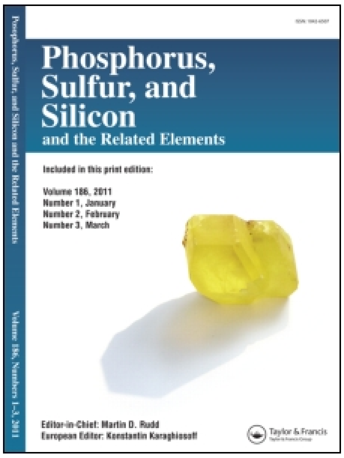

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Rings with and Without Carbon Atoms

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RINGS WITH AND WITHOUT CARBON ATOMS

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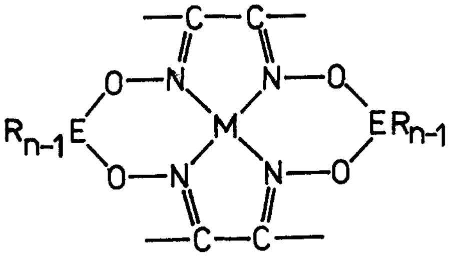
Abstract Rings with and without carbon atoms were obtained by substitution of hydrogen bridges from dioximates with organometallic bridges. The reaction of the same dioximates with organochlorosilanes takes place by the ligand substitution and the formation of silicon derivatives of the free oxime.

INTRODUCTION

It is known that some dioximes form internal chelates with transition metal ions.[1,2] The Ni(II) and Pd(II) bisdimethylglyoximates exhibit very strong intramolecular hydrogen bonds. Because the strength of these bonds, the features of the oxime hydroxyl group are screened and the identification reactions of the active hydrogen do not take place.[3,4]

RESULTS AND DISCUSSION

According to our studies, the reaction of Ni(II) and Pd(II) bisdioximates with some organometallic derivatives takes place by the substitution of hydrogen bridges with organometallic ones:[5-10]

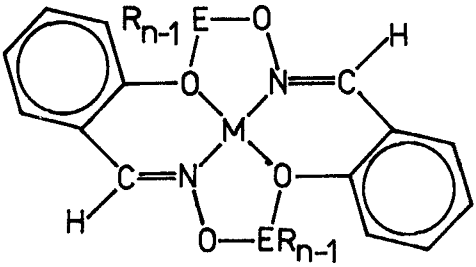


where: E = Al, B, Zn; n - E metal valence,

R = CH_3, C_2H_5, C_6H_5, i-C_4H_9, Cl.

The introduction of the organometallic bridges into the molecule of bisdioximate determines the closure of two hexaatomic rings without carbon atoms, adjacent to other two pentaatomic rings with carbon atoms.

Also, the reaction between Ni(II) and Pd(II) bis-salicylaldoximates and the same organometallic derivatives occurs by the substitution of the hydrogen bridges through organometallic ones. Thus, the closure of some pentaatomic rings without carbon atoms occurs here:



The sudies on the reaction of some organochlorosilanes with Ni(II) and Pd(II) bisdimethyl- and bisdiphenylglyoximates show that this reaction is going according to another way than that described previously.

The reaction between bisdioximates and organochlorosilanes affects the central metal ion and determines the substitution of the ligand from chelate with chlorine atoms:

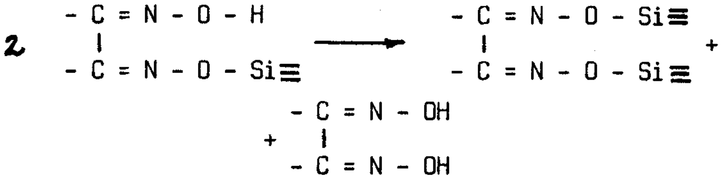
$$M(II)(DOxH)_2 + R_nSiCl_{4-n} \longrightarrow M(II)(DOxH)Cl + \begin{array}{ll} & -C=N-O-Si\equiv \\ + & \;\;| \\ & -C=N-O-H \end{array}$$

where: n = 1,2,3; R = CH_3, C_6H_5; and

DOxH is the coordinated dioxime radical.

A solid compound with unitary composition and which do not contain silicon results from this reaction. Also, we obtain a liquid colourless fraction, which is a mixture containing silicon derivatives of the oxime, of the free oxime and polymer compounds.

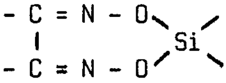
The disubstituted silicon derivatives of the oxime result probably from the following reaction:



$$2\ \begin{array}{l}-C=N-O-H\\ \ \ |\\ -C=N-O-Si\equiv\end{array} \longrightarrow \begin{array}{l}-C=N-O-Si\equiv\\ \ \ |\\ -C=N-O-Si\equiv\end{array} + \begin{array}{l}-C=N-OH\\ \ \ |\\ -C=N-OH\end{array}$$

what can explain the formation of free oxime, appearing in all the cases.

Taking into account the di- and trifunctional organochlorosilanes, the reaction can take place with the formation of some cyclic compounds:

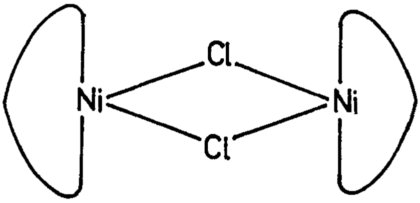


as well as of polymer compounds, containing Si-O-Si bonds.

These statements were postulated based on elemental analyses and spectral data. The ^{1}H-NMR spectra evidenced the formation of the above-mentioned cyclic compounds by the signals at 0.4 and 2.05 ppm assigned to H_3C-Si- and H_3C-C= protons, for the disubstituted organochlorosilane derivative.

The reaction of Ni(II) bisdioximates with silicon derivatives leads to a strong modification of the metal state and the molecule geometry. The magnetic measurements show that the Ni(II) compound is paramagnetic (μ = 2.8 BM), indicating that an octahedral or tetrahedral configuration was formed in lieu of a planar structure.

In all the cases, a solid compound is obtained by the substitution of the ligand with a chlorine atom, having the following probable structure:



CONCLUSIONS

The substitution of hydrogen bonds from coordinated oximes through organometallic bridges determines the closure of some rings without carbon atoms.

The reaction of some organochlorosilanes with Ni(II) and Pd(II) dioximates takes place in a different way of the known reaction for another organometallic derivatives.

The first reaction step involves probably the formation of a monosubstituted silicon compound, which by a disproportionation reaction leads to the formation of the disubstituted derivative and the free oxime.

In all the cases, for these reactions, we would not evidenced silicon derivatives of the coordinated oximes.

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