ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 9, pp. 607–617. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © N.A. Ovchinnikova, A.E. Sinyakov, 2015, published in Koordinatsionnaya Khimiya, 2015, Vol. 41, No. 9, pp. 566–576.

Regioselectivity of the Insertion of RNSO(S) and RCN into the M–L Bonds of the Tungsten Chlorocomplexes

N. A. Ovchinnikova* and A. E. Sinyakov
Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
Leninskii pr. 31, Moscow, 119991 Russia
**e-mail: talan@igic.ras.ru*

Received December 15, 2014

Abstract—The results of studying the reaction behavior of tungsten hexachloride toward organic iso(thio)cyanates and their combinations with nitriles are generalized. The factors determining the multiplet insertion of iso(thio)cyanates at the W–Cl bond and the conditions of symmetrical or asymmetrical cross-linking of the inserted fragments into heterocycles upon their trimerization (on the basis of the X-ray structural data on the products of the partial or complete hydrolysis of the complexes) are discussed. The reasons determining the direction of the combined insertion of heterocumulenes and nitriles at the W–Cl or W–N bond are considered, which is important for the targeted design of complexes of various architecture and new poorly accessible related heterocyclic compounds.

DOI: 10.1134/S1070328415090031

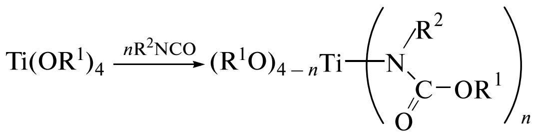
Many transformations involving transition metal complexes are based on the insertion of unsaturated compounds into the metal–ligand bond [1]. In addition to the traditional sphere (investigation of insertion reactions of unsaturated compounds into metal–carbon and metal–hydrogen bonds) [2], increasing attention is given to the possibility of their addition to the metal–heteroatom bonds [3, 4]. However, examples for insertion reactions into metal–oxygen and metal–nitrogen bonds are rare, and those for metal–halogen bonds are single.

The results of our studies of the possibility of insertion of a series of unsaturated compounds into the M–Hal bonds, in particular, the addition of combinations of acetonitrile with organic isocyanates or sulfur dioxide to higher niobium, tantalum, and molybdenum chlorides, are the first examples of reactions of this type for compounds of transition metals of Groups V–VII of the periodic table.

We found that heterocatenation chain closure can be accomplished for products of the multiple insertion of iso(thio)cyanates with the formation of the cyclic ligand or heterocyclic compound, depending on the conditions. The latter can find use in the fabrication of dyes, herbicides, thermostable polymers, and biologically active drugs used for the treatment of malignant tumors [5, 6].

The cases of insertion into the M–L bond, when addition occurs due to the opening of one of the double bonds, are known for heterocumulenes of the general formula X=C=Y (X, Y = O, NR, or S). If the coordination possibilities of the central atom are favorable, the second heteroatom can also coordinate to the metal to form a four-membered metallocycle.

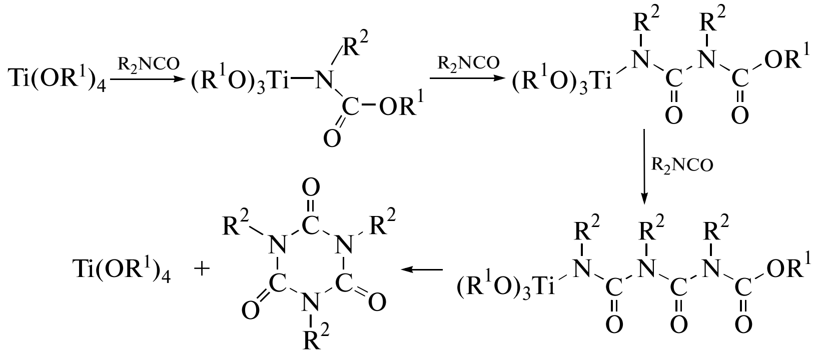
It is known that the insertion of organic isocyanates at M–O(R) bonds of alkoxides of transition metals of Groups V and IV affords stable insertion products. The reactions of titanium alkoxide $Ti(OR)_4$ with isocyanates are accompanied by the insertion of one to four molecules (depending on the component ratio) to form the corresponding carbamate derivatives **(I)** [7]:



(I)

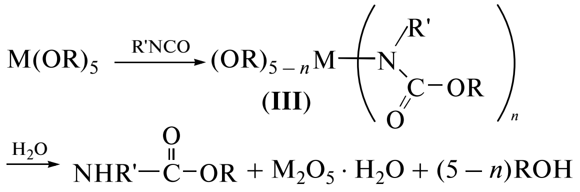
$R^1 = Pr^i, Bu^t, Ph; R^2 = Ph, Bu, PhCH_2, Et,$
α-naphthyl, cyclohexyl; $n = 1–4$

It is remarkable that the cyclic trimer of isocyanate, isocyanurate **(II)** (IR: 1690 cm^{-1}), is formed upon the prolonged storage of the reaction mixture in the presence of an isocyanate excess. This occurs, most likely, due to the trimerization (in the course of hydrolysis) of the primarily formed product of the cooperative addition of three isocyanate molecules into the same Ti–O bond.



(II)

Both reactions of isocyanates with niobium [8] and tantalum [9] pentaalkoxides and the subsequent cyclization of the inserted fragments proceed similarly. The hydrolysis of the insertion products **(III)** with water is accompanied by their decomposition to the corresponding urethane and hydrated metal oxide:

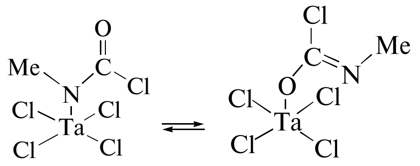


(III)

$$M(OR)_5 \xrightarrow{R'NCO} (OR)_{5-n}M\left(N(R')C(=O)OR\right)_n \xrightarrow{H_2O} NHR'-\overset{O}{\overset{\|}{C}}-OR + M_2O_5 \cdot H_2O + (5-n)ROH$$

M = Nb, Ta

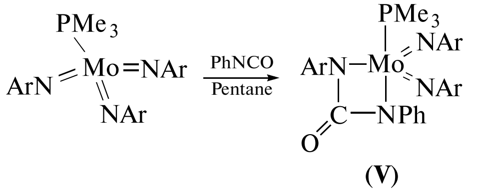
The insertion of MeNCO into $TaCl_5$ into the metal–chlorine bond in benzene (the latter being both the medium and reactant in this case) carried out by us can serve as the first example of organic isocyanate insertion into the transition metal–chlorine bond. According to the data of IR spectroscopy, the formed monomolecular insertion product $[TaCl_4\{(MeNCO)Cl\} \cdot C_6H_6]$ **(IV)** exists as two equilibrated bond isomers [10]:



(IVa) **(IVb)**

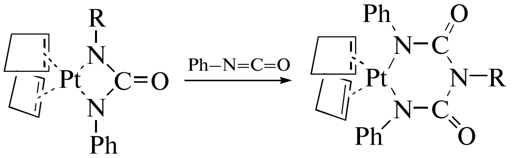
The IR spectrum of N-bonded isomer **IVa** contains a band at 1740 cm^{-1} characteristic of ν(C=O) of the chloroanhydride group, whereas the band at 1670 cm^{-1} typical of ν(C=N) of inserted isocyanate corresponds to O-bonded isomer **IVb**. According to the ^1H NMR data for adduct **IV**, these tautomeric forms of the insertion product also coexist in solution.

Organic isocyanates can also add to the M=NR imido bond. The reaction of $[Mo(NAr)_3(PMe_3)]$ with an excess of PhNCO in pentane [11] gave the monomolecular addition product **(V)** (its IR spectrum exhibits absorption bands characteristic of ν(C=O)) formed due to the opening of one of the components of the Mo=N(Ar) in the ligand:



(V)

The capability of heterocumulenes of inserting at the M–N ordinary bond of the complexes containing ureate ligands is also known. The reaction of [Pt{*N*,*N*'–N(Ph)–C(O)–N(R)}(Cod)] with an excess of PhNCO gives the biureate derivative **(VI)** [12]:



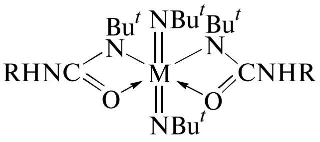
(VI)

R = Me, Ph

Several factors affecting the ability of the ligands to insertion were revealed. First, the nucleophilicity of the amido ligand increases with an increase in the number of *d* electrons of the central atom because of the competition of the lone pair of the nitrogen atom with *d* electrons of the metal. Second, the presence of aromatic substituents in the amido ligand results in a decrease in the reactivity because of a decrease in the nucleophilicity. Third, insertion occurs more rapidly for aromatic isocyanates, since the stronger electron-acceptor properties of the R'' group enhance the electrophilicity of the isocyanate carbon atom. For example, the diphenylamide complex $[Re(NPh_2)(CO)_3(Bipy)]$ does not react with RNCO (R = Et, *tert*-Bu, Ph) even on prolonged reflux [13], whereas its methylphenylamide analog

[Re{N(Me)Ph}$(CO)_3$(Bipy)] readily adds *p*-Tol-NCO.

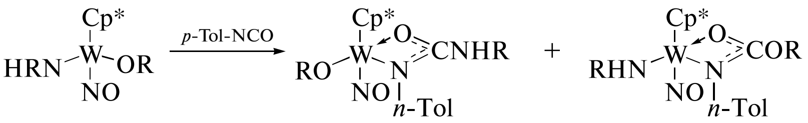
The reactions of the amidoimido complexes of transition metals of Group VIB of the general formula $[M(N\text{-}tert\text{-}Bu)_2(NHR)_2]$ (M = Mo, R = *tert*-Bu; M = Cr, R = $C_6H_3Cl_2$-2,6) with an excess of *tert*-butyl isocyanate are accompanied by the selective insertion of heterocumulene into the M–N ordinary bonds to form two chelate N,O-ureate ligands **(VII)** [14]:



(VII)

An assumption about the N,O-coordination of the ligands formed upon insertion (the IR spectra of complex **VII** contain the band in a range of 1550–1540 cm^{-1} characteristic of the coordinated carbonyl group) was also confirmed by the X-ray diffraction data for the molybdenum derivative.

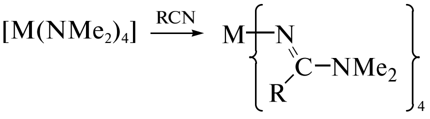
When the complexes contain M–O and M–N bonds, heterocumulenes are inserted more readily at the bond containing a more nucleophilic heteroatom. According to the ^1H NMR data, the reaction of [Cp*W(NRH)(OR)(NO)] (R = *tert*-Bu) with *p*-Tol-NCO affords two insertion products: at the W–N bond **(VIII)** and at the W–O bond **(IX)** in a ratio of 8 : 1 [15]:



(VIII) **(IX)**

The presence of an intense band in a range of 1556–1538 cm^{-1} in the IR spectra of insertion products **VIII** and **IX** indicates the chelate structure of these compounds.

For the interaction of benzo- and 4-methylbenzonitrile with metal amides of Group IVB, nitrile is inserted at all four M–N bonds, which is indicated by the ν(C=N) band (1558–1590 cm^{-1}) in the IR spectra of the insertion products **(X)** and their mass spectrometric parameters [16]:



(X)

M = Ti, Zr, Hf; R = C_6H_5, 4-Me–C_6H_4

It is remarkable that nitrile reacts with titanium amide only at 100°C, which contradicts the reaction behavior of zirconium and hafnium amides, whose insertion proceeds exothermally already at room temperature.

Unlike metal amides of Group IVB, the multiplicity of nitrile insertion into Nb and Ta pentaamides (see compounds **XI**) [17] is determined by the component ratio and occurs only on reflux of the reaction mixture:

$$[M(NMe_2)_5]$$

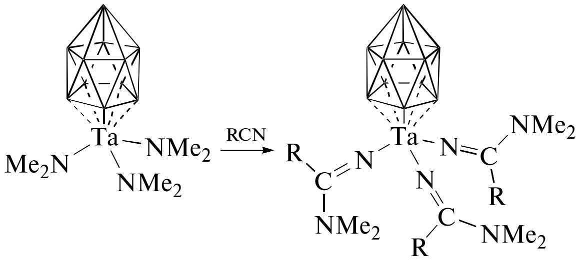
$$\xrightarrow{MeCN} [M\{N{=}C(Me){-}NMe_2\}_x(NMe)_{5-x}]$$

(XI)

M = Nb, Ta; x = 1–5

The IR spectra of compound **XI** contain an absorption band in a range of 1577–1587 cm^{-1} characteristic of stretching vibrations of the $N\overset{\cdots}{-}C\overset{\cdots}{-}N$ group of the amidinate ligand with the delocalized double bond.

This assumption was confirmed by the X-ray diffraction results for the acetonitrile and *p*-fluorobenzonitrile derivatives of the tantalum amidocarborane complex **(XII)** [18].

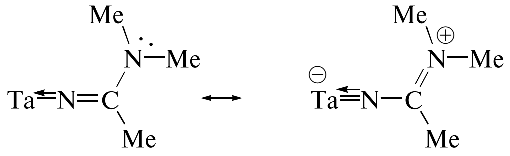


(XII)

R = Me, *p*-F-C_6H_4

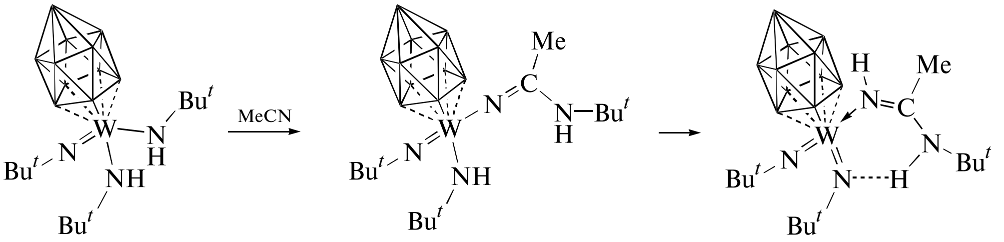
The average value of Ta–N bond lengths in these compounds is ~1.90 Å, which intermediate between the lengths of typical amide (Ta-NR_2, d_{av} = 1.99 Å) and imide (Ta–NR, d_{av} = 1.79 Å) bonds.

The results obtained in the work combined with the planarity of the amidinate ligand framework and the enhanced multiplicity of the C–NMe_2 bond make it possible to consider the structure of this ligand as an equilibrium structure between two ultimate resonance forms (amide and imide) with bond delocalization inside the Ta–N–C–N group



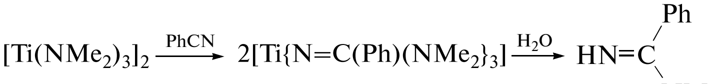
Shorter Ta–N bonds (~1.86 Å) are typical of the substitution products of one of the amidinate ligands by the chloride anion in the *p*-fluorobenzonitrile derivative: [*closo*-3,2,1-Ta{N=C(*p*-F–C_6H_4)NMe_2}$_2$Cl($C_2B_9H_{11}$). This can be explained by the weakening of the competition between the amidinate ligands in the internal sphere of the complex as their number decreases.

The coordinated amidinate ligands have strong basic properties, which affects the structures of the final insertion products. The dissolution of complex [W(N-*tert*-Bu)(NH-*tert*-Bu)$_2$($C_2B_9H_{11}$)] in acetonitrile is accompanied by the insertion of an acetonitrile molecule into one of the amide bonds W–N, and the proton migrates from the second amide group to the nitrogen atom of the amidinate ligand to form complex **XIII** containing two imide bonds along with neutral coordinated amidine [19]:



(XIII)

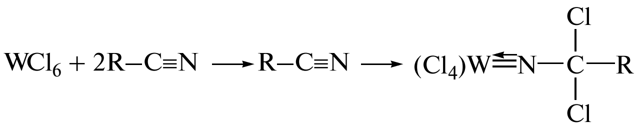
Since the IR spectrum shows product **XIV** synthesized by the insertion of benzonitrile into binuclear titanium amide and an intense absorption band corresponding to ν(C=N) at 1570 cm^{-1} and free amidine is formed by the hydrolysis of this product, one can conclude that the addition of nitrile into the M–N bonds of the amide groups is similar in this case:



$$[Ti(NMe_2)_3]_2 \xrightarrow{PhCN} 2[Ti\{N{=}C(Ph)(NMe_2\}_3] \xrightarrow{H_2O} HN{=}C(Ph)(NMe_2)$$

(XIV)

The coordination of nitriles by higher transition metal (mainly of Group VIB) chlorides can be accompanied by the migration of two halogen atoms to the carbon atom of the nitrile group to form the imido derivatives; i.e., insertion into the M–X bond occurs. For example, the reactions of WCl_6 with a series of aliphatic and aromatic nitriles are accompanied by the addition of two ligand molecules to form the dichloroimidonitrile derivatives **(XV)** [20, 21]:



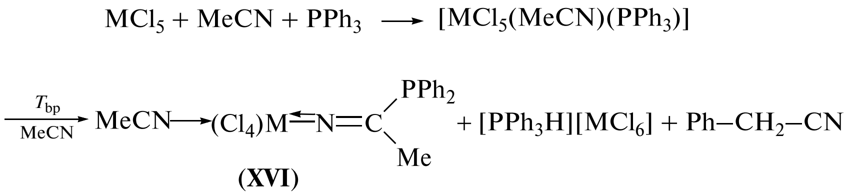
$$WCl_6 + 2R{-}C{\equiv}N \longrightarrow R{-}C{\equiv}N \longrightarrow (Cl_4)W{\equiv}N{-}CCl_2{-}R$$

(XV)

R = Me, CH_2Cl, $CHCl_2$, CCl_3,CH_2CCl_2, CH_2=CH, CMe_3, Ph, C_6H_4Cl-4, C_6H_4Me-2, C_6H_4Me-4

The IR spectra of all insertion products **XV** contain two intense bands: the band in a range of 2310–2255 cm^{-1} characteristic of the ν(C≡N) vibrations of the coordinated nitrile molecule and the band in a range of 1310–1262 cm^{-1} corresponding to the ν(W≡N) vibrations of the imido ligand.

It is found that tertiary amines and phosphines affect the capability of organic nitriles of inserting into higher chlorides of transition metals of Groups V and VI. For example, in the absence of other donor molecules, acetonitrile reacts with niobium and tantalum pentachlorides to give only adducts [MCl_5(NCMe)] [22, 23]. The introduction of triphenylphosphine into the reaction mixture first results in the formation of the heptacoordinated chloronitrilephosphine complex [MCl_5(NCMe)(PPh_3)] and then, on reflux, in the addition of acetonitrile to one of the P–Ph bonds with the formation of insertion products **XVI** [24]:



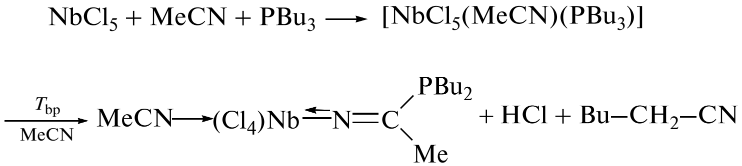
$$\mathrm{MCl_5 + MeCN + PPh_3 \longrightarrow [MCl_5(MeCN)(PPh_3)]}$$

$$\xrightarrow[\mathrm{MeCN}]{T_{\mathrm{bp}}} \mathrm{MeCN{\longrightarrow}(Cl_4)M{\Leftarrow}N{=}C(PPh_2)(Me) + [PPh_3H][MCl_6] + Ph{-}CH_2{-}CN}$$

(XVI)

M = Nb, Ta

The IR spectra of insertion products **XVI** exhibit the ν(C=N) band (~1650 $\mathrm{cm^{-1}}$) characteristic of the phosphinomethyleneamide complexes containing the M=N bond. In addition, by-products of this reaction are the hexachlorotriphenylphosphonium derivative and benzylnitrile. In the case of using tributylphosphine, a similar insertion product (**XVII**) is formed, but hydrogen chloride is evolved as one of the by-products instead of a hexachloro complex:

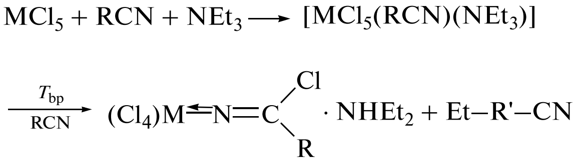


$$\mathrm{NbCl_5 + MeCN + PBu_3 \longrightarrow [NbCl_5(MeCN)(PBu_3)]}$$

$$\xrightarrow[\mathrm{MeCN}]{T_{\mathrm{bp}}} \mathrm{MeCN{\longrightarrow}(Cl_4)Nb{\Leftarrow}N{=}C(PBu_2)(Me) + HCl + Bu{-}CH_2{-}CN}$$

(XVII)

Niobium and tantalum pentachlorides react with nitriles in the presence of triethylamine in a different manner [25]. If heptacoordinated complex $\mathrm{[MCl_5(MeCN)(NEt_3)]}$ is obtained at the first stage of these reactions, as for the participation of phosphines, its heating results in the insertion of nitrile into the metal–chlorine bond to form products **XVIII**:



$$\mathrm{MCl_5 + RCN + NEt_3 \longrightarrow [MCl_5(RCN)(NEt_3)]}$$

$$\xrightarrow[\mathrm{RCN}]{T_{\mathrm{bp}}} \mathrm{(Cl_4)M{\Leftarrow}N{=}C(Cl)(R) \cdot NHEt_2 + Et{-}R'{-}CN}$$

(XVIII)

M = Ta, R = Me, Et, Ph; M = Nb, R = Me;
R' = deprotonated radical R

The IR spectra of insertion products **XVIII** exhibit absorption bands ν(C=N) in a range of 1618–1640 $\mathrm{cm^{-1}}$ and ν(N–H) (3130–3082 $\mathrm{cm^{-1}}$) characteristic of coordinated diethylamine along with the absorption bands (1570–1544 $\mathrm{cm^{-1}}$) corresponding to δ(N–H).

The formation of similar insertion products in the reactions of acetonitrile with tungsten hexachloride in the presence of diethyl- (**XIX**) and triethylamine (**XX**) is accompanied by the reduction of tungsten(VI) to tungsten(V) with the evolution of gaseous chlorine [26]:

$$\mathrm{WCl_6 \xrightarrow{MeCN + NHEt_2} [WCl_4\{N{=}C(Me)Cl\}(NHEt_2)] + 1/2Cl_2}$$

(XIX)

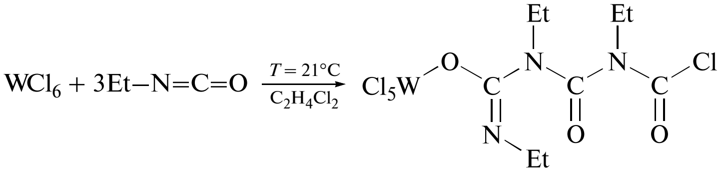
$$\mathrm{WCl_6 \xrightarrow{MeCN + NEt_3} [WCl_4\{N{=}C(Me)Cl\}(MeCN)(NHEt_2)] + 1/2Cl_2}$$

(XX)

In the IR spectra of these reaction products, the band at ~1660 cm^{-1} corresponds to the ν(C=N) vibrations of the inserted nitrile fragments.

Organic isonitriles are also capable of inserting at the metal–chlorine bond, which was demonstrated by the reactions of $TiCl_4$, $HfCl_4$, VCl_3, $NbCl_5$, and $TaCl_5$ with *tert*-butylisonitrile [27]. An attempt to obtain similar insertion products for molybdenum and tungsten chlorides was unsuccessful.

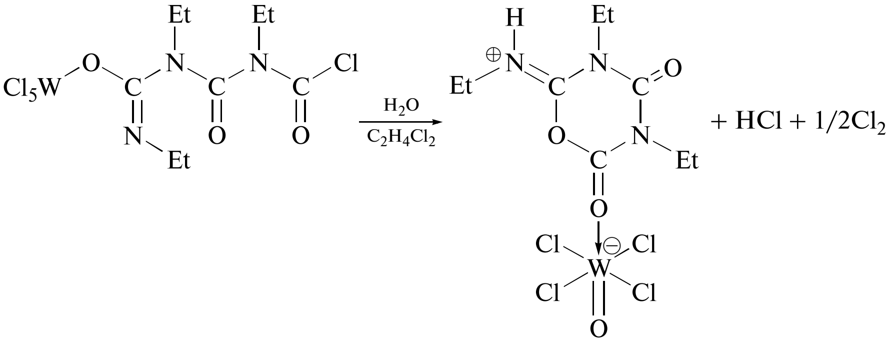
We found [28] that the reaction of WCl_6 with EtNCO in dichloroethane at room temperature, regardless of the component ratio, resulted in the addition of three isocyanate ligands into one W–Cl bond to form complex **XXI**:



(XXI)

This is indicated by the presence of three intense absorption bands in the IR spectrum of insertion product **XXI**. Two of the bands correspond to stretching vibrations of the uncoordinated carbonyl group (1776 and 1722 cm^{-1}), and the third band (1570 cm^{-1}) corresponds to ν(C=N) with a decreased multiplicity.

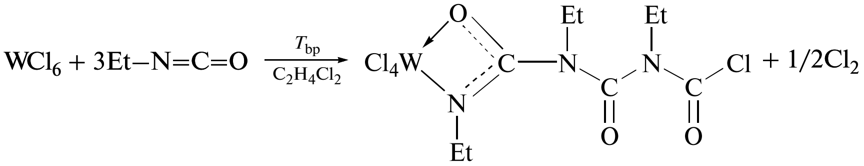
The partial hydrolysis of compound **XXI** results in the reduction of tungsten to W(V) and in the formation of the oxochloro complex [$WOCl_4LH$] (**XXII**) (Fig. 1) containing the asymmetrical cyclic trimer of ethyl isocyanate (L) as a cation in which the isocyanate fragments are bound due to the opening of one of the components of two C=N bonds and one C=O bond [28]:



(XXII)

The presence of the band in a range of 1850–1798 cm^{-1} in the IR spectrum of compound **XXI** corresponding to the ν(C–O) vibrations of the ester group is characteristic of nonsymmetrical cyclotrimers of isocyanates.

It turned out [29] that the reaction carried out at the boiling point of the reaction mixture also resulted in the addition of three ethyl isocyanate molecules to the same tungsten–chlorine bond, regardless of the component ratio. The distinction from the previous reaction is that the reaction is accompanied, in this case, by the reduction of tungsten W(VI) to W(V) and gaseous chlorine evolution and results in the formation of insertion product **XXIV** via the Scheme:



(XXIII)

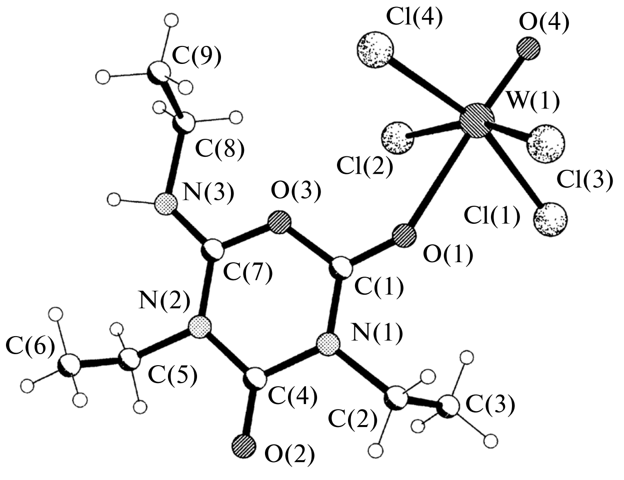


Fig. 1. Structure of complex $[WOCl_4\{(EtNCO)_3H\}]$ (**XXII**).

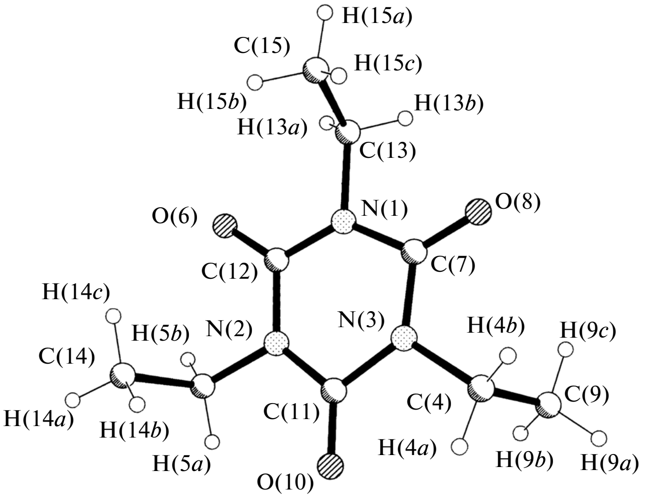
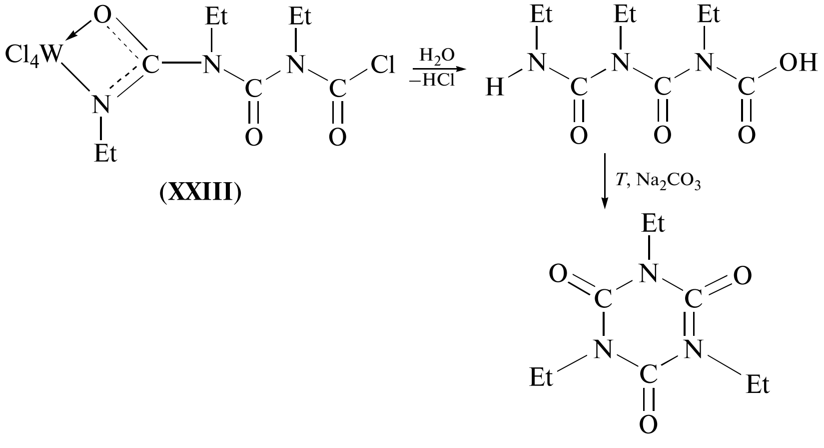


Fig. 2. Structure of triethyl isocyanurate (**XXIV**).

The results of studying complex **XXIII** by MALDI mass spectrometry also indicate that the isocyanate molecules in the insertion product are bound to each other and are inserted into the same W–Cl bond [30]. This assertion is consistent with the data of IR spectroscopy, namely, with the presence of three absorption bands in a range of 1800–1550 cm^{-1} in the spectrum of complex **XXIII**, and these bands correspond to the stretching vibrations of the double bonds of the inserted isocyanate fragments. The single ν(C–Cl) band at 834 cm^{-1} is also observed and confirms the above assertion.

The alkaline hydrolysis of complex **XXIII** affords triethyl isocyanurate (**XXIV**). Unlike the heterocyclic ligand in the hydrolysis product of complex **XXI** (synthesized without heating), in **XXIV** all isocyanate fragments are linked through the C–N bonds (Fig. 2).

According to the data of IR spectroscopy, ^1H and ^{13}C NMR spectroscopy, and X-ray diffraction analysis [29], the following scheme of **XXIV** decomposition can be proposed:



(**XXIII**)

(**XXIV**)

The formation of cyclic ethyl isocyanate trimers of different structures by the hydrolysis of insertion products **XXI** and **XXIII** (acting as a ligand and a free molecule, respectively) can serve as a convincing proof for our assumption that the variation of the temperature parameters for the multiple insertion of ethyl isocyanate into tungsten hexachloride leads to various bonding modes of individual isocyanate fragments in the chain. The synthesis with heating is accompanied by the bond rearrangement and, as a consequence, the formation of a more ordered structure of the heterocatenation chain in the insertion product.

The insertion of ethyl isothiocyanate into tungsten hexachloride at room temperature proceeds in a different way [31].

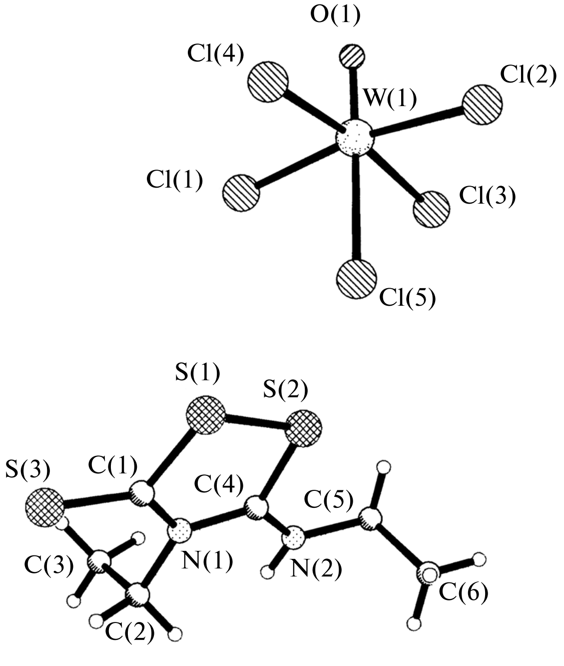
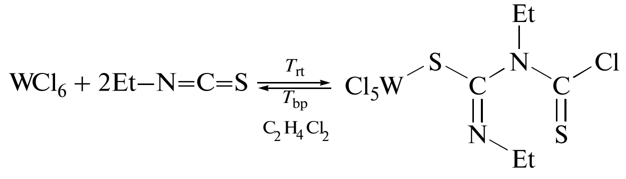


Fig. 3. Structure of complex $[WOCl_5][C_6H_{11}N_2S_3]$ (**XXVI**).

All the data of IR spectroscopy for compound XXV, namely, the presence of absorption bands corresponding to the stretching vibrations of the C=N and C=S bonds (1596 and 1531 cm^{-1}, respectively) and the single ν(C–Cl) band (850 cm^{-1}), and the elemental analysis results indicate the consecutive insertion of two isothiocyanate molecules to give the chain ligand:

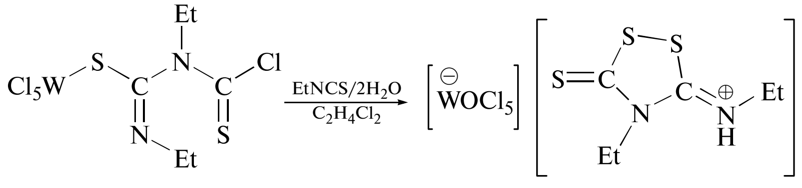


(**XXV**)

It should be mentioned that the band at 1596 cm^{-1} is characteristic of ν(C=N) of the imino group formed by the insertion of organic isothiocyanate into the metal–ligand bond due to the opening of one of the bonds of the C=S group, whereas the band at 1531 cm^{-1} is typical of stretching vibrations of the thioamide group N–C(S)–Cl bound to the chlorine atom. It is most likely that the chain ligand in insertion product **XXV** contains two differently bound isothiocyanate fragments.

We believe that this structure of the ligand is formed by the insertion of the first isothiocyanate molecule at the W–Cl bond due to the opening of one of the components of the C=S bond of the thiocarbonyl group. The second isothiocyanate molecule is inserted into the already formed C–Cl bond, due to which one of the components of the CN bond of the imino group is cleaved.

At the same time, the X-ray diffraction results for the hydrolysis product of complex **XXV** show that complex **XXV** undergoes a deeper hydrolysis than its isocyanate analog. In this case, complex $[WOCl_5][C_6H_{11}N_2S_3]$ (**XXVI**) (Fig. 3) is formed in which the $[C_6H_{11}N_2S_3]^+$ cation represents a heterocycle: the dithiazolidine derivative formed due to the condensation of two ethyl isothiocyanate molecules according to the "head-to-head" type and the sulfur ion. The latter is present in an aqueous solution due to the formation of hydrogen sulfide by the hydrolysis of an ethyl isothiocyanate excess in the reaction mixture.



(**XXV**) (**XXVI**)

The structure of compound **XXVI** reveals the fact that the asymmetrical condensation of heterocumulenes takes place for the synthesis of the insertion products at the W–Cl bond of isothiocyanates under mild conditions, as in the case of the addition of isocyanates. This means that a combinatory synthesis of novel complicated ligands formed by their combined condensation proceeding in different manners is possible on the basis of the insertion of several unsaturated compounds at the metal–heteroatom bond. The compositions and structures of the formed insertion products are determined by both the nature of the initial reactants and temperature parameters.

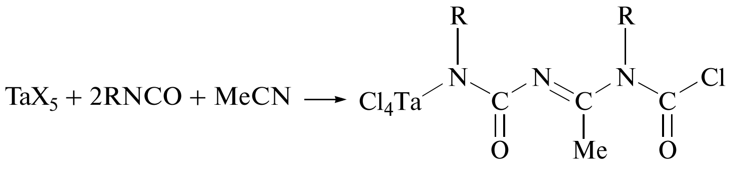
The cyclization of the chain of inserted fragments upon their removal from the coordination sphere of the complex is of special interest. This provides new possibilities for the target synthesis of novel and poorly accessible heterocyclic ligands and compounds in one stage, selectively, and under mild reaction conditions.

Therefore, one of the most promising tasks of coordination chemistry is the study of the mutual influence of unsaturated compounds of different classes (which do not interact with each other in the free state) on their capability of combined inserting into metal–ligand bonds.

We have earlier found that organic isocyanates are capable of inserting at the metal–halogen bond in Ta [32, 33] and Nb [34] pentahalides and can also activate the combined addition of acetonitrile with the formation of the heteromolecular chain of inserted ligands. At the same time, only coordination is observed for isothiocyanates in this case.

The insertion of two isocyanate molecules and one acetonitrile molecule at the same Ta–Hal bond of tantalum pentahalide results in the formation of a series of compounds containing chain ligands (**XXVII**) [32, 33].

The presence of absorption bands in a range of 1790–1550 cm^{-1} corresponding to the stretching vibrations of the C=O and C=N groups of the inserted isocyanate and nitrile fragments in the IR spectra of insertion products **XXVIIa** and **XXVIIb** in a combination with the intense absorbance in a range of 800–700 cm^{-1} characteristic of stretching vibrations of the C–Cl bond indicates that the insertion of all three ligands occurs at the same Ta–Cl bond.

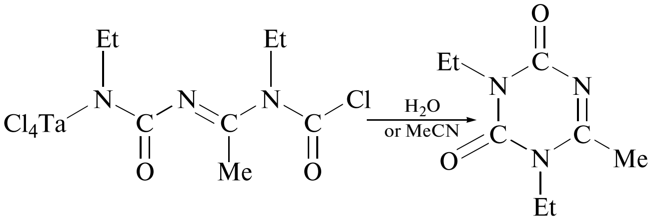


(XXVII)

X = Cl, R = Me (a), Et (b); X = F, R = Me (c)

The elemental analysis of insertion product **XXVIIa** could not unambiguously answer the question about the composition of the heteromolecular chain because of an insignificant difference in masses of its fragments. Therefore, this problem was refined by additional studies. The ^1H NMR study of the analog synthesized with the replacement of CH_3CN by CD_3CN shows the disappearance of one of three singlets, which unambiguously confirms our assumption that the composition of the chain of the inserted ligands of **XXVII** includes two methyl isocyanate fragments and one acetonitrile fragment.

Later it was proved chemically and by the multinuclear NMR study of complex **XXVIIb** [34] that its hydrolysis or transition to an acetonitrile solution led to the removal of the condensed ligands from the coordination sphere of the complex accompanied by heterocatenation chain cyclization to form the s-triazine derivative (**XXVIII**):



(XXVIIb) **(XXVIII)**

Unlike niobium and tantalum halides, both ethyl isocyanate and its thio derivative can insert into tungsten hexachloride, which allowed one to expect the addition of heterocumulenes of both types in to the W–L bond and in combination with other ligands, in particular, with nitriles.

This was accomplished for the first time as the addition of EtNCX (X = O, S) and RCN (R = Me, Ph) to tungsten hexachloride. The regioselectivity of heterocumulene insertion is interesting: into the tungsten–nitrogen or tungsten–chlorine bond, depending on the nature of the organic radical nature in nitrile.

Since the result of acetonitrile addition is adduct $WCl_4 \cdot 2MeCN$ [35], as for the derivatives of transition metals of Group V, it is natural to assume that the addition of the ligand into the W–Cl bond has no alternatives for the tungsten acetonitrile derivatives.

It is known [36] that the coordinated donor molecules activate acetonitrile to insert into the tungsten–chlorine bond of tungsten hexachloride. In particular,

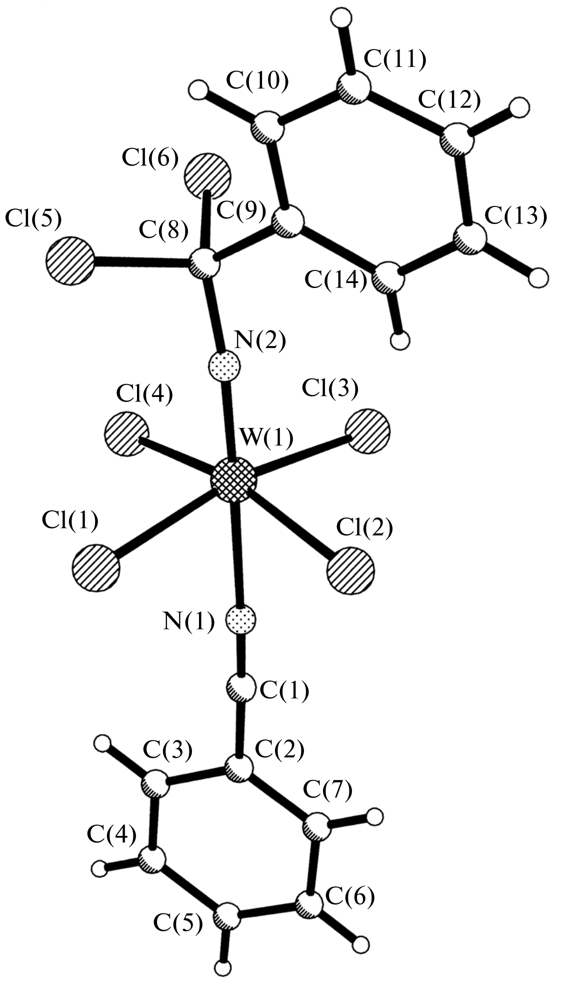
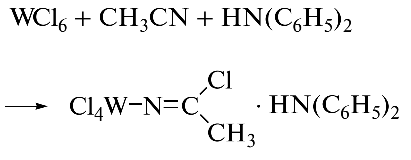


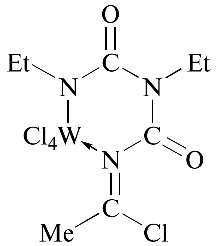
Fig. 4. Structure of $[WCl_4(NCPh)(CNCl_2Ph)]$ (**XXIX**).

in the presence of $HN(C_6H_5)_2$, the reaction proceeds via the Scheme:



$$\mathrm{WCl_6 + CH_3CN + HN(C_6H_5)_2} \longrightarrow \mathrm{Cl_4W{-}N{=}C\overset{Cl}{\underset{CH_3}{}}\cdot HN(C_6H_5)_2}$$

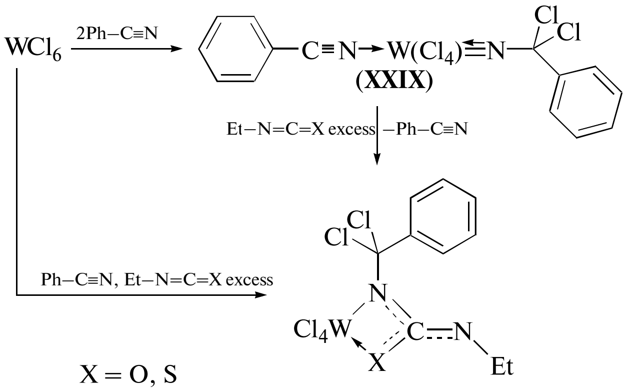
We believe that, as in similar reactions of tantalum pentahalides, the insertion of ethyl isocyanate in combination with acetonitrile into tungsten hexachloride proceeds via the primary insertion of an acetonitrile molecule, then two ethyl isocyanate molecules are consecutively inserted into the already formed W–N bonds to form the chain ligand, after which the additional coordination to the central atom occurs due to the electron pair of the nitrogen atom of the imide fragment to form the six-membered metallocycle:



The reaction of tungsten hexachloride with benzonitrile turned out to give stable nitriledichloroimido complex $[WCl_4(NCPh)(NCCl_2Ph)]$ (**XXIX**) [37] isostructural to that obtained by us using the high-temperature synthesis [38], which was confirmed by the X-ray diffraction data (Fig. 4). The coordination polyhedron of the tungsten atom in complex **XXIX** is a distorted octahedron with four chlorine atoms in the equatorial plane. The N(1) atom of coordinated benzonitrile and the N(2) atom of the $NCCl_2Ph$ ligand occupy the axial positions. The W–N(2) distance (1.732(13) Å) and the value of angle WN(2)C(8) (169.0°) indicate an additional involvement of the lone pair of the imide nitrogen atom in the bond with tungsten and, hence, this bond can be interpreted as nearly triple.

The reaction of compound **XXIX** with an ethyl iso(thio)cyanate excess results in the insertion of one heterocumulene molecule and displacement of coordinated benzonitrile from the coordination sphere of the complex (data of elemental analysis, IR spectroscopy, and mass spectrometry).

According to the mechanism proposed by us for these reactions, iso(thio)cyanate is added due to the opening of one of the (thio)carbonyl bonds to form *N*,*O*(*S*)-*iso*(thio)ureate:



This result contradicts the known cases of the insertion of isocyanates and isothiocyanates [39] into the imido complexes giving, as a rule, *N*,*N*-ureato compounds.

To conclude, the multiplet insertion of heterocumulenes into the W–Cl bond provides new possibilities for the targeted design and synthesis (depending on the temperature parameters) of both symmetrical and asymmetrical chain and heterocyclic ligands and for the synthesis of novel and poorly accessible organic compounds using these reactions.

It is remarkable that the introduction of nitrile into the reaction mixture leads to the heteromolecular insertion into the W–Cl bond only in the case if the intermediate imido derivative is unstable. In the opposite case, the addition of heterocumulene becomes preferable into one of the W=N bonds of the stable imido complex. This, in turn, makes it possible to construct complicated molecular architectures of specified composition and structure using these reactions and varying organic radicals of nitriles introduced into the reaction mixture.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 15-03-08685.

REFERENCES

1. Braunstein, P. and Nobel, D., *Chem. Rev.,* 1989, p. 1927.
2. Ballivet-Tkatchenko, D., Chermette, H., Plasserauda, L., et al., *Dalton Trans.*, 2006. p. 5167.
3. Fowles, G.W.A., Rice, D.A., and Shanton, K.J., *Dalton Trans.*, 1977, no. 7, p. 1212.
4. Drew, M.G.B., Moss, K.C., and Rolf, N., *Inorg. Nucl. Chem. Lett.*, 1971, vol. 7, no. 12, p. 1219.
5. Afonso, C., Lourenço, N., and Rosatella, A., *Molecules*, 2006, vol. 11, no. 1, p. 81.
6. Pacak, J., *Uvod do studia Organické chemie*, Praha: Nakladatelstvi technicke literatury, 1982.
7. Meth-Cohn, O., Thorpe, D., and Twitchelt, H.J., *J. Chem. Soc. C.*, 1970, p. 132.
8. Mehrotra, R.C., Rai, A.K., and Bohra, R., *J. Inorg. Nucl. Chem.*, 1974, vol. 36, no. 8, p. 1887.
9. Bohra, R., Rai, A.K., and Mehrotra, R.C., *Inorg. Chim. Acta*, 1977, vol. 25, p. L147.
10. Ovchinnikova, N.A., Ermakov, V.A., and Glushkova, M.A., *Zh. Neorg. Khim.*, 1987, vol. 33, no. 4, p. 1056.
11. Morrison, D.L. and Wigley, D.E., *Inorg. Chem.*, 1995, vol. 34, no. 10, p. 2610.
12. Dinder, M.B. and Henderson, W., *Dalton Trans.*, 1998, no. 11, p. 1763.
13. Hevia, E., Pérez, J., Riera, V., et al., *Organometallics*, 2002, vol. 21, no. 9, p. 1966.
14. Lam, H.-W., Wilkinson, G., Hussain-Bates, B., et al., *Dalton Trans.*, 1993, p. 781.
15. Legzdins, P., Rettig, S.J., and Ross, K.J., *Organometallics*, 1994, vol. 13, no. 2, p. 569.
16. Lappert, M.F. and Sanger, A.R., *J. Chem. Soc. A*, 1971, no. 9, p. 1314.
17. Bradley, D.C. and Ganovkar, M.C., *Chem. Ind.*, 1968, no. 2, p. 1521.
18. Broder, C.K., Goeta, A.E., Howard, J.A.K., et al., *Dalton Trans.*, 2000, no. 20, p. 3526.
19. Batsanov, A.S., Goeta, A.E., Howard, J.A.K., et al., *Dalton Trans.*, 2001, no. 8, p. 1210.
20. Fowles, G.W.A., Rice, D.A., and Shanton, K.J., *Dalton Trans.*, 1977, no. 7, p. 1212.
21. Drew, M.G.B., Moss, K.C., and Rolf, N., *Inorg. Nucl. Chem. Lett.*, 1971, vol. 7, no. 12, p. 1219.
22. Legzdins, P., Rettig, S.J., and Ross, K.J., *Organometallics*, 1994, vol. 13, no. 2, p. 569.
23. Buslaev, Yu.A., Glushkova, M.A., Chumaevskii, N.A., et al., *Koord. Khim.*, 1982, vol. 8, no. 4, p. 457.
24. Ershova, M.M., Glushkova, M.A., Chumaevskii, N.A., et al., *Koord. Khim.*, 1981, vol. 7, no. 4, p. 556.
25. Glushkova, M.A., Chumaevskii, N.A., Khmelevskaya, L.V., et al., *Koord. Khim.*, 1987, vol. 13, no. 13, p. 349.
26. Glushkova, M.A., Chumaevskii, N.A., Ershova, M.M., et al., *Koord. Khim.*, 1985, vol. 11, no. 2, p. 193.
27. Behnam-Dehkordy, M., Crociani, B., Nicolini, M., and Richards, R., *J. Organomet. Chem.*, 1979, vol. 181, no. 1, p. 69.
28. Ovchinnikova, N.A., Sinyakov, A.E., Sergienko, V.S., et al., *J. Coord. Chem.*, 2003, vol. 56, no. 11, p. 995.
29. Ovchinnikova, N.A., Sinyakov, A.E., Reznik, A.M., et al., *Russ. J. Coord. Chem.*, 2002, vol. 28, no. 9, p. 673.
30. Ovchinnikova, N.A., Sinyakov, A.E., and Streletskii, A.B., *Russ. J. Coord. Chem.*, 2004, vol. 30, no. 2, p. 84.
31. Ovchinnikova, N.A., Sinyakov, A.E., et al., *Crystallogr. Rep.*, 2003, vol. 48, p. 602.
32. Ovchinnikova, N.A., and Glushkova, M.A., *Zh. Neorg. Khim.*, 1991, vol. 36, p. 131.
33. Ovchinnikova, N.A., Sakharov, S.G., et al., *Koord. Khim.*, 1991, vol. 17, p. 658.
34. Ovchinnikova, N.A., Sakharov, S.G., et al., *Russ. J. Coord. Chem.*, 2000, vol. 26, no. 3, p. 181.
35. Ovchinnikova, N.A. and Sinyakov, A.E., *Russ. J. Coord. Chem.*, 2006, vol. 32, p. 761.
36. Glushkova, M.A., Chumaevskii, N.A., Ershova, M.M., et al., *Koord. Khim.*, 1985, vol. 11, no. 2, p. 193.
37. Fowles, G.W.A. and Rice, D.A., *Dalton Trans.*, 1977, no. 12, p. 1212.
38. Sinyakov, A.E., Aleksandrov, G.G., and Ovchinnikova, N.A., *Crystallogr. Rep.*, 2004, vol. 49, no. 4, p. 649.
39. Morrison, D.L. and Wigley, D.E., *Inorg. Chem.*, 1995, vol. 34, p. 2610.

Translated by E. Yablonskaya