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N.S. Zefirov on His 70th Anniversary

Synthesis, Structure, and Hydrophosphorylation of π-Complexes of Hexacarbonyltungsten(0) with Cyclohexanone, Cyclohexanethione, and *N*-Cyclohexylideneaniline

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Abstract—New carbonyl π-complexes of tungsten(0) with cyclohexanone, cyclohexanethione, and *N*-cyclohexylideneaniline were synthesized. Geometric and electronic parameters of the ligands, as well as energy parameters of the complex formation process, were determined by quantum-chemical calculations. Hydrophosphorylation with diethyl phosphonate changed the reactivity of coordinated *N*-cyclohexylideneaniline, while no analogous effect was observed for cyclohexanone and cyclohexanethione.

An actual problem of modern chemistry is selective functionalization of compounds possessing several potential reaction centers; solution of this problem makes it possible to develop procedures for target-oriented synthesis of polyfunctional organic and organometallic compounds with a specified structure. A promising method for design of new organophosphorus compounds is based on hydrophosphorylation reactions involving multiple carbon–heteroelement bonds in α,β-unsaturated oxo, thioxo, and imino derivatives. These reactions lead to formation of the corresponding unsaturated α-hydroxy, α-amino, and α-sulfanyl phosphonates which attract interest from the viewpoint of their practical applications. In addition, they are convenient intermediate products for further modifications [1]. However, the synthesis of such compounds is often complicated due to competition between carbon–carbon and carbon–heteroelement bonds in the hydrophosphorylation processes [1–4].

Chemo- and regioselectivity in reactions of polyenes and heteropolyenes may be controlled via their functionalization within the coordination sphere of organometallic compounds [5]. We previously reported that oxo, aza, and thioxo dienes coordinated to zerovalent chromium subgroup metals take up dialkyl phosphonates at the double carbon–heteroelement bond, regardless of the mode of heterodiene coordination to the metal center [4, 6–8]. On the other hand,

phosphorylation of unsaturated compounds as free ligands follows mainly the Pudovik scheme: P–H compounds add as a rule at the carbon–carbon bond. Our studies on numerous η^x-heterodiene complexes with various *x* values showed that the reasons for change in the reactivity of heteropolyenes coordinated to a transition metal include not only steric factors (shielding of a potential reaction center by the metal–ligand moiety) but primarily variation of the electronic structure of the ligand due to its coordination to metal. First of all, this is distortion of conjugation in the heterodiene system of unsaturated ketones and their analogs within the coordination sphere of transition metals, as was confirmed by the results of nonempirical quantum-chemical calculations [9].

In the present work we examined variations in the geometric and electronic structure of unsaturated systems possessing double carbon–oxygen, carbon–sulfur, and carbon–nitrogen bonds due to their coordination to metal complexes. We also studied the effect of coordination with metals on the reactions of the ligands with diethyl phosphonate. The study was performed using IR spectroscopy and empirical and nonempirical quantum-chemical calculations.

It is known that vibrations of multiple carbon–heteroelement bonds give rise to characteristic absorption bands in the IR spectra and that the position and intensity of these bands are sensitive to the coordina-
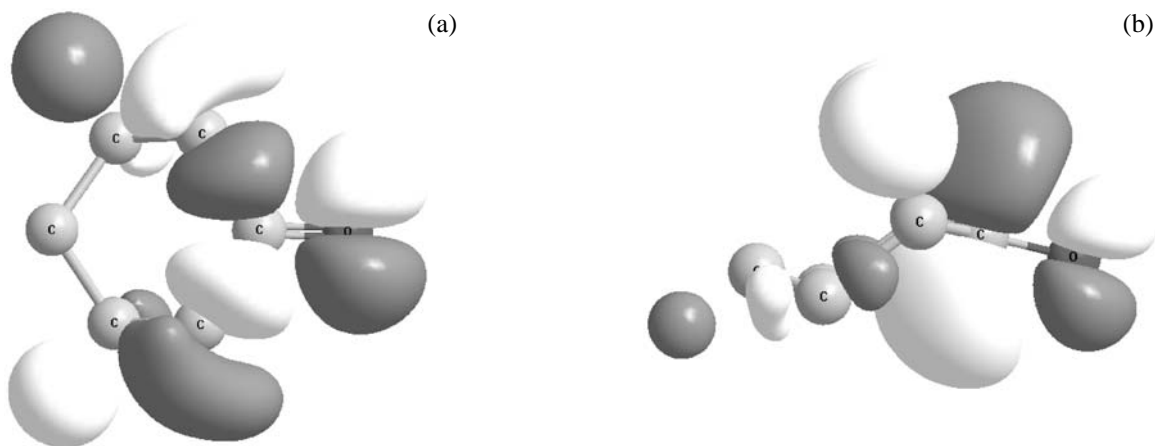
(a)

(b)

Fig. 1. (a) HOMO and (b) LUMO of cyclohexanone.
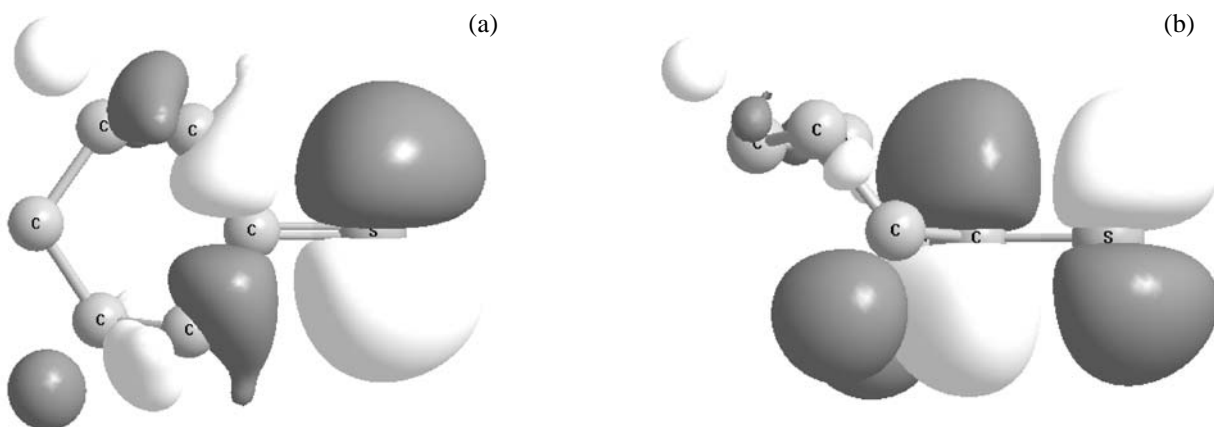
(a)

(b)

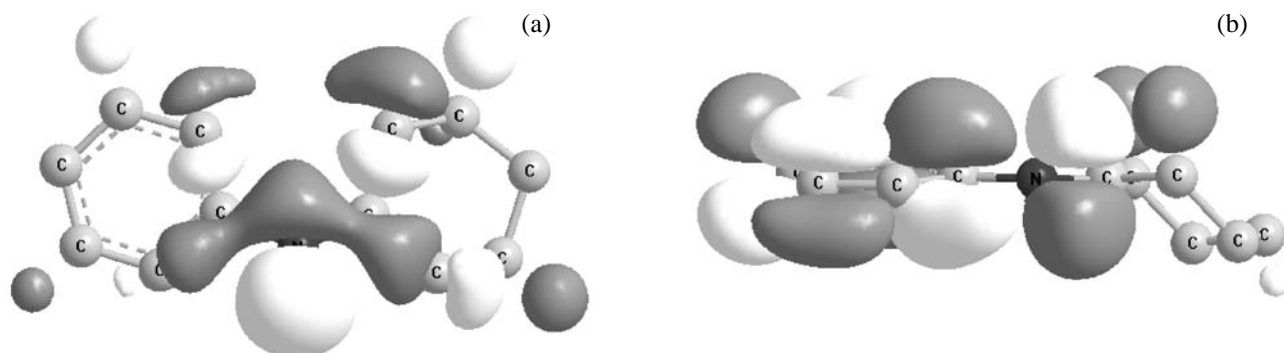**Fig. 2.** (a) HOMO and (b) LUMO of cyclohexanethione.

(a)

(b)

Fig. 3. (a) HOMO and (b) LUMO of *N*-cyclohexylideneaniline.

tion mode [10]. Functional groups like C=X can be involved in coordination in two modes: terminal (through the X heteroelement) and lateral (through the carbon–heteroelement π-bond) [11]. Each of the above coordination modes is characterized by reduction of vibration frequency of the corresponding multiple bond in the IR spectrum, but terminal coordination of

C=X bond induces a smaller change of the vibration frequency than does lateral coordination [10].

As model unsaturated compounds having a C=X bond, we selected cyclohexanone (**I**), cyclohexanethione (**II**), and *N*-cyclohexylideneaniline (**III**). The electronic and steric structures of their molecules were determined by PM3 semiempirical calculations. The

frontier orbitals in molecules **I–III** are localized mainly on the multiple carbon–heteroelement bonds, and the lowest unoccupied molecular orbitals (LUMO) are characterized by low energies: 0.8532 (**I**), 0.1121 (**II**), and −1.309 eV (**III**). However, their highest occupied molecular orbitals (HOMO) are located at a fairly deep level, the corresponding energies being equal to −10.48, −9.062, and −8.991 eV, respectively. The frontier orbital fragments localized on the C=O, C=N, and C=S groups become less symmetric in the series **I** > **III** > **II**. The electron and orbital densities in the frontier orbitals of cyclohexanone are distributed almost symmetrically over the carbonyl carbon and oxygen atoms. The orbital density of both HOMO and LUMO of cyclohexanethione is localized almost completely on the sulfur atom (Figs. 1–3).

According to [12, 13], replacement of carbonyl ligands in hexacarbonyl complexes of chromium subgroup metals is a dissociative process which begins with fast elimination of carbon(II) oxide from the metal coordination sphere [13]. The subsequent formation of coordination compound $(R–C=X–R')M(CO)_5$ involves interaction between the π-system of the C=X bond or lone electron pair (LEP) of the X heteroatom and metal-containing fragment $M(CO)_5$ (M = Cr, Mo, W). We examined the localization and energies of frontier orbitals of pentacarbonyl metal-containing fragments formed by elimination of CO ligand from the coordination sphere of chromium subgroup metal:
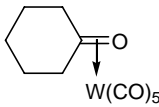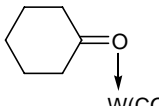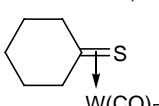
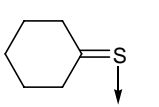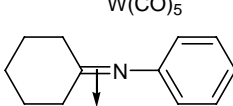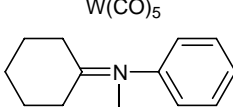$$M(CO)_6 \rightarrow M(CO)_5 + CO$$

The structure and energy parameters were calculated in terms of the Hartree–Fock theory using the ECP (SBK) basis set in which inner-shell electrons are described by the Stevens–Basch–Krauss model potential. Hydrogen atoms were treated at the 6-31G level, and valence shells of heavy atoms were described using quadruple and triple zeta basis sets for *s*, *p*, and *d* electrons, respectively; *d*-polarizing function was also used for heavy atoms. This basis set was used to perform full geometry optimization of the complexes [14]. The applicability of the above approach to analysis of the structure and energy of formation of π-organometallic compounds was substantiated by us previously [9].

The results of calculations showed that the structure of frontier orbitals of the $M(CO)_5$ fragments is almost similar to that of *d* orbitals of transition metals. The LUMO energies of coordinately unsaturated 16-electron $M(CO)_5$ species are −2.57 (Cr), −2.85 (Mo), and 2.60 eV (W); i.e., their LUMOs are readily accessible for interaction with HOMOs of ligands. The HOMO energy may stimulate π-dative metal–ligand interaction. Analysis of the structure and energy of frontier orbitals of potential ligands and pentacarbonylmetal fragments led us to conclude that the C=O and C=N groups are capable of coordinating in both lateral and terminal modes and that terminal coordination is preferred for the C=C fragment.

Table contains the Gibbs energies of formation of the $W(CO)_5L$ complexes (where L is cyclohexanone, cyclohexanethione, or *N*-cyclohexylideneaniline) with different modes of coordination of the ligand. These data confirm the conclusion drawn from analysis of the frontier orbital structure: only the complexes with cyclohexanethione show a considerable difference in the Gibbs energies of formation of coordination compounds with *n*- and π-bonding of the metal with the ligand. The difference in the Gibbs energies of formation of complexes with participation of C=O and C=N groups is so small that we can suppose competing formation of compounds with terminal and lateral modes of coordination for ketone **I** and Schiff base **III**.

Gibbs energies of the reaction $W(CO)_6 + L \rightarrow W(CO)_5L + CO$, where L is cyclohexanone, cyclohexanethione, or *N*-cyclohexylideneaniline coordinated in different modes

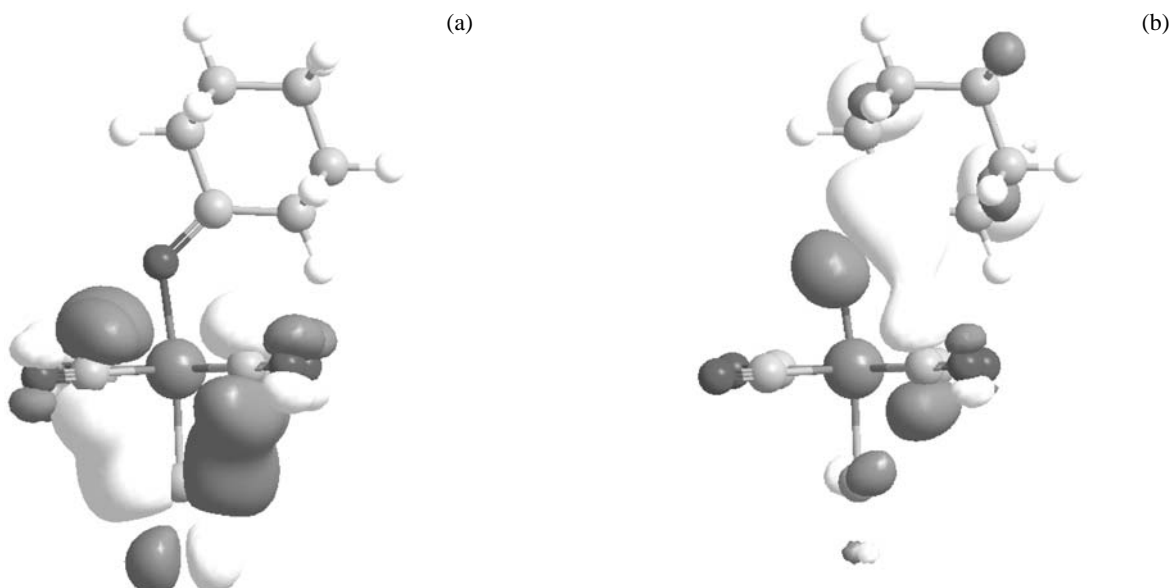| Complex $W(CO)_5L$	ΔG, kJ/mol
	−7.8
	−8.1
	−5.3
	−12.0
	−8.0
	−8.5

(a)

(b)

Fig. 4. (a) HOMO ($E = -4.34$ eV) and (b) LUMO ($E = -1.28$ eV) of the complex (η^1-$C_6H_{10}O$)Mo(CO)$_5$, .

(a)

(b)
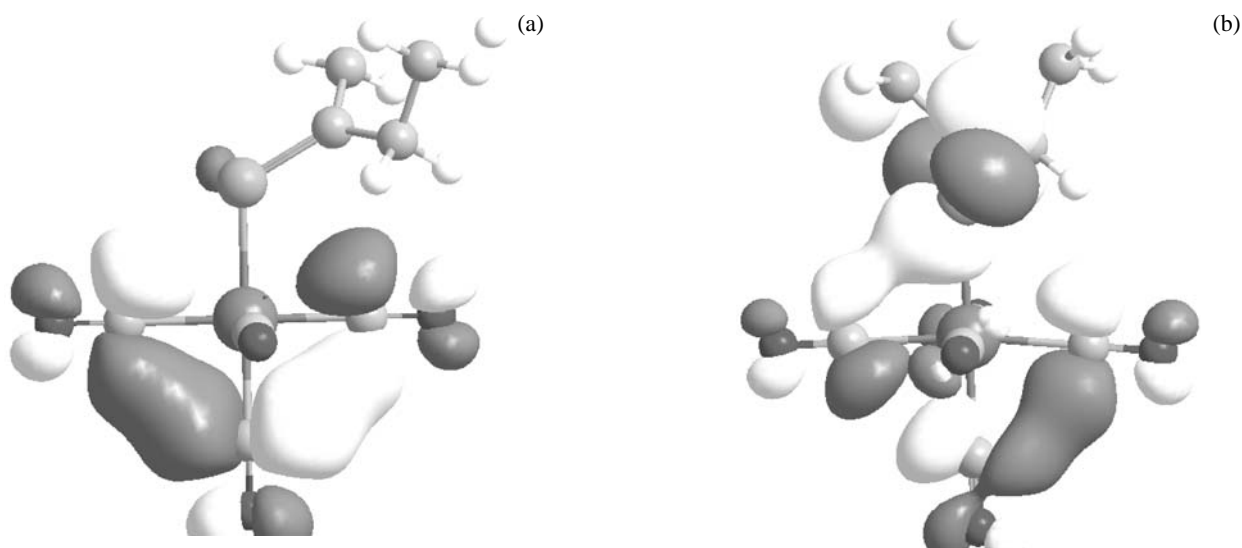
Fig. 5. (a) HOMO ($E = -4.27$ eV) and (b) LUMO ($E = -3.42$ eV) of the complex (η^1-$C_6H_{10}S$)Mo(CO)$_5$.

Moreover, interconversion between isomeric complexes with η^1- and η^2-coordinated ligands seems to be possible.

Figures 4 and 5 show the structure of frontier orbitals of the complexes formed by unsaturated compounds **I** and **II** and pentacarbonylmetal fragment. The HOMOs of these complexes are localized almost completely on the metal-containing fragments, while their LUMOs reside mainly on the double C=X bonds of the ligands. We can thus presume that HOMO of a nucleophile should interact with LUMO of the metal complex (which is localized on the double bond of the ligand) provided that the reaction is orbital-controlled. This is consistent with our previous conclusion that the metal center not only acts as a protecting group but strongly affects the electronic properties of the reaction center in the coordinated unsaturated reagent [4, 6–8]. Charge distribution between the carbon and heteroelement atoms in η^1- and η^2-coordinated C=X groups in the complexes derived from compounds **I** and **II** should also favor attack by nucleophile on the electrophilic carbonyl (or thiocarbonyl) carbon atom when the reaction is charge-controlled. For example, the charge on the oxygen atom in free cyclohexanone

Scheme 1.
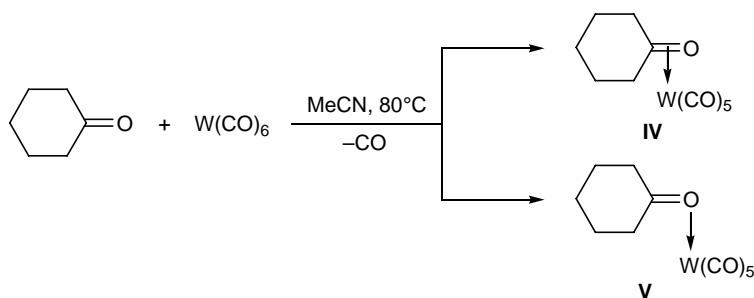
molecule is –0.323 a.u., and the charge on the carbonyl carbon atom is +0.298 a.u. η^1-Coordination of cyclohexanone to tungsten only slightly changes these charges, the C=O bond polarization remaining unchanged: –0.287 (O) and +0.231 a.u. (C).

According to the calculations, coordinated ligand **III** is characterized by a different distribution of electron density. In uncoordinated Schiff base **III**, the negative end of the C=N dipole is the nitrogen atom ($q_N = -0.051$, $q_C = +0.017$ a.u.); in going to the η^1-coordinated ligand, the charges on the carbon and nitrogen atoms change their signs so that excess electron density is localized on the carbon atom ($q_C = -0.115$ a.u.), while the nitrogen atom becomes electron-deficient ($q_N = +0.098$ a.u.). Such charge distribution in the coordinated Schiff base leads to inversion of the direction of nucleophilic attack: nucleophile adds at the nitrogen atom rather than at the carbon atom, as in reactions with the free ligand. Analogous inversion of polarization of the C=N bond as a result of coordination was observed for 1-aza-1,3-diene complexes with chromium subgroup metals [8].

In order to obtain experimental support to the results of theoretical calculations we examined reactions of cyclohexanone (**I**) and its analogs **II** and **III** with hexacarbonyltungsten(0), which were performed according to the procedure developed by us previously for thermochemical activation of complex formation processes [6–8]. In the reaction with cyclohexanone we succeeded in isolating a mixture of crystalline products corresponding to η^1- and η^2-coordination to tungsten. The products were unstable in the presence of atmospheric oxygen and moisture, and their composition implied replacement of one carbonyl ligand in W(CO)$_6$ by the ketone (Scheme 1). The IR spectrum of the isolated mixture contained two well defined absorption bands in the region of carbonyl stretching vibrations, at 1610 and 1660 cm^{-1}. These bands were assigned, respectively, to the π-coordinated C=O group in complex **IV** and *n*-coordinated C=O group in

complex **V**. Uncoordinated cyclohexanone is characterized by a carbonyl stretching vibration frequency of 1710 cm^{-1}.

The above assignment is supported by the following considerations. Lateral (η^2) coordination of the double bond induces not only electron density redistribution but also extension of that bond, leading to considerable variation of its stretching vibration frequency. Terminal coordination of the C=X group through the heteroatom is accompanied by insignificant variation of the electronic structure, and the vibration frequency should change only slightly. Approximately equal intensities of the bands at 1610 and 1660 cm^{-1} in the IR spectrum suggest equal or (at least) comparable amounts of complexes **IV** and **V** in the product mixture. This is consistent with the equilibrium constant for isomerization of complex **IV** into **V**, calculated from the Gibbs energies of formation of these complexes (see table), $K_{eq} = 1.14$.

The mixture of coordination compounds obtained from cyclohexanone and hexacarbonyltungsten(0) was analyzed by thin-layer chromatography. Elution with acetonitrile revealed two compounds with R_f values of 0.100 and 0.154. The first of these was assigned to η^2-complex **IV**, and the second, to η^1-(cyclohexanone)-pentacarbonyltungsten(0) (**V**). The assignment was based on the calculated dipole moments of compounds **IV** and **V**, 0.302 and 2.93 D, respectively. Unfortunately, we failed to isolate individual complexes **IV** and **V** by column chromatography due to their sensitivity to atmospheric oxygen and moisture.

Crystalline products obtained by the reaction of cyclohexanone with hexacarbonyltungsten(0) were isomeric coordination compounds of the general formula L$_2$W(CO)$_4$ (Scheme 2). However, in this case, lateral coordination of the C=S fragment to the metal center may be ruled out. Both initial cyclohexanethione and mixture of products of its reaction with W(CO)$_6$ showed in the IR spectra a weak absorption
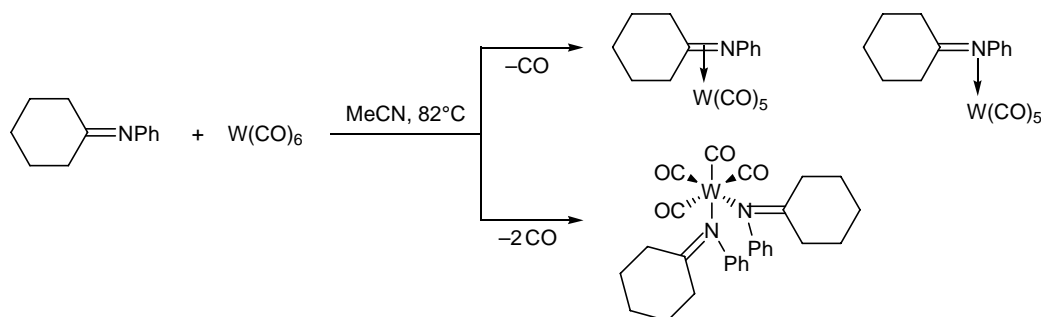
Scheme 2.

VI

VII
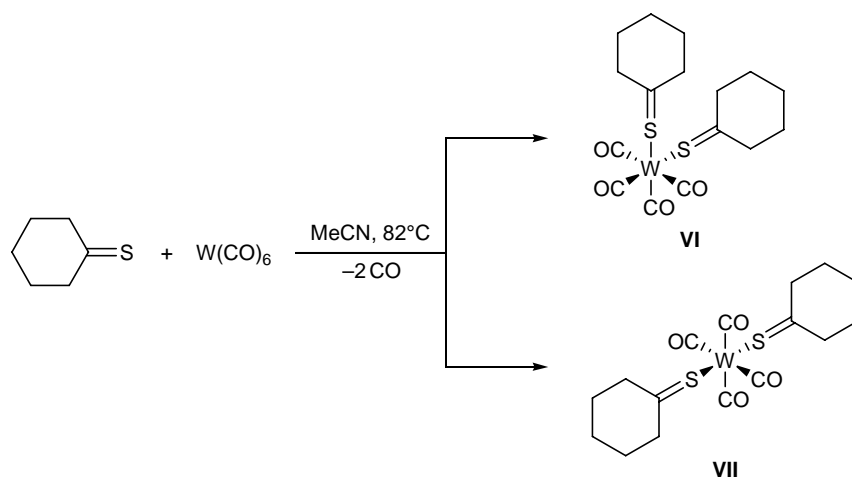
band at 1140 cm^{-1} corresponding to the C=S bond. We thus concluded (in keeping with the results of quantum-chemical calculations), that cyclohexanethione coordinates to the metal through the sulfur atom to give isomeric *cis*- and *trans*-bis(η^1-cyclohexanethione) tetracarbonyltungsten(0) **VI** and **VII**. In the IR spectrum of a crystalline mixture of complexes **VI** and **VII** we observed a system consisting of 4 well resolved absorption bands in the region 2100–1950 cm^{-1}; these bands were assigned to carbon(II) oxide molecules coordinated to tungsten in the terminal mode. No bands assignable to bridging C=O groups were present. The long-wave region of the spectrum contained two strong bands at 374 and 364 cm^{-1}, which are likely to arise from vibrations of the sulfur–tungsten dative bond. Insofar as the sulfur atom is known to exert a stronger *trans* effect than CO, the band at 374 cm^{-1} was assigned to *trans* isomer **VI**, and the band at 364 cm^{-1}, to *cis*-bis(η^1-cyclohexanethione)tetracarbonyltungsten(0) (**VII**).

In the reaction of *N*-cyclohexylideneaniline with hexacarbonyltungsten(0) we isolated a mixture of crystalline products **VIII** whose elemental analysis did not allow us to assign them a definite formula. The ligand–metal ratio in the products varies from 1:1.2 to 1:1.6. The IR spectrum contained poorly resolved absorption bands in the region corresponding to terminally coordinated carbonyl groups, while no absorption typical of bridging carbonyl groups was observed. These data led us to presume that the product mixture contains mononuclear coordination compounds with the compositions LW(CO)$_5$ and L$_2$W(CO)$_4$ (Scheme 3).

Two absorption bands in the IR spectrum of the products belong to stretching vibrations of the C=N bond: the band at 1610 cm^{-1} belongs to the uncoordinated double C=N bond, and that located at 1580 cm^{-1} corresponds to the π-coordinated C=N bond. In the long-wave region we observed absorption bands at 567, 582, and 588 cm^{-1} due to vibrations of the dative nitrogen–metal bond [8]. A complex absorption pattern in the carbonyl ligand region and the presence of several W–N bands suggest the occurrence of different coordination modes in the complexes, presumably due to strongly reduced symmetry of the C=N bond orbitals. Unfortunately, the products were very unstable in the presence of atmospheric oxygen and moisture,
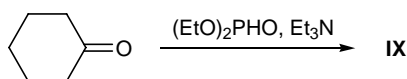
Scheme 3.

Scheme 4.
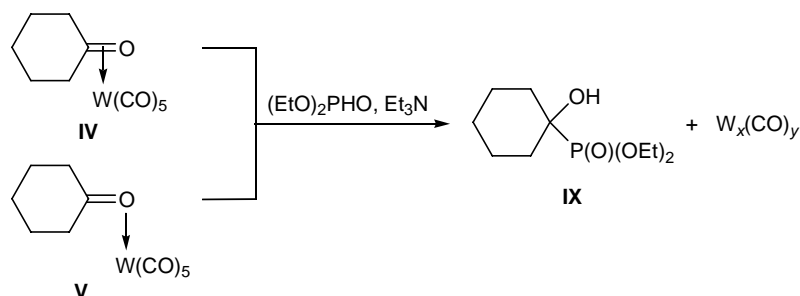
and we failed to isolate individual complexes and even to analyze the composition of the product mixture by thin-layer chromatography.

We examined the behavior of complexes **IV–VIII** with different modes of coordination of the C=X groups in reactions with diethyl phosphonate in the presence of triethylamine. In all cases, addition of the P–H reagent at the double bond occurred. Hydrophosphorylation of cyclohexanone complexes **IV** and **V** was accompanied by decomposition of the coordination compounds with liberation of diethyl 1-hydroxy-cyclohexylphosphonate (**IX**) and formation of a metal-containing residue with the composition $W_x(CO)_y$ (Scheme 4); the latter product results from increase in the nuclearity due to formation of coordinately unsaturated species $W(CO)_5$. Phosphonate **IX** showed in the ^{31}P NMR spectrum a singlet at δ_P 24 ppm; the same signal was observed in the spectrum of a product obtained by model reaction of uncoordinated cyclohexanone with diethyl phosphonate in the presence of triethylamine (Scheme 5).
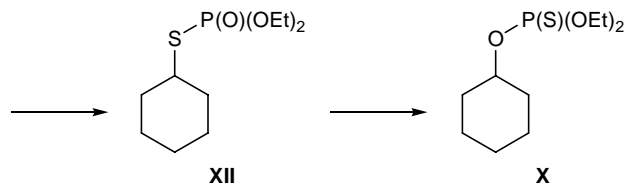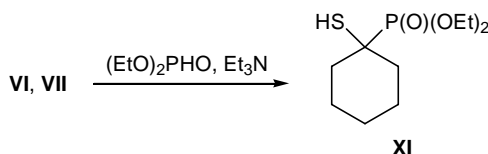
Scheme 5.

Under analogous conditions, hydrophosphorylation of a mixture of complexes **VI** and **VII** in benzene also involved addition of diethyl phosphonate at the double C=S bond (Scheme 6). However, in this case we isolated *O*-cyclohexyl *O,O*-diethyl thiophosphate (**X**) as product of two successive rearrangements: sulfanyl-phosphonate–thiophosphate **XI** → **XII** and thiol–thione **XII** → **X**. Analogous ligand transformations were observed previously while studying hydrophosphorylation of 1,3-diphenyl-2-propenethione in the coordination sphere of carbonyl and carbonyl cyclo-pentadienyl complexes of chromium subgroup metals [14]. The ^{31}P NMR spectrum of the hydrophosphorylation product of coordination compounds **VI** and **VII**

contained a singlet at δ_P 65 ppm. Hydrophosphorylation of uncoordinated cyclohexanethione gives a product with the same ^{31}P chemical shift (Scheme 7). As with complexes **IV** and **V**, reactions of diethyl phosphonate with cyclohexanethione complexes **VI** and **VII** are accompanied by decomposition of the coordination compounds and formation of a solid metal-containing residue with the composition $W_x(CO)_y$.

Scheme 6.

Scheme 7.
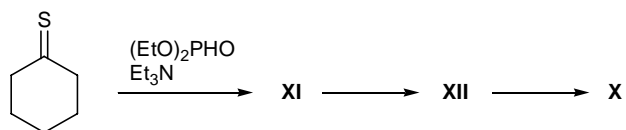
A mixture of tungsten complexes **VIII** with *N*-cyclohexylideneaniline also reacted with diethyl phosphonate in benzene, resulting in decomposition of the coordination compounds and increase in the nuclearity of carbonyltungsten complexes. In the ^{31}P NMR spectrum of the reaction mixture we observed two singlets. One of these is typical of α-aminophosphonates (δ_P 14.7 ppm); obviously, it belongs to diethyl 1-(phenylamino)cyclohexylphosphonate (**XIII**). The other signal was located in the amidophosphate region, δ_P 2.3 ppm; it was assigned to diethyl *N*-cyclohexyl-*N*-phenylamidophosphate (**XIV**) (Scheme 8). Uncoordinated *N*-cyclohexylideneaniline **III** reacted with di-

Scheme 8.
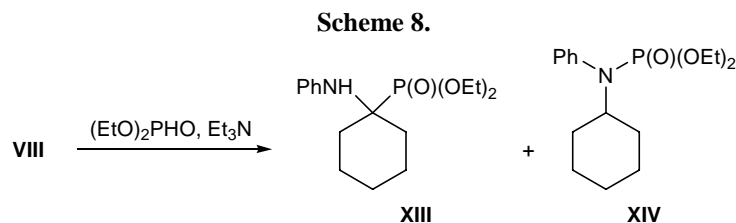
ethyl phosphonate to give exclusively the corresponding Pudovik reaction product, α-aminophosphonate **XIII**, which was identified by the presence of a singlet at δ_P 14.8 ppm in the ^{31}P NMR spectrum.

Our experimental data are very consistent with the above described charge distribution in coordinated Schiff base, determined by quantum-chemical calculations. Change in the polarization of the nitrogen–carbon bond, leading to increased electrophilicity of the nitrogen atom, makes the latter the target for attack by nucleophile. It should be noted that we have already observed formation of P–N bond via addition of diethyl phosphonate at the C=N bond of 1-aza-1,3-diene in the coordination sphere of a carbonylmetal complex [8]. Moreover, we have shown that the amidophosphate ligand undergoes rearrangement into the corresponding unsaturated α-aminophosphonate on prolonged storage at room temperature. As concerns the formation of α-aminophosphonate **XIII**, the available experimental data do not allow us to distinguish between alternative pathways including the imine version of the Pudovik reaction and the isomerization **XIV → XIII**. Also, we cannot rule out simultaneous formation of isomeric products via inner-sphere Ad_N reaction since the difference between the charges on the nitrogen and carbon atoms in the coordinated Schiff base is very small, 0.007 a.u.

Thus the results of our theoretical and experimental studies on the structure and reactivity of ligands having a multiple carbon–heteroelement bond and coordinated in different modes to carbonyl-containing complexes of Group VI metals showed almost complete similarity in the behavior of heterocumulenes, on the one hand, and cyclic ketones and their sulfur and nitrogen analogs, on the other. In both cases, the carbonylmetal fragment strongly affects the electronic (and, in the case of heterodienes, steric [8, 9]) structure of unsaturated ligands, stimulating their regioselective functionalization exclusively at the carbon–heteroelement multiple bond. Hydrophosphorylation of oxo and thioxo ligands follows the Abramov reaction pattern, leading to the corresponding phosphorylated alcohols and thiols. The same reaction pattern is typical of the

free ketones and thioketones. However, coordination to a metal induces some specificity in the synthetic results. α-Sulfanylphosphonates readily undergo intramolecular rearrangements within the coordination sphere of a metal. The effect of coordination is especially strong in the case of Schiff bases: inversion of polarization of the C=N bond, induced by the carbonylmetal fragment, changes the regioselectivity of hydrophosphorylation, and the reaction proceeds in a direction untypical of the free ligand. Here, apart from the expected formation of α-aminophosphonate according to the imine version of the Pudovik reaction, nucleophile adds to the C=N bond in the inversed mode, leading to amidophosphate. Therefore, involvement of oxo compounds and their analogs in inner-complex functionalization opens new prospects in the purposeful synthesis of substances with a specified structure.

The results obtained in the present work, together with our previous data on the addition of dialkyl phosphonate to alkenes coordinated to chromium subgroup metals [15], cast doubt on the assumption [7–9, 15, 16] that change in the reactivity of coordinated heterodienes is induced by the metal acting as protecting group. We believe that the most probable reason is profound geometric and electronic reorganization of ligands as a result of coordination with transition metal.

EXPERIMENTAL

The following commercial reagents and solvents were used: pentane, hexane, benzene, toluene, acetone, acetonitrile, tetrahydrofuran, ethanol, and triethylamine; they were additionally purified according to standard procedures [17]. Initial hexacarbonyltungsten(0) was purified by vacuum sublimation (0.05 mm) at 60–80°C. The complexes were purified by reprecipitation with hexane or pentane from benzene or by recrystallization from hexane or pentane.

The IR spectra were recorded on Specord M-80 (from samples dispersed in mineral oil or films) and Bruker Vector 2-2 Fourier spectrometers (from

samples prepared as KBr pellets; resolution 1 cm^{-1}, scan number 64, frequency range 200 to 4000 cm^{-1}). The ^{31}P NMR spectra were measured on a Varian Unity-300 spectrometer (121.4 MHz) using 85% phosphoric acid as external reference. TLC analysis was performed on Silufol plates using 2-propanol–benzene (3:1) as eluent; development with iodine vapor. All experiments were carried out under dry argon. Quantum-chemical calculations were performed with the aid of GAMESS 98 program [18].

(η^2-Cyclohexanone)pentacarbonyltungsten(0) (IV) and η^1-(cyclohexanone)pentacarbonyltungsten(0) (V). A mixture of 1 g of hexacarbonyltungsten(0) and 5 ml of cyclohexanone was heated for 15 h at the boiling point under argon. The colorless needle-shaped crystals were filtered off. Yield 66.3%, mp 165°C (decomp.). IR spectrum (mineral oil), ν, cm^{-1}: 1600 (C=O, π-coordinated), 1660 (C=O, *n*-coordinated). Found, %: C 31.80; H 2.37. C$_{11}$H$_{10}$O$_6$W. Calculated, %: C 31.31; H 2.39.

***cis*- and *trans*-Bis(η^1-cyclohexanethione)tetracarbonyltungsten(0) (VI/VII).** A solution of 0.16 g of cyclohexanethione in 5 ml of 2-propanol was added to a solution of 0.50 g hexacarbonyltungsten(0) in 5 ml of 2-propanol. The pale yellow crystals were filtered off. Yield 75.6%, mp 183°C (decomp.). IR spectrum (mineral oil), ν, cm^{-1}: 1140 (C=S, uncoordinated); 374, 364 (W–S); 1950, 1980, 2000, 2100 (CO ligands). Found, %: C 36.48; H 4.37; S 12.09. C$_{16}$H$_{24}$O$_4$SW. Calculated, %: C 36.37; H 4.58; S 12.14.

Reactions of free ligands and coordination compounds with diethyl phosphonate. The reactions were carried out at 20°C in benzene in the presence of 10 mol % of triethylamine. Diethyl phosphonate was taken in an amount equimolar to the coordinated substrate containing a C=X bond. After 24 h, the reaction mixtures were analyzed by ^{31}P NMR spectroscopy.

REFERENCES

1. Konovalova, I.V. and Burnaeva, L.M., *Reaktsiya Pudovika* (The Pudovik Reaction), Kazan: Kazan. Univ., 1991.
2. Arbuzov, B.A., Tudrii, G.A., and Fuzhenkova, A.V., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, p. 1585.
3. Tudrii, G.A. and Fuzhenkova, A.V., *Zh. Obshch. Khim.*, 1978, vol. 48, p. 490.
4. Galkin, V.I., Galkina, I.V., Kurdi, Kh.A., Denisov, B.V., and Cherkasov, R.A., *Metalloorg. Khim.*, 1990, vol. 3, p. 1429.
5. Beletskaya, I.P. and Kazankova, M.A., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 1391.
6. Kuramshin, A.I., Karpenko, E.A., and Cherkasov, R.A., *Russ. J. Gen. Chem.*, 2001, vol. 71, p. 191.
7. Kuramshin, A.I., Pavlova, I.V., and Cherkasov, R.A., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 45.
8. Kuramshin, A.I., Kuramshina, E.A., and Cherkasov, R.A., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 1265.
9. Kuramshin, A.I., Mushkin, V.B., Karpenko, E.A., and Cherkasov, R.A., *Russ. J. Gen. Chem.*, 2001, vol. 71, p. 348.
10. Faller, J.W., Ma, Y., Smart, C.J., and Di Verdi, M.J., *J. Organomet. Chem.*, 1991, vol. 420, p. 237.
11. Caldarelli, J.L., Wagner, L.E., White, P.S., and Templeton, J.L., *J. Am. Chem. Soc.*, 1994, vol. 116, p. 2878.
12. *Comprehensive Organometallic Chemistry*, Wilkinson, G., Ed., Oxford: Pergamon, 1980, vol. 3, p. 799.
13. Pardue, J.E. and Dobson, G.R., *Inorg. Chim. Acta*, 1976, vol. 20, p. 207.
14. Kuramshin, A.I., Pavlova, I.V., Sokolov, Yu.A., and Cherkasov, R.A., *Karbonil'nye soedineniya v sinteze geterotsiklov* (Carbonyl Compounds in the Synthesis of Heterocycles), Saratov, 2004, p. 223.
15. Kuramshin, A.I., Kuramshina, E.A., and Cherkasov, R.A., *Russ. J. Gen. Chem.*, 2001, vol. 71, p. 354.
16. Schmidt, Th., Bienewald, F., and Goddard, R., *J. Chem. Soc., Chem. Commun.*, 1994, vol. 35, p. 1857.
17. *Organikum. Organisch-chemisches Grundpraktikum*, Berlin: Wissenschaften, 1976, 15th ed. Translated under the title *Organikum*, Moscow: Mir, 1979, vol. 2, p. 353.
18. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A, Su, S.J., Windus, T.L., Dupuis, M., and Montgomery, A., *J. Comput. Chem.*, 1993, vol. 14, p. 1347.