesting to compare the reaction in DMF with that in acetone (see Section 3.2.). Thus, interaction between the complexes *trans*-$[PtX_2(RR'C=NOH)_2]$ and MCPBA in Me_2CO gives rise to oxidation of the central ion and addition of



Scheme 10.

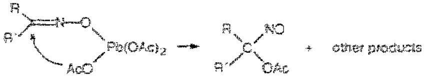


Scheme 11.



A B

Fig. 2. Compounds A and B.



Scheme 12.

acetone which acts as both the solvent and reagent. The same process in DMF leads to oxidation of the oxime ligand while the Pt^{II} oxidation state remains the same.

It is useful to compare the oxidation of coordinated oxime ligands in $[PtX_2(RR'C{=}NOH)_2]$ with the oxidation of free ketoximes. Ingold and co-workers [88] examined the silver oxide oxidations of a number of $RR'C{=}NOH$ compounds in benzene. They concluded that the reaction probably involves the intermediate formation of iminoxyl radicals. Rather complex mixtures of products are generally obtained, due to the relative instability of the $RR'C{=}NO\cdot$ radicals. Thus, upon treatment of acetoneoxime with Ag_2O the identified products were Me_2CO, N_2 and N_2O, while a very small amount of N-methylacetamide was also detected in the reaction mixture. In the case of $^tBu_2C{=}NOH$ a moderately stable iminoxyl radical was formed. Remarkably, $^iPr_2C{=}NOH$ behaves in a different way in comparison to the above mentioned oximes. Indeed, its oxidation by Ag_2O gives N_2, N_2O, $^iPr_2C{=}O$ and also the compounds A and B (Fig. 2).

Compound A is structurally similar to the chelating nitroso species in the complex $[PtX_2\{(N{=}O)CRR'ONCRR'\}]$ cited above. Although the oxidation conditions for free and coordinated oximes are not comparable, some differences in the pathways suggest a process assisted by the metal ion for the oxidation of coordinated $RR'C{=}NOH$ ligands. Apparently the platinum ion plays the role of a center which facilitates the template-type reaction.

Oxidations of ketoximes $RR'C{=}NOH$ by $Pb(OAc)_4$ have been reviewed by Butler and colleagues [6]. These reactions give the *gem*-nitrosoacetates [6,89], $RR'C(N{=}O)OAc$ and the parent ketones as the main products. A mechanism involving a Pb-intermediate has been suggested to account for the formation of nitrosoacetates (Scheme 12).

Some similarities with the Pt-assisted oxidations of coordinated ketoximes are obvious: the two-electron oxidation of the ligand is concerted with a nucleophilic attack at the carbon atom.

5.2. *Oxidative deoximation*

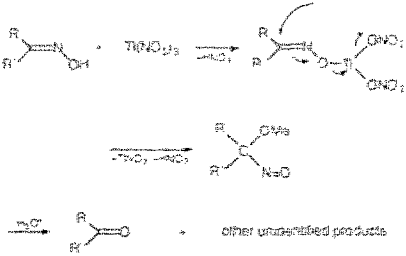
It has been demonstrated that direct hydrolysis of oximes to carbonyl compounds does not proceed in high yields or is very slow and subject to side reactions [5–7].

Alternative methods have been sought among reduction (see Section 6) and oxidative reactions. The latter will be considered later in this article.

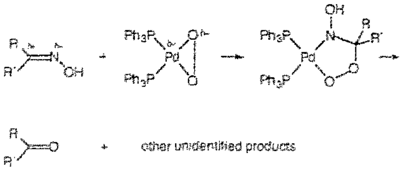
A variety of oxidants have been employed for the oxidative deoximation of oximes [5–7]. Among them, one of the most representative classes of reagents is the high oxidation state metal ions. In the vast majority of cases, the mechanisms of these reactions were neither studied nor suggested. However, when the mechanisms were investigated and discussed, all the suggested pathways included a stage of coordination of the oxime to a metal ion prior to oxidation. This means that oxidative deoximation involving high oxidation state metal ions is a metal-assisted process. Thus, McKillop et al. [90] have described the direct conversion of various aldoximes and ketoximes into the corresponding aldehydes and ketones by treatment with thallium(III) nitrate in methanol. The progress of the reaction was rapid and the process was completed within a few minutes at room temperature. The precipitated $TlNO_3$ was removed by filtration and subsequent workup with the filtrate afforded the appropriate organic carbonyls in high yields. The authors convincingly argued that the overall process involves the intermediate formation of the thallium oximato complex (Scheme 13).

This mechanism was partially supported by a kinetic study [91]. Some other works on oxidative deoximation by Bi^{V} [92], Cr^{VI} [93–97], Mn^{III} [98,99], Mn^{VII} [100–104], Fe^{III} [105], Co^{III} [106], U^{VI} [107], Ce^{IV} [108], Np^{VI} [109] and Am^{V} [110] can be informative.

Other methods of oxidative deoximation are known. Baruah and Sen [111] studied the reactivity of the oximes Ar(H)C=NOH, $Ar_2C=NOH$ and ArMeC=NOH towards a mixture of $Cu(O_2CCH_3)_2 \cdot H_2O$ and benzoyl peroxide in MeCN. Products of this reaction were separated by chromatography and identified. The authors reported that oximes derived from ketones, e.g. $Ar_2C=NOH$ and ArMeC=NOH, undergo oxidative deoximation to form the appropriate ketones. The aldoximes Ar(H)C=NOH give Ar(H)C=O, nitriles ArCN and carboxamides $ArC(=O)NH_2$. A radical mechanism was postulated [111] to explain the reaction path. Maeda et al. [112] and concurrently Sedzik-Hibner [113] reported a procedure for the oxidative deoximation of various alkyl, aryl and benzyl oximes catalyzed by



Scheme 13



Scheme 14.

the [$PdO_2(PPh_3)_2$] complex. The reaction is fast and highly efficient to produce the corresponding ketones. It is anticipated that the process follows a 1,3-dipolar cycloaddition path (Scheme 14).

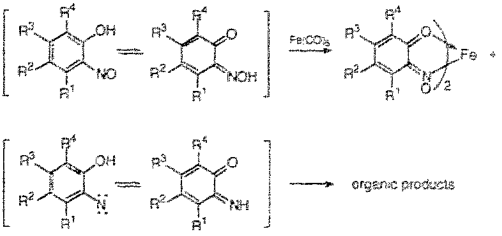
Unfortunately, no data supporting this mechanism were given and the oxidation fate of the oxime nitrogen was not elucidated. Nevertheless, the above mechanism seems to be reasonable from the point of view of recently described addition reactions of oximes discussed in Section 3.

6. Reduction of oximes

6.1. Deoxygenations involving metal carbonyls

Most likely, the initial impetus towards the investigation of deoxygenation reactions of oximes promoted by homoleptic transition metal carbonyls was given by Alper and Edward [114] who, as early as 1970, studied deoxygenation of nitrosophenols (⇌quinonemonoximes) by $Fe(CO)_5$. They found that *p*-quinonemonoxime is reduced under treatment with $Fe(CO)_5$ giving 4,4'-dihydroxyazobenzene as the only isolable product. 5-Methyl-4-nitroso-2-isopropylphenol, which exists almost exclusively in the quinonemonoxime form, reacts with $Fe(CO)_5$ to afford 5-isopropyl-2-methyl-1,4-benzoquinone as the deoximation and 5-methyl-4-amino-2-isopropylphenol as the reduction product. The authors assumed that the reduction products arise from deoxygenation of the corresponding nitrosophenols by the iron complex. Later, Charalambous and co-workers [115] demonstrated deoxygenations of 1,2-naphthoquinone-2-oxime (**1**), 1,2-naphthoquinone-1-oxime (**2**) and 5-methoxy-1,2-quinone-2-oxime (**3**) with $Fe(CO)_5$ in refluxing tetrahydrofuran. Along with the iron(II) quinone mono-oximato complex the authors isolated some organic products of the reaction (Scheme 15).

Thus, in the reaction of **1** with $Fe(CO)_5$, 2-amino-N^4(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine and 5-hydroxy-dibenzo[b,i]phenazin-12(6H)-one were identified. For the reaction involving **3** the predominant organic product turned out to be 2-amino-7-methoxy-3H-phenoxazin-3-one. The complexity of the mixture of organic products from **2** + $Fe(CO)_5$ hindered characterization. The authors [115] accounted for the appearance of the above organic products in terms of deoxygenation of the protonated ligands to give the "quinoneimine⇌nitrene"



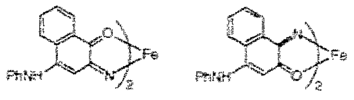
Scheme 15.

intermediate (Scheme 15) followed by hydrogen abstraction and/or coupling reactions.

It was also reported [115] that in the presence of aniline, both **1** and **2** react with $Fe(CO)_5$ to generate the iron(II) quinone mono-oximato complex as the main product. Remarkably, other complexes, **C** and **D**, were isolated from the reaction mixture (Fig. 3). Both of them contain chelating ligands with deoxygenated nitrogen atoms.

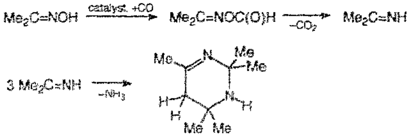
Dondoni and Barbaro [116] observed deoxygenation of methyl mesityl oxime, $Me(2,4,6\text{-}Me_3C_6H_2)C{=}NOH$, which—in contrast to previously discussed quinone-monoximes—does not tautomerize to the corresponding nitroso compound. Reaction of the oxime with $Fe(CO)_5$ in refluxing THF produces the appropriate imine, $Me(2,4,6\text{-}MeC_6H_2)C{=}NH$. The latter was isolated as its hydrochloride in 65% yield. Nitta and co-workers [117] studied similar reactions between the oximes $R^1R^2C{=}NOH$ (R^1/R^2 means Ph/Ph, Me/Ph, Me/CH_2CH_2Ph, CH_2Ph/CH_2Ph) and $Fe(CO)_5$ or $Fe_2(CO)_9$ in anhydrous methanol at 60°C. The process presumably proceeds via the formation of the imines $R^1R^2C{=}NH$ followed by their hydrolysis with H_2O which is considered to be one of the reaction products. After workup, the corresponding ketones were isolated as the final products of a chain of chemical transformations.

The deoxygenation of ketoximes to imines was also observed by Süss-Fink and co-workers [118]. They showed that in the presence of $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}Me_2C{=}NO)_2(Me_2C{=}NOH)_2]$ as a catalyst, acetone oxime is deoxygenated by CO to give a mixture of 2,3,4,5-tetrahydro-2,2,4,4,6-pentamethylpyrimidine, CO_2 and NH_3. The authors argued that the reaction proceeds via carbonylation of coordinated acetone oxime to the unstable intermediate $Me_2C{=}N\text{-}OCHO$. The latter undergoes



C **D**

Fig. 3. Complexes **C** and **D**.



Scheme 16.

decarboxylation to afford the imine $Me_2C{=}NH$ followed by its trimerization, with elimination of NH_3 (Scheme 16).

The authors [118] proved the intermediacy of the imine by carrying out the analogous reaction with $PhMeC{=}NOH$, which gives the stable imine $PhMeC{=}NH$.

The deoxygenation of aldoximes involving other metal carbonyls proceeds in a different way. Thus, Kaneda and co-workers [119,120] have studied the catalytic deoxygenation of various compounds containing N–O bonds including the aldoximes listed in Table 3. The processes were carried out under water gas shift reaction conditions (8 atm., $CO+H_2O$, room temperature) by use of the catalytic system consisting of the rhodium cluster $Rh_6(CO)_{16}$ and N,N,N′,N′-tetramethyl-1,3-propanediamine (TMPDA). After completion of the reaction, the liquid phase was analyzed by chromatography, and the results are summarized in Table 3.

Inspection of the data presented in Table 3 shows that all aldoximes studied, except $PhCH{=}NOH$, were selectively deoxygenated to produce the appropriate nitriles (the formation of nitriles from oximes via deaquation has already been described above in Section 4). It is believed that benzaldehyde oxime afforded $PhCH_2OH$ as the main product, because of its facile hydrolysis to PhCHO under the reaction conditions. In general, alcohols formed in the reaction originated from hydrolysis of the oximes followed by reduction.

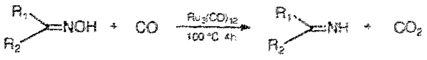
The authors detected CO_2 and H_2 among the reaction products, and concluded that the overall process is deoxygenation rather than water abstraction

$$R\text{-}CH{=}NOH+CO \xrightarrow{Rh_6(CO)_{16}} R-C{\equiv}N+CO_2+H_2 \qquad (3)$$

In contrast to $Rh_6(CO)_{16}$, ruthenium and iron carbonyl clusters, e.g. $Ru_3(CO)_{12}$ and $Fe(CO)_5$, showed poor catalytic activity in the deoxygenation of aldoximes

Table 3
Substrates/products in the reaction of oximes with $Rh_6(CO)_{16}$/TMPDA in the presence of $CO+H_2O$

Substrate	Deoxygenated products/Yields, %	
$MeCH{=}NOH$	$MeC{\equiv}N/64$	$EtOH/11$
$EtCH{=}NOH$	$EtC{\equiv}N/61$	$C_3H_7OH/20$
$CyCH{=}NOH$	$CyC{\equiv}N/71$	$CyCH_2OH/12$
$PhCH{=}NOH$	$PhC{\equiv}N/22$	$PhCH_2OH/75$
$PhC_2H_4CH{=}NOH$	$PhC_2H_4C{\equiv}N/84$	$PhC_3H_7OH/5$



Scheme 17.

[119]. Nevertheless, it has been found later [121] that $Ru_3(CO)_{12}$ exhibits high catalytic activity for the deoxygenation of various ketoximes to the corresponding ketimines under carbon monoxide pressure (Scheme 17).

The reaction gives the ketimines $R_1R_2C{=}NH$ (R_1/R_2 means Ph/Et, Ph/i-Pr, Ph/Ph, 4Cl–C_6H_4/Me, *n*-Bu/*n*-Bu; R_1R_2 means $CHMe(CH_2)_3CHMe$) which were isolated in 70%–100% yields. Other transition metal carbonyl complexes, such as $Ru(CO)_3(PPh_3)_3$, $Fe(CO)_5$ and $Fe_3(CO)_{12}$ showed a little catalytic activity; $RuCl_2(PPh_3)_3$ and $RuCl_3{\cdot}nH_2O$ were inactive for the deoxygenation. When $Rh_6(CO)_{16}$ and $Co_2(CO)_8$ were employed in the conversion, the selectivities of the formation of ketimines were low. Watanabe and co-workers [121] did not study the mechanism for the deoxygenation. However, they observed that O-benzyl propiophenone oxime and O-acetyl acetophenone oxime do not react under the same reaction conditions. This finding led the authors [121] to the conclusion that the initial step of the reaction involves the cleavage of the ketoxime O–H bond.

Recently, Watanabe's group [122] has established conditions for the $Ru_3(CO)_{12}$-catalyzed conversion of aldoximes into the appropriate imines and then to nitriles. When the reaction is conducted in the presence of allylic compounds, the imines formed can be trapped as their N-allylated derivatives having the C=N bond.

6.2. *Formation of azavinylidene complexes*

This type of reactivity of oxime complexes was discovered by Werner and co-workers [78,123–125], and allowed the first preparation of azaalkenylidene-metal complexes. The synthesis of the azavinylideneosmium complexes $[(\eta^6$–$C_6H_6)Os({=}N{=}CRR')(PMe^tBu_2)][PF_6]$ can be performed by the reaction of the hydride $[(\eta^6$–$C_6H_6)OsHI(PMe^tBu_2)]$ with the oximes $HON{=}CRR'$ (R/R′ means Ph/Ph, Me/Ph, Me/Me; R/R′ means cyclohexadiyl) in the presence of $AgPF_6$ as the halide-abstracting reagent [78]. The process proceeds via the oxime intermediates $[(\eta^6$–$C_6H_6)OsH(HON{=}CRR')(PMe^tBu_2)][PF_6]$ which were isolated in the cases of CRR′ means CMe_2 and cyclohexadiyl. The oxime-containing complexes react further with Al_2O_3 with abstraction of water to give the final azavinylidene products. X-ray structure analysis of $[(\eta^6$–$C_6H_6)Os({=}N{=}CPh_2)(PMe^tBu_2)][PF_6]$ reveals an allene-like arrangement of the ligands and substituents around the Os=N=C unit (Fig. 4).

Ruthenium azavinylidenes. $[(\eta^6$–$C_6Me_6)Ru({=}N{=}CR'_2)(PR_3)_2][PF_6]$ (R′/PR_3 means Me or Ph/PMe_3 or $PMe_2{}^tBu$) were prepared by the same route starting from the hydrides $[(\eta^6$–$C_6Me_6)RuHCl(PR_3)_2]$ [126] (Scheme 18).

The synthesis of azavinylidenemetal complexes can be carried out by an alternative way. Thus, the reaction of $[(\eta^6$–$C_6H_6)RuCl_2(P^iPr_3)_2]$ with $NaON{=}CRR'$ (R/R′ means Me/Me, Ph/Ph, H/Me, Me/^{t}Bu) in the presence of KPF_6 affords

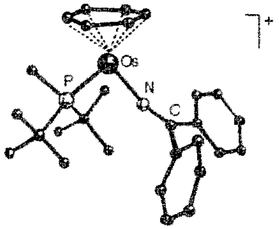
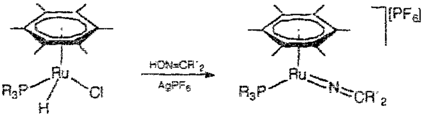


Fig. 4. An allene-like arrangement of the ligands and substituents around the Os=N=C unit.



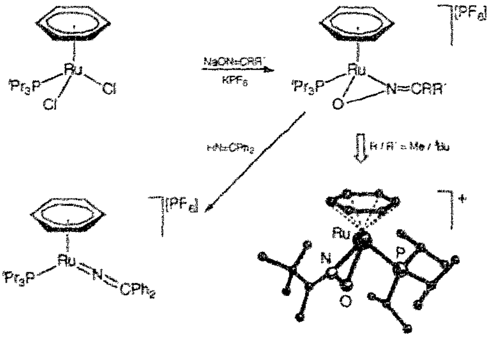
Scheme 18.

oximatoruthenium(II) complexes; one of them has been structurally studied (Scheme 19) [126].

The oximate $[(\eta^6\text{-}C_6H_6)Ru(\eta^2\text{-}ON{=}CRR')(P^iPr_3)][PF_6]$ reacts further with $HN{=}CPh_2$ via ligand exchange to give the azavinylidene complex (Scheme 19).

6.3. *Formation of imine and μ_2-imido complexes*

Ketimine complexes were first isolated by Fischer and Knauß [127]. For their preparation the authors explored the novel reaction between the carbene complex $[(OC)_5Cr{=}C(OMe)Me]$ and the oximes $HON{=}CRR'$ (R/R′ means Me/Me, Me/Et, Et/Et, Me/Ph, Ph/Ph; RR′ means $(CH_2)_4$, $(CH_2)_5$), which affords

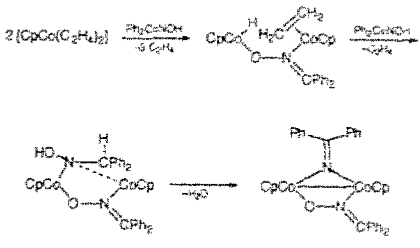


Scheme 19.

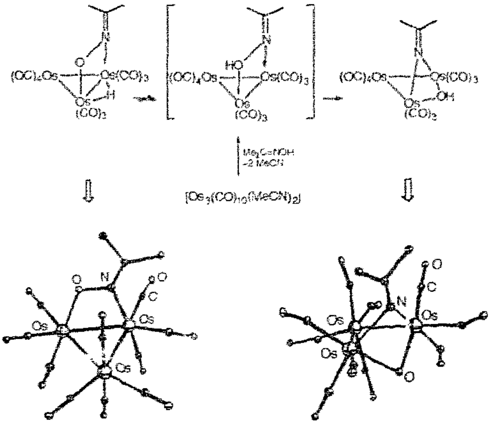
$[(OC)_5Cr(NH{=}CRR')]$. Alternatively, imine complexes were later obtained from metal carbonyls and oximes. Thus, the tungsten complex $[W(CO)_5(THF)]$ in a THF solution reacts with aliphatic or aromatic ketoximes and aldoximes to give the appropriate ketimine and aldimine complexes $[W(NH{=}CRR')(CO)_5]$ in 10–20% yields [81]. The authors [81] recognized that the mechanism of this reaction is unclear. A balanced reaction of the starting complex and an oxime requires oxygen as a product, for example assuming oxygenation of coordinated CO and elimination of CO_2. However, it was also demonstrated that methyl ethers of oximes react with $[W(CO)_5(THF)]$ in the same way as the parent oximes. This and other observations [128] probably rule out the common mechanism [129] for deoxygenation of N–O donors by metal carbonyls.

Floriani and co-workers [130] studied the reaction of $[CpCo(C_2H_4)_2]$ and benzophenone oxime, $Ph_2C{=}NOH$, in toluene at room temperature. The process proceeds presumably through a preliminary oxidative addition of the O–H bond to the metal, and leads to the formation of the μ_2-imido Co–Co complex, $[\{CpCo\}_2(\mu_2\text{-}N{=}CPh_2)(\mu_2\text{-}ON{=}CPh_2)]$ with evolution of ethylene. A plausible mechanism for deoxygenation of the $Ph_2C{=}NOH$ ligand involves three principal steps: (i) oxidative addition of O–H to cobalt(I), (ii) addition of the hydride ligand to the imino functionality, and (iii) dehydration of the hydroxylamine intermediate (Scheme 20).

Acetoxime reacts with the bis-acetonitrile osmium compound $[Os_3(CO)_{10}(MeCN)_2]$ to give the μ_2-oximato cluster $[Os_3(\mu_2\text{-}H)(\mu_2\text{-}Me_2C{=}NO)(CO)_{10}]$ formed via oxidative addition of the oxime with O–H bond cleavage [131]. The authors suggested a possible route for the formation of this cluster with the oxime complex $[Os_3(CO)_{10}(Me_2C{=}NOH)]$ being an intermediate (Scheme 21). A range of clusters $[Os_3(\mu_2\text{-}H)(\mu_2\text{-oximato})(CO)_{10}]$ were synthesized analogously from $[Os_3(CO)_{10}(MeCN)_2]$ and the oximes $Ph_2C{=}NOH$, $C_5H_{10}C{=}NOH$, $MeCH{=}NOH$, $PhCH{=}NOH$ and $NH_2CH{=}NOH$. It was also established [131] that $[Os_3(\mu_2\text{-}H)(\mu_2\text{-}Me_2C{=}NO)(CO)_{10}]$ isomerizes at 125°C in boiling octane to the μ_2-imido cluster $[Os_3(\mu_2\text{-}OH)(\mu_2\text{-}Me_2C{=}N)(CO)_{10}]$ probably via the oxime intermediate (Scheme 21). X-ray structures for both $[Os_3(\mu_2\text{-}OH)(\mu_2\text{-}Me_2C{=}N)(CO)_{10}]$ and $[Os_3(\mu_2\text{-}H)(\mu_2\text{-}Me_2C{=}NO)(CO)_{10}]$ were reported; the hydride ligand in $[Os_3(\mu_2\text{-}H)(\mu_2\text{-}Me_2C{=}NO)(CO)_{10}]$ was not located



Scheme 20



Scheme 21.

but bond lengths and angles indicate that it bridges Os atoms bonded to the oximato ligand (Scheme 21).

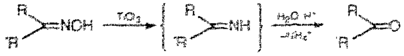
Thus, the overall process can be considered as deoxygenation of coordinated oxime with the formation of the μ_2-imido cluster.

6.4. Reduction of oximes involving low and medium oxidation state metal ions

Apart from the above mentioned low oxidation state metal carbonyls and other organometallic complexes, inorganic complexes or metal ions with low or medium oxidation states can also behave as reducing agents of oximes.

McMurray indicated in his review [132] that Ti^{III} compounds are mild, specific and effective reducing agents. Titanium has a strong affinity for oxygen and this is partly responsible for its remarkable ability to deoxygenate (reduce) nitro- and nitroso-compounds, aromatic and aliphatic N-oxides, azoxy compounds and, finally, oximes. The first reduction of oximes was carried out by Timms and Wildsmith [133] when they faced the problem of conversion of the complex antibiotic erythromycin into erythromycylamine. They chose to examine the action of buffered, aqueous $TiCl_3$ on erythromycin oxime. The progress of this reaction was rapid and erythromicin imine was obtained. Remarkably, Ti^{III} had effected a deoxygenation but had not reduced the oxime C=N bond. Since imines formed on deoxygenation are easily hydrolized to give the appropriate ketones at low pH values, the reaction is also useful as a mild deoximation process (Scheme 22).

Among other works on reduction of oximes by Ti^{III}, attention should be paid to (i) the report of Tuck and co-workers [134] who employed electrochemically generated titanium(III) species for the reductive deoximation of acetophenone oxime to afford the parent ketone; (ii) a paper by Barton et al. [135] where reduction of



Scheme 22.

various ketoximes using anhydrous titanium(III) acetate in the presence of mixed formic-acetic anhydride was studied (a reaction yielding N-formyl enamines [135]); (iii) a mild and convenient procedure for the reduction of oximes to amines in a single step involving treatment of the oxime with aqueous $TiCl_3$ in the presence of $Na[BH_3CN]$ [136].

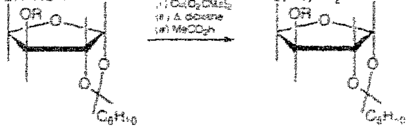
In concluding Section 6.4. we note that the reduction of oximes can also be achieved using low oxidation state samarium(II) [137–140], chromium(II) [141], vanadium(II) [142], cobalt(I) [143] and titanium(II) [144–146].

7. Miscellaneous reactions of oximes and oxime complexes

In this Section we have compiled material which does not belong to the categories described above.

The most familiar and extensively investigated of the rearrangements involving the azomethine group is the Beckmann rearrangement-conversion of oximes to amides. Usually, this reaction proceeds under the catalytic action of protic or Lewis acids. Metal ions, like typical Lewis acids, can also promote the rearrangement. However, examples of metal-ion assisted Beckmann rearrangement are fairly scarce so far. Thus, Zhdanov et al. [147] have studied the Cu(II)-mediated Beckmann rearrangement of the aldoximes (R is H, Me) into the appropriate amides (Scheme 23).

The preparative method consists of heating the oximes and copper(II) acetate in a 2:1 molar ratio in dioxane at 70°C, followed by the addition of acetic acid, extraction of the amides with ethyl acetate and removal of the solvent in vacuum. The authors [147] reported that they isolated copper(II)-oxime complexes as intermediates of the reaction, but no details of their conversion were given. Buslaev and co-workers [148] demonstrated that interaction of a suspension of $TaCl_5$ or $ReCl_5$ in benzene with acetoxime, $Me_2C{=}NOH$, gives rise to $[TaCl_5(MeCONHMe)]$ and $[ReCl_4(MeCONHMe)]$, respectively. It is believed [148] that the methylacetamide ligand comes from the Beckmann rearrangement, but the mechanistic pathway of the reaction has not been studied. The reaction of AlI_3 with $Ph_2C{=}NOH$ or



Scheme 23.

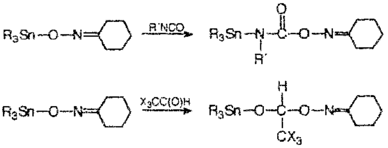
PhMeC=NOH proceeds via the Beckmann rearrangement and gives the appropriate anilides, Ph–C(=O)NHR (R is Ph, Me) [80]. However, the aliphatic oximes $Me_2C{=}NOH$ and $Me^tBuC{=}NOH$ did not undergo the rearrangement, and in both cases the starting materials were recovered from the reaction mixture. In contrast, the aldoximes ArCH=NOH and $PhCH_2{=}NOH$ were dehydrated into the corresponding nitriles [80] (see Section 4). The hydrosilylation of alkyl aryl ketoximes with H_2SiPh_2, in the presence of $[RhCl(PPh_3)_3]$ as catalyst, gives the corresponding N-silylamines via N-siloxyimine intermediates [149–151]. Although a possible mechanism of the hydrosilylation was suggested, the rôle of the $[RhCl(PPh_3)_3]$ is not completely understood.

Trialkyltin oximato complexes, $R_3SnONCC_5H_{10}$, undergo insertion reactions of aryl and alkyl isocyanates R′NCO and aldehydes $X_3CC(=O)H$ (X is Cl, Br) [152] (Scheme 24).

Additions of this type are well known for both organotin [153] and organic chemistry [154].

The lone electron pairs on both nitrogen and oxygen atoms enable oximes to act as multisite ligands and coordinate to different metal ions. In this review we have not considered reactions of *vic*-dioxime complexes with Lewis acids which generate clathrochelates, multicyclic ligand systems that completely encapsulate a metal ion. From our viewpoint these interactions may be considered as a complicated type of substitution reactions and their analysis is not a goal of the article. However, one example can be cited in order to show the diversity of reactivity modes of oxime complexes. Thus, the treatment of $^{99}TcO_4^-$ with dimethylglyoxime and tin(II) chloride in a EtOH/HCl mixture leads to the tin-capped complex $[Tc(DMG)_3(\mu\text{-}OH)SnCl_3]$ [155]. The X-ray structure of the final compound was solved but the H-atoms were not located (Fig. 5).

Other reactions of dioximato complexes with tin(IV) [156] as well as their



Scheme 24.

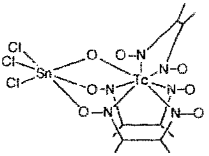


Fig. 5. Structure of the final compound.

interactions with titanium(IV) [157], aluminium(III) [158], germanium(IV) [159], boron(III) [160–162], and silicon(IV) compounds [163] have also been studied.

Bleaupré and Holland have investigated the extraction of $H_2[PtCl_6]$ from aqueous solutions of low pH by methylethylketone oxime and 4-heptanone oxime [164]. The efficiency of this extraction turned out to be pH dependent. Moreover, in very acidic solutions, Pt^{IV} species are reduced to give Pt^{II} species. The nature of the reducing agent was not elucidated, but the authors suggested the occurence of hydrolysis of the oximes followed by reduction of Pt^{IV} by NH_2OH formed in situ.

8. Conclusions

The information discussed in this article shows that the chemistry of oxime ligands and oxime containing metal complexes is impressively rich. Despite this fact, only very few systematic investigations related to the metal-ion assisted reactivity of oximes have been reported. Among others, some areas, which from the viewpoint of the authors, need further research are listed here.

(i) An improved understanding of the relationship between the coordination modes and reactivity of oxime ligands and/or oxime complexes is crucial for a broadening of thought on oxime chemistry. In this respect, theoretical and computational methods should be developed to predict the structural requirements for one or another reactions to take place.

(ii) It is well documented that N-bonded oximes are subject to deprotonation at fairly low pH values. Nevertheless, all these studies were carried out without special investigations of possible structural changes, e.g. N → O isomerization. Works in this direction would give a useful information.

(iii) Two reported examples of metal-ion assisted addition of oximes to nitriles and vice versa provide a route for the preparation of a new type of unusual chelates. However, the mechanisms of these processes are not yet clear. Thus, there are not enough data to judge whether reactions proceed via addition of an oxime to a coordinated nitrile or via addition of a free nitrile to a coordinated oxime ligand. Undoubtedly, this information would be important not only for the correct choice of starting materials and reaction conditions, but also for predicting the occurrence of other metal-ion assisted addition reactions of oximes.

(iv) Data discussed in this review show that metal-promoted dehydration of oxime species leads to nitriles. In turn, hydration of coordinated nitriles does not regenerate the corresponding oximes but gives rise to carboxamides. Thus, studies on succesive dehydration of coordinated oximes and hydration of the corresponding nitrile ligands may open up a broader pathway for conversion of oximes into amides.

(v) More attention needs to be focussed on oxidations of coordinated oxime ligands. A few reports have shown that these reactions give rise to unusual and little explored nitrosoalkyl complexes. There is still some groundwork to be done in this field, as demonstrated by some synthetic, structural and physicochemical reports.

(vi) The current level of understanding of the deoxygenation reactions by metal carbonyls is far from complete. Oximes as oxygen donors are different from many other oxygen donors commonly employed for nucleophilic oxygenation of metal carbonyls, for example from trimethylamine N-oxide, due to the availability of a proton at the O atom. This may lead to different mechanisms for the deoxygenation. Future research could well be aimed at improving our understanding of the mechanistic pathways involved in the above discussed processes. Kinetic studies would not only provide valuable fundamental information, but also give further impetus for the development of new synthetic methods for the preparation of a variety of complexes starting from metal oxime compounds.

(vii) Electrochemical studies of oxime complexes have not yet been developed in spite of the recognized interest [165] of electrochemical methods for the understanding of the electron donor/acceptor ability of ligands and their activation by electron-transfer to further reactivity.

Certainly, there is still a good deal of progress to be done, and it is hoped that this review will stimulate interest towards metal-assisted reactions of oximes.

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