Preparation of Complexes η^4-4-(1,3-Diphenyl-2-propen-1-one)-η^3-3-(1,3,5-triorganyl-1,3,5-triazacyclohexane)carbonyltungsten(0) and Their Reactions with Diethyl Phosphite

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Abstract—New tungsten complexes were prepared of a composition η^3-[(1,3,5-triorganyl)-1,3,5-triazacyclohexane]-tricarbonyltungsten(0) where a tridentate coordination of the triazinane fragment to the metal center was found. The reaction of tricarbonyltriazinane tungsten complexes with 1,3-diphenyl-2-propen-1-one (chalcone) under thermochemical activation resulted in replacement of two carbon monoxide molecules in the coordination sphere of tungsten by a chalcone molecule linked to the transition metal atom through a system of π-bonds C=C and C=O. The phosphorylation of η^4-(1,3-diphenyl-2-propen-1-one)-η^3-[(1,3,5-triphenyl)-1,3,5-triazacyclohexane]-monocarbonyltungsten(0) with diethyl phosphite occurred at the carbonyl group of the coordinated heterodiene; the phosphonate thus formed underwent intracomplex phosphonate-phosphate rearrangement affording an organometallic phosphate.

Although a long time has elapsed since the 1,3,5-triorganyl-1,3,5-triazacyclohexanes (triazinanes) have been described for the first time the chemistry of these heterocyclic tridentate ligands just now starts to develop [1–5]. Triazacyclohexane system should apparently be regarded as the smallest representative of the triaza-macrocyclic ligands. Therefore its tridentate coordination with the metal center is characterized by a certain strain that might result in unpredictable changes in reactivity of the complexes including these systems. Relatively simple procedures for preparation of complexes (1,3,5-trialkyl-1,3,5-triazacyclohexane)metal(CO)$_3$ were reported in [2–5], and it was shown that notwithstanding the character of substituents at the nitrogen atom, for instance, alkyne [4] or hydroxyalkyl groups [5], in the chromium and in some cases in molybdenum complexes a tridentate *n*-coordination of the triazinane with metal was observed occurring at the expense of the unshared electron pairs of nitrogen.

We formerly developed preparation procedures for organometallic compounds starting from α-enones and homoligand hexacarbonyl complexes of metals from the chromium subgroup and investigated hydrophosphorylation of unsaturated ligand within the coordination sphere of metal [6, 7]. This study permit us establishing a fundamental possibility to govern hydrophosphorylation regio-

selectivity of α-enones included into the coordination sphere of a transition metal. Aiming at evaluation of the influence of ligands surrounding the transition metal atom, in particular, at replacement of carbonyl ligands by a triazinane, on the readiness to form heterodiene η^4-complexes and on the features of the unsaturated ligand reactivity toward intracomplex hydrophosphorylation we performed reactions of 1-oxo-1-heterodienes with coordination compounds (triazinane)W(CO)$_3$. The choice of tungsten as the complexing metal was due first of all to the presence in the natural isotope mixture of tungsten a magnetically-active isotope ^{183}W that facilitated the study of phosphorylation by appearance in the NMR spectra of the spin-spin coupling phosphorus–tungsten. Besides the chemistry of triazinane complexes of the zero-valent metals from the VIB group was studied mainly on the chromium and molybdenum compounds [2–5], whereas the information on the similar tungsten(0) derivatives was scanty.

The compounds we used as ligand, 1,3,5-tris-*sec*-butyl-1,3,5-triazacyclohexane (**Ia**), 1,3,5-triphenyl-1,3,5-triazacyclohexane (**Ib**), and 1,3,5-tri(2-hydroxyethyl)-1,3,5-triazacyclohexane (**Ic**), were obtained by condensation of primary amines with paraformaldehyde as described [8]. The homogeneity of the compounds was tested by TLC, their physicochemical and spectral characteristics were consistent with the published data.
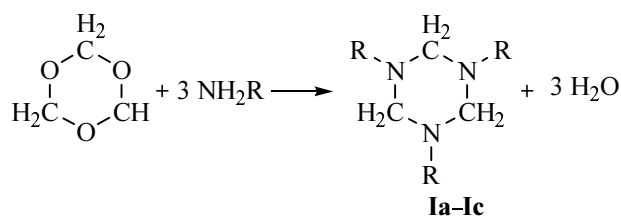
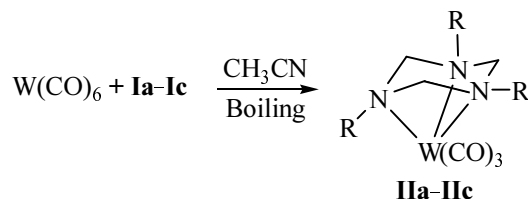R = *s*-Bu (**a**), Ph (**b**), CH₂CH₂OH (**c**).

We used two approaches to preparation of carbonyl tungsten complexes with 1,3,5-tris-*sec*-butyl-1,3,5-triazacyclohexane (**Ia**): a direct reaction of the latter with the hexacarbonyltungsten, and also substitution of three carbonyl ligands in the hexacarbonyltungsten by acetonitrile followed by replacement of the nitrile ligands by triazinane.
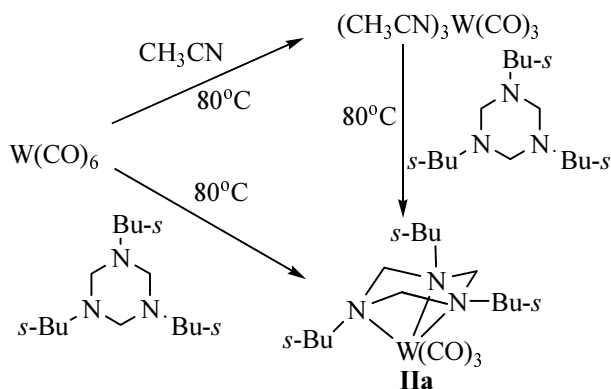
In both cases formed η^3-[(1,3,5-tris-*sec*-butyl)-1,3,5-triazacyclohexane]tricarbonyltungsten(0) (**IIa**) where the nitrogen ligand was in a tridentate coordination to tungsten. The direct reaction of hexacarbonyltungsten(0) with triazinane **Ia** gave rise to complex **IIa** in a 65% yield, and by the alternative "acetonitrile" procedure the product of the ligand exchange **IIa** was obtained in 80% yield. However taking into account relatively low conversion of the hexacarbonyltungsten into the product of acetonitrile substitution not exceeding 30% [9] the direct reaction between the hexacarbonyltungsten(0) with triazinane is preferable. We further used just this procedure, the reaction of substituted triazacyclohexanes with hexacarbonyltungsten in a boiling acetonitrile solution, in prepartion of tungsten(0) triazinanetricarbonyl complexes.

As already mentioned, the hexacarbonyltungsten(0) reacted with triazinanes **Ia** and **Ib** with replacement of three carbon monoxide molecules and formation of crystalline complexes **IIa** and **IIb**. Their homogeneity was confirmed by TLC. In the IR spectra of compounds **IIa** and **IIb** three well resolved absorption bands of the carbonyl ligands linked to tungsten are observed at 1850–

1990 cm⁻¹, and also absorption bands in the region 580–600 cm⁻¹ assigned to vibrations of the donor-acceptor W–N bonds. ^{1}H NMR spectra show that in compounds **IIa** and **IIb** hydrogen atoms are present in the same chemical environment as in trialkyltriazinanes **Ia** and **Ib**. These findings evidence the tridentate coordination of the nitrogen-containing ligand substituting three carbon monoxide molecules in the coordination sphere of the hexacarbonyltungsten(0).

R = *s*-Bu (**a**), Ph (**b**), CH₂CH₂OH (**c**).

In contrast to 1,3,5-trialkyl-1,3,5-triazacyclohexanes with alkyl or aryl substituents attached to the nitrogen atoms the coordination of triazinane **Ic** in its reaction product with hexacarbonyltungsten(0) might occur not only through the nitrogen atoms: the presence of additional potential coordination centers, oxygens of the hydroxy groups, might complicate the complex structure. In reaction of hexacarbonyltungsten(0) with hydroxyethyl derivative **Ic** we obtained an amorphous metal complex where a coordination of tungsten with carbon monoxide was retained, and also appeared a new coordination bond tungsten–nitrogen. In the IR spectrum of complex **IIc** like in those of his analogs **IIa** and **IIb** appear three bands at 1880, 1920, 1980 cm⁻¹ from carbonyl groups linked to tungsten and a medium band at 590 cm⁻¹ belonging to vibrations of the donor-accepton bond nitrogen–tungsten. However alongside these bands an additionsl absorption band is observed at 880 cm⁻¹ corresponding to the tungsten–oxygen bond, and the broadening of hydroxy group bands of the triazinane ligand demonstrates the formation of a hydrogen bonds net. We presume that the amorphous state of triazinanetricarbonyltungsten complex **IIc** may be due to its polymeric structure originating both from the existence of intermolecular hydrogen bonds between the hydroxy groups of the coordinated ligand and also by coordination of tungsten atoms with the oxygen of hydroxy groups.

The obtained coordination compounds of tungsten **IIa–IIc** are considerably more soluble in various organic solvents than hexacarbonyltungsten(0). The solubility of the latter in benzene and ethanol (0.10 and 0.50 mg/ml respectively) is far less than the corresponding data for the least soluble among the complexes we obtained,

triphenyltriazacyclohexane derivative **IIb**: 1.26 and 1.37mg/ml. This fact significantly facilitates a synthesis based on these compounds of heterodiene derivatives of the zero-valent tungsten and the study of the intracomplex phosphorylation of unsaturated ligands that was the goal of the present investigation.

η^3-[(1,3,5-Triphenyl)-1,3,5-triazacyclohexane]tricarbonyltungsten(0) (**IIb**) and its hydroxyethyl analog **IIc** we brought into reaction with chalcone under conditions of thermochemical initiation: the reaction of the α-enone with the metal complex was carried out in boiling acetonitrile solution [6, 7]. According to published data [2, 4] with the growing size of substituents attached to the nitrogen atoms of the trialkyltriazinanes increases the conformational rigidity of the ligands, and it stabilizes the organometallic compounds obtained therefrom. Therefore we expected to obtain a stable organometallic derivative in reaction of the heterodiene and (triazinane)tricarbonyltungsten containing sterically loaded phenyl substituents.

To the products of reactions of compounds **IIb** and **IIc** with chalcone we assigned a structure of η^4-(1,3-diphenyl-2-propen-1-one)-η^3-(1,3,5-triorganyl)-1,3,5-triazacyclohexane)monocarbonyltungsten(0) (**IIIb** and **IIIc**).


IIIb, IIIc
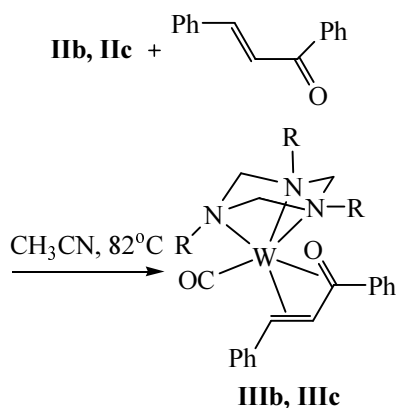
In the IR spectrum of compound **IIIb** a characteristic absorption band is observed at 1520 cm^{-1}, corresponding to vibrations of the C=C bond of chalcone coordinated to tungsten, and a band at 1620 cm^{-1} belonging to the carbonyl group of 1,3-diphenyl-2-propen-1-one involved into the coordination with the metal [7]. In the IR spectrum of complex **IIIc** vibrations of these bonds coordinated to the metal appear as bands at 1580 and 1655cm^{-1}. In the IR region of vibration bands characteristic of carbon monoxide coordinated to tungsten appears a single band for each complex at 1970 (**IIIb**) and 1930 cm^{-1} (**IIIc**).

The absorption bands from vibrations of bonds tungsten–nitrogen and carbon–nitrogen characteristic of initial metal complexes **IIb** and **IIc** are retained in the IR spectra of derivatives **IIIb** and **IIIc**.

The π-complexes of chalcone we obtained proved to be more stable, and the unsaturated ligand turned out to be conformationally more stable compared to the previously studied carbonyl analogs [6, 7]. In the ^{1}H NMR spectrum of compound **IIIb** the hydrogen atoms of the olefin fragment of chalcone appeared, for instance, as two sufficiently well resolved doublets with the chemical shifts equal to 3.70 and 3.90 ppm, $^3J_{H,H}$ 7.0 and 20.0 Hz respectively which were assigned to hydrogens located *cis-* and *trans-* with respect to the double bond of chalcone coordinated to the transition metal atom. In the free chalcone these hydrogen signals appear at 6.7 ppm. The possibility to observe in solution by spectral method separate geometrical isomers of the oxodiene present in the coordination sphere of a metal is due to the low rate of ligand exchange in compounds **IIIb** and **IIIc** and eventually testifies to the stability of the organometallic compounds obtained. We previously [6, 7] observed only broadened signals of the olefin protons of 1-hetero-1,3-dienes coordinated to metals from the chromium subgroup, and we undersood it as kinetic lability of these compounds and the possibility of intracomplex rotation of the α-enone [10]. Thus we may conclude that the replacement of three carbon monoxide molecules by one tridentate chelating ligand of triazinane series containing bulky substituents on the nitrogen increases the stability of π-complexes and opens an opportunity to isolate these compounds and the products of their intracomplex functionalization.

We attempted to phosphorylate the chalcone bound to the triazinanecarbonyl metal-containing core in compound **IIIc** with diethyl phosphite under conditions described in [6,7,11]. The reaction was carried out in benzene solution at room temperature in the presence of a basic catalyst triethylamine. We demonstrated by special experiments that under these conditions the dialkyl phosphite did not react either with the metal center or with the triazinane ligand. In 4 h after mixing the reagents in the ^{31}P NMR spectrum of the reaction mixture appeared a signal with the chemical shift 16.3 ppm, $^2J_{P,W}$ 35 Hz (from the satellite splitting ^{31}P–^{183}W) that we assigned by analogy with [6,7] to the phosphorus atom in the product of dialkyl phosphite addition to the carbonyl group of chalcone **IV**. In the compound the α-hydroxyphosphonate ligand is linked to tungsten via the olefin fragment and the phosphoryl oxygen atom.

IV   **V**
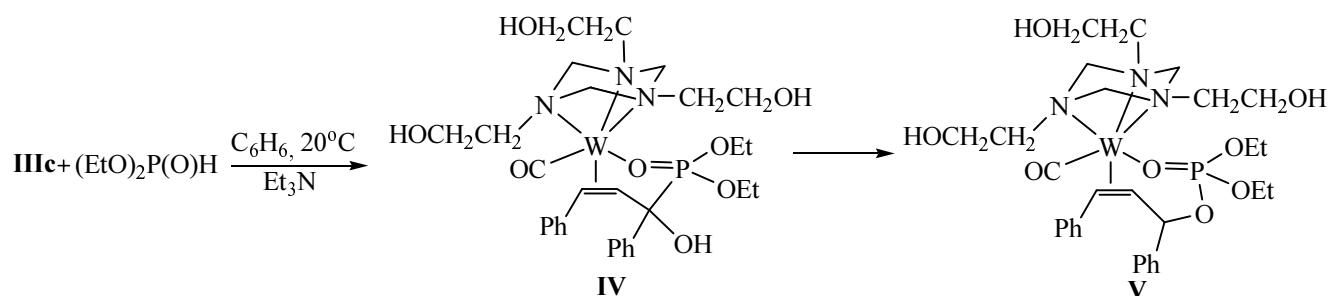
After 3 days of keeping the reaction mixture at room temperature in the ^{31}P NMR spectrum alongside the signal at 16.3 ppm appeared one more stronger signal at –3.7 ppm, $^2J_{P,W}$ 33Hz; the intensity ratio of the signals was 1:7. We suggested that the second upfield signal might correspond to a phosphate structure **V** also connected to tungsten through the oxygen of the phosphoryl group [12, 13]. The formation of phosphate **V** is apparently caused by phosphonate-phosphate rearrangement characteristic of Abramov reaction in the presence of a base [13]. It should be indicated that this unusually ready isomerization occurring via nucleophilic substitution by the hydroxy group oxygen at the tetrahedral phosphorus atom is apparently due to the increased effective positive charge on the phosphoryl center as a result P=O group coordination to the metal.

We succeeded to isolated resinous compound **V** by distilling off the solvent in a vacuum from the reaction mixture. Based on the data of NMR spectroscopy the compound was characterized as η^3-[(1,3-diphenyl-prop-2-enyl)diethylphosphate]-η^3-[1,3,5-tri-(2-hydroxyethyl)-1,3,5-triazinane]monocarbonyltungsten(0). In the ^{1}H NMR spectrum the proton signals of benzene rings appear in the downfield region as a multiplet at 6.2–7.2 ppm, the protons of the hydroxy groups of the triazinane ligand give rise to a broad signal at 3.7 ppm, to the methylene protons from the group POCH$_2$ corresponds a quartet at 3.8 ppm. Two doublets at 4.1 and 4.2 ppm we assigned to the hydrogens of the double bond of chalcone coordinated to tungsten. In the ^{31}P NMR spectrum an only signal is observed with the chemical shift –3.7 ppm, $J_{P,W}$ 33Hz. The organometallic phosphate **V** obtained by us is the first stable product of an α-enone hydrophosphorylation in the coordination sphere of a transition metal. Also the reaction we studied, chalcone hydrophosphorylation when the substrate was bound to the triazinanecarbonyl metal-containing framework, resulting in an unsaturated phosphate coordinated to the metal, was the first example of intercomplex hydroxyphosphonate-phosphate rearrangement . The results we obtained once

more show that the control of phosphorylation regio-selectivity of polyfunctional unsaturated compounds by introducing them into a coordination sphere of a transition metal is a promising opportunity.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord M-80 from mulls in mineral oil. ^{1}H NMR spectra were registered on spectrometers Varian UNITY-300 (299.94 MHz), Bruker 100 (100 MHz), Brucker Gemini-200 (199.827 MHz) at 25°C in acetone-d_6 and deutero-chloroform; chemical shifts were measured from the residual proton signals of the deuterated solvents. ^{31}P NMR spectra were obtained on spectrometer Varian UNITY-300 (121.4 MHz) with 85% water solution of H$_3$PO$_4$ as external reference. TLC was carried out on Silufol plates, eluent a mixture of 2-propanol with benzene, 3:1 by volume, development in iodine vapor. All experiments were performed under argon atmosphere.

η^3-(1,3,5-Triphenyl-1,3,5-triazacyclohexane)-tricarbonyltungsten(0) (IIb). To 1.000 g (0.003 mol) of hexacarbonyltungsten in 15 ml of THF was added 0.897 g (0.003 mol) of 1,3,5-triphenyl-1,3,5-triazinane **(Ib)**, and the mixture was boiled for 1.5–2 h. On cooling the separated light-yellow crystals were filtered off. Yield 65%, mp 200°C (decomp.). IR spectrum, ν, cm^{-1}: 580 (W–N), 1380 (Ph–N), 1580 (C$_6$H$_5$); 1920, 1950, 1980 (carbonyl ligands linked to tungsten). ^{1}H NMR spectrum [(CD$_3$)$_2$C(O)], δ, ppm: 6.5–7.3 m (5H, C$_6$H$_5$), 4.25 s (2H, NCH$_2$N).

η^3-(1,3,5-Tris-*sec*-butyl-1,3,5-triazacyclohexane)-tricarbonyltungsten(0) (IIa) was prepared as described for compound **IIb**. Light-brown crystals, yield 61%, mp 200°C. IR spectrum, ν, cm^{-1}: 600 (W–N), 1170 (*s*-Bu group0, 1920, 1990 (carbonyl ligands linked to tungsten). ^{1}H NMR spectrum [(CD$_3$)$_2$C(O)], δ, ppm: 1.00 (3H, CH$_2$CH$_3$), 1.15 (3H, CHCH$_3$), 1.25(2H , CH$_2$), 3.46 s (2H, NCH$_2$N).

η^3-[1,3,5-Tris(2-hydroxyethyl)-1,3,5-triazacyclohexane]tricarbonyltungsten(0) (IIc) was

prepared as described for compound **IIb**. Amorphous dark-brown substance. IR spectrum, ν, cm^{-1}: 590 (W–N), 880 (W–O), 1050 (C–O), 1180 (C–N); 1880, 1920, 1980 (carbonyl ligands linked to tungsten).

η⁴-(1,3-Diphenyl-2-propen-1-one)-η³-(1,3,5-triphenyl-1,3,5-triazacyclohexane)monocarbonyltungsten(0) (IIIb). In 10 ml of acetonitrile 0.05 g (0.018 mol) of compound **IIb** and 0.0158 g (0.018 mol) 1,3-diphenyl-2-propen-1-one were boiled for 6 h. We obtained light-yellow crystals, yield 45%, mp 190°C. IR spectrum, ν, cm^{-1}: 580 (W–N), 1410 (PhN), 1580 (Ph), 1600 (C=C of chalcone coord. to W), 1620 (C=O of chalcone coord. to W), 1970 (carbonyl ligands linked to tungsten). ^{1}H NMR spectrum [(CD$_3$)$_2$C(O)], δ, ppm: 3.70 d (2H, *trans*-C$\underline{H}$=C$\underline{H}$, $^3J_{H,H}$ 6.96 Hz), 3.90 d (2H, *cis*-C$\underline{H}$=C$\underline{H}$, $^3J_{H,H}$ 20.1Hz).

η⁴-(1,3-Diphenyl-2-propen-1-one)-η³-[1,3,5-tris-(2-hydroxyethyl)-1,3,5-triazacyclohexane]-monocarbonyltungsten(0) (IIIc). In 10 ml of acetonitrile 0.05 g (0.018 mol) of 1,3,5-tri(2-hydroxyethyl)-1,3,5-triazacyclohexanetricarbonyltungsten(0) and 0.011 g (0.018 mol) of 1,3-diphenyl-2-propen-1-one were boiled for 6 h. We obtained viscous substance of brown color, yield 37%. IR spectrum, ν, cm^{-1}: 570 (W–N), 1600 (C=C of chalcone coord. to W), 1655 (C=O of chalcone coord. to W), 1930 (carbonyl ligand linked to tungsten).

η³-[(1,3-Diphenylprop-2-enyl)diethylphosphate]-η³-[1,3,5-tris(2-hydroxyethyl)-1,3,5-triazacyclohexane]carbonyltungsten(0) (V). To a solution of 0.20 g of compound **IIIc** in 5 ml of anhydrous benzene was added 0.2 ml of diethyl phosphite and 1–2 drops of triethylamine. The reaction mixture was stored at room temperature for 72 h. The benzene was distilled off in a vacuum of a roughing pump. We obtained amorphous substance of dark-brown color. IR spectrum, ν, cm^{-1}: 600 (W–N), 1610 (C=C, coord. to W), 1900 (carbonyl ligand linked to tungsten), 1300 (P=O). ^{1}H NMR spectrum (CCl$_3$), δ, ppm: 3.7 s (O$\underline{H}$), 3.8 q (POCH$_2$), 4.10 d (2H, *trans*-C$\underline{H}$=C$\underline{H}$, $^3J_{H,H}$ 6.96 Hz), 4.20 d (2H, *cis*-C$\underline{H}$=C$\underline{H}$, $^3J_{H,H}$ 20 Hz), 6.2–7.2 m (C$_6$H$_5$). ^{31}P NMR spectrum (CCl$_3$), δ, ppm: –3.7 s ($^1J_{P,W}$ 35Hz).

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